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Physicochemical and Structural Properties of Starch Isolated from Different Cultivars of Potato

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Abstract: Potato cultivars originating from the Andes region of South America, France, Japan and North America are becoming increasingly popular with consumers in Japan. The objective of this study was to investigate the physicochemical and structural properties of the starches isolated from twelve potato cultivars from various regions of the world. In addition, the correlation among the starch properties was examined in order to gain a better understanding of this research. The average granule size ranged from 30.7 to 39.3 μm , and was negatively correlated with the peak gelatinization temperature by DSC and the pasting temperature by RVA. The phosphorus content ranged from 614 $\mu\text{g/g}$ starch (dry weight) to 833 $\mu\text{g/g}$ starch (dry weight), and the phosphorus content in four starch samples originating from France was lower than in all of the other samples. The swelling power (70°C) was negatively correlated with the pasting temperature by RVA and apparent amylose content, and positively correlated with the breakdown by RVA. The solubility (70°C) was negatively correlated with the peak viscosity and the breakdown by RVA. The digestibility after 24 h exposure to pancreatin was negatively correlated with the gelatinization temperature (the peak gelatinization temperature by DSC and pasting temperature by RVA), and positively correlated with the swelling power (70°C). It was observed many digested starch granules with rough surfaces and fine wrinkles by FE-SEM. The endo-corrosion on the surface of the starch sunk into the granules and made up of layered structures.

Key words: different potato cultivars, starch, physicochemical and structural properties, FE-SEM

Potato tubers are one of the most important crops in terms of food supply and food processing materials in many parts of the world. Several kinds of potatoes exist, which differ in shape, color, taste and texture, and are cultivated in different areas.

In 2007, the global potato production was 322 million tons per annum, and the per annum food supply quantity of potato was 31.7 kg per capita. In the same year, the annual per capita food supply quantity of potatoes by region was 91.4 kg in Europe, 36.5 kg in America, 23.7 kg in Asia, 1.5 kg in Oceania and 14.0 kg in Africa. In Japan, the food supply quantity of potatoes per capita is 22.6 kg, which is relatively low among foreign countries (FAO: <http://faostat.fao.org/site/368/default.aspx#ancor>, 2011.5.6) and is thought to be due to differences in dietary culture. As with many Asian countries, rice has been the basic food staple in Japan,

and the popularity of potatoes is relatively recent. Therefore, the introduction of new potato cultivars for domestic cultivation and other measures should be implemented in order to increase the supply of potatoes for processing foods such as french fries that have relatively recently become popular in Japan.

The color of the skin and flesh of potatoes sold on the open market in Japan is mainly light yellow. In recent years, various potato cultivars originating from the Andes region have been introduced and sold after adapting to a Japanese climate. The colors of their skin and flesh are red or violet derived from anthocyanin pigment, or saffron yellow derived from carotenoid pigment. These improvements have been made in order to create demand for new food varieties. Some of these colored varieties, like Andes Red, Inkanomezame, Jaga Kids Purple and Violetta, all originating from Peru, are becoming increasingly popular in Japan. Furthermore, in addition to colored varieties originating from the Andes region, many potato cultivars from France have been improved sold in the Japanese market for a variety of specialized cooking purposes in recent years. Their skin and flesh

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Abbreviations: B.V., Blue Value; DSC, differential scanning calorimetry; RVA, Rapid Visco Analyzer; FE-SEM, field emission scanning electron microscope.

range in color from white to light yellow or to light red.

The characteristics of potatoes are affected by cultivar origin and cultivation environment,¹⁻⁴⁾ and the properties of starch, the main component of potato also vary according to these factors.⁵⁾ Therefore, a better understanding of the properties of the starches from these increasingly popular potato cultivars could provide valuable information which could be used to increase demand for new food varieties and contribute to the increase of the supply of potatoes for processing in the Japanese market.

The objective of this study was to investigate the physico-chemical and structural properties of the starches isolated from twelve potato cultivars which are becoming increasingly popular in Japan. In addition, the correlation among the starch properties was examined in order to gain a better understanding of this research.

MATERIALS AND METHODS

Materials. Twelve potato cultivars, Inkanomezame, Jaga Kids Purple, Jaga Kids Red, Northern Ruby, Red Andes, Shadow Queen (origin: Andes region), Cynthia, Dorothy, Sassy, Sherry (origin: France), Kita-akari (origin: Japan) and Irish Cobbler (origin: North America) were grown at the Kinki University Institute of Resource Recycling at Eniwa in Hokkaido and harvested in October 2008.

Starch granules from the twelve cultivars of potato were isolated by homogenizing peeled fresh tubers in a blender with three parts ion-exchanged water to one part tubers. The slurry was filtered through a nylon cloth and precipitated. After removing the supernatant solution, the precipitate was passed through a stainless-steel sieve (150 μm), stirred with three parts distilled water, and precipitated again. The starch granules were washed and decanted ten times with distilled water, and dried at room temperature.

Measurement of starch granule size. Starch granule size was analyzed with a laser diffraction particle size analyzer (SALD-2200, Shimadzu, Co., Ltd., Kyoto, Japan) after dispersing the starch granules in water. The granule size was measured at 25, 50 and 75% on the frequency distribution of granule size. The 50% on the frequency distribution of granule size represents the average granule size.

X-ray diffraction patterns. X-ray diffraction of the starch granules was performed using a X-ray diffractometer (Rint 2500, Rigaku, Co., Ltd., Tokyo, Japan) with copper radiation ($\text{CuK}\alpha = 1.54 \text{ \AA}$) operating at 30 kV and 26 mA. The diffractograms were obtained from $2\theta = 4-32^\circ$ with a scanning speed of $1^\circ/\text{min}$ and scanning step of 0.02° .

Measurement of phosphorus content. Starch phosphorus content was measured as inorganic phosphorus according to the method of Noda *et al.*⁴⁾ Starch samples were burnt to ashes by the wet ashing method, and the phosphorus content was determined by the vanadomolybdate method.

Measurement of iodine absorption spectra. Measurement of the iodine absorption spectra of the starch granules was performed using the method of Suzuki *et al.*⁶⁾ The starch granules were gelatinized with 1 M sodium hydroxide overnight at 5°C and neutralized with dilute acetic acid. A starch solution, containing 1 mg of starch, was added to 1 mL of 0.2% iodine-2% potassium iodine solution and filled up to 25 mL with distilled water. The absorption curves of

the starch-iodine complexes were obtained by recording the spectra from 700 to 500 nm.

The apparent amylose content was calculated using the blue value (B.V.) at 680 nm of the absorption spectra of iodine-starch complexes according to the equation specified in Takeda *et al.*⁷⁾ The average B.V.s of amylose and amylopectin isolated from potatoes reported by Suzuki *et al.*²⁾ (amylose, 1.40 and amylopectin, 0.243) were also used for calculation of the apparent amylose content in the starch.

Thermal analysis. Measurement of the thermal properties of the starch granules was conducted using differential scanning calorimetry (DSC) (DSC60, Shimadzu, Co., Ltd., Kyoto, Japan). A sample of approximately 5 mg (dry weight) was weighed and placed in an aluminum pan. Distilled water (2 parts water to 1 part starch) was added and the pan was sealed. A sealed pan, which contained 10 μL distilled water, was used as a reference. The measurements were carried out at a heating rate of $5^\circ\text{C}/\text{min}$ from 40 to 90°C . The onset temperature (T_0), the peak temperature (T_p), the conclusion temperature (T_c) and the heat of gelatinization (ΔH) were determined from the endothermic curves.

Pasting properties of the starch granules. Gelatinization, pasting, breakdown and setback of the starch suspension (4% w/w on a dry weight basis) were determined using a Rapid Visco Analyzer (RVA) (RVA-Super3, Newport Scientific Pty., Ltd., Australia) by holding at 30°C for 1 min, heating from 30 to 95°C at $5^\circ\text{C}/\text{min}$, holding at 95°C for 6 min, cooling from 95 to 50°C at $5^\circ\text{C}/\text{min}$ and holding at 50°C for 10 min.

Starch swelling power and solubility. The swelling power and solubility of the starch granules were determined by the method of Kainuma *et al.*⁸⁾ The experimental temperatures were 60 and 70°C . The swelling power was determined by heating a weighed dry starch sample in excess water and was defined as the swollen sediment weight (g) per gram of dry starch. Starch solubility was expressed as the percentage (by weight) of dissolved starch from the heated solution.

Measurement of digestibility by pancreatin. Starch digestibility by pancreatin was measured as described by Fuwa *et al.*⁹⁾ The starch granules (50 mg on a dry weight basis) were suspended in 0.5 mL of 0.02 M phosphate buffer (pH 7.2, Japan) and 1 mL of pancreatin (animal pancreas-derived, amylase activity; more than 2,800 U/g, Amano Enzyme Inc., Nagoya, Japan) solution (3% pancreatin: 0.03M sodium chloride: 0.03M calcium acetate = 2:2:1) was added. The mixture was incubated at 37°C with shaking (85 rpm/min). After the reaction time (3, 24 or 48 h), the total carbohydrate content of the reaction mixture supernatants was determined by the phenol-sulfuric acid method.

Observation by field emission scanning electron microscope (FE-SEM). Observation of the digested residue of the starch granules was performed using a field emission scanning electron microscope (FE-SEM; S-4800, Hitachi, Ltd., Tokyo, Japan). The samples were coated with evaporated osmium (coating thickness 10 nm) using an osmium coater (HPC-30type hollow cathode plasma CVD, Vacuum device Inc., Mito, Japan) and observed at 2.0 kV of accelerating voltage and 10 μA of electrical current.

Statistical analysis. The correlation coefficients among the physicochemical properties of starches from twelve

potato cultivars were calculated using SPSS 11.5J for Windows.

RESULTS AND DISCUSSION

Average granule size and X-ray diffraction patterns.

The average starch granule size ranged from 30.7 μm in Inkanomezame to 39.3 μm in Shadow Queen (Fig. 1). The starch granules from Jaga Kids Red had the widest distribution range, whereas those from Northern Ruby had the

Fig. 1. Particle size distribution of starches prepared from twelve potato cultivars.

The granule size was measured at 25, 50 and 75% on the frequency distribution of granule size. The 50% on the frequency distribution of granule size represents the average granule size. ■, 25% granule size; ●, 50% granule size; ◆, 75% granule size.

Fig. 2. X-ray diffraction patterns of starches prepared from twelve potato cultivars.

It was performed with copper radiation ($\text{CuK}\alpha = 1.54 \text{ \AA}$) operating at 30 kV and 26 mA. The diffractograms were obtained from $2\theta = 4\text{--}32^\circ$ with a scanning speed of $1^\circ/\text{min}$ and scanning step of 0.02° .

narrowest range.

The X-ray diffraction patterns of the starch granules indicated that they were all the B type (Fig. 2).

Phosphorus content and apparent amylose content.

The phosphorus content, the absorption maximum wavelength (λ_{max}) of the spectra, the B.V. and the apparent amylose content of twelve starch samples are given in Table 1. Table 2 summarizes the presence or absence of correlations among the physicochemical and structural properties of starches from twelve potato cultivars.

The phosphorus content ranged from 614 $\mu\text{g/g}$ starch (dry weight) in Sherry to 833 $\mu\text{g/g}$ starch (dry weight) in Kita-akari. The range of the phosphorus content in this study was comparable to the results of the previous studies (400–1,100 $\mu\text{g/g}$ starch).^{3,10,11} Furthermore, the phosphorus content in the four cultivars originating from France ranged from 614 $\mu\text{g/g}$ starch (dry weight) in Sherry to 687 $\mu\text{g/g}$ starch (dry weight) in Sassy, which was lower than in the samples originating elsewhere, and the result confirmed our previous report.¹⁾

The B.V. represents apparent amylose content in starch. Determination of apparent amylose content from B.V. revealed that the starch from Sherry had the highest amount of amylose (23.5%), and that from Northern Ruby had the lowest amount of amylose (16.4%) in this study. The λ_{max} of

Table 1. Phosphorus content, iodine absorption spectra and amylose content of starches prepared from twelve potato cultivars.

	Phosphorus content ^{a)} ($\mu\text{g/g}$ Starch)	$\lambda_{\text{max}}^{\text{b)}$ (nm)	Blue value ^{b)} (O.D. at 680 nm)	Amylose content ^{b)} (%)
Inkanomezame	801 $\pm$ 10.8	595	0.46	18.9
Jaga Kids Purple	679 $\pm$ 12.9	589	0.49	21.2
Jaga Kids Red	731 $\pm$ 6.3	588	0.49	21.0
Northern Ruby	762 $\pm$ 10.2	596	0.43	16.4
Red Andes	708 $\pm$ 7.9	597	0.45	18.2
Shadow Queen	795 $\pm$ 12.0	588	0.47	19.3
Cynthia	658 $\pm$ 14.5	585	0.48	20.7
Dorothy	629 $\pm$ 11.7	590	0.46	19.1
Sassy	688 $\pm$ 13.6	587	0.46	19.1
Sherry	614 $\pm$ 20.6	584	0.52	23.5
Kita-akari	833 $\pm$ 14.6	583	0.51	23.4
Irish Cobbler	737 $\pm$ 23.9	581	0.47	19.7

^{a)} Mean values $\pm$ SD ($n = 3\text{--}5$). ^{b)} Mean values ($n = 2$).

Table 2. Presence or absence of correlations among the physicochemical and structural properties of starches prepared from twelve potato cultivars.

	1	2	3	4	5	6	7	8	9	10
1 Average granular size										
2 Amylose content										
3 T_p	—**									
4 Pasting temperature	—**	+++								
5 Peak viscosity										
6 Breakdown					+++					
7 Setback					++					
8 Swelling power (70°C)		—*	—**			++				
9 Solubility (70°C)					—*	—*				
10 Digestibility (24 h)			—*	—**				+++		

** Significant difference at $p < 0.01$. * Significant difference at $p < 0.05$. +, Positive correlation; —, negative correlation.

certain kinds of potato starches in this study were inversely related to B.V. (Table 1). These starches from Northern Ruby and Red Andes had lower apparent amylose content and longer $\lambda_{\max}$, and those from Sherry and Kita-akari had a higher apparent amylose content and relatively shorter $\lambda_{\max}$ than the other starch samples. This means that the $\lambda_{\max}$ and B.V. were influenced by the chain composition of amylose and amylopectin. Further examination is needed to evaluate the real amylose content using an enzymatic and chromatographic methods^{12,13)} to clarify the composition of amylose and amylopectin.

Thermal properties by DSC and pasting properties by RVA.

The DSC-determined thermal properties of twelve starch samples are shown in Table 3. The differences between the two extreme values in these three parameters (T_o , T_p , T_c) were 3–4°C. These starches from Jaga Kids Red, Shadow Queen and Sassy had a relatively low gelatinization temperature compared to the others, whereas those from Inkanomezame, Red Andes, Cynthia and Kita-akari had a high gelatinization temperature among twelve starch samples.

The heat of gelatinization (ΔH) ranged from 12.0 J/g in Shadow Queen to 14.8 J/g in Northern Ruby. It indicated that the starch from Shadow Queen was easy to gelatinize, and it was thought that this might be due to its relatively low gelatinization temperature.

Table 3. Thermal properties by DSC of starches prepared from twelve potato cultivars.

Starch source	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Inkanomezame	63.6	66.8	73.3	13.2
Jaga Kids Purple	61.6	64.9	70.9	14.3
Jaga Kids Red	61.1	64.3	69.7	14.1
Northern Ruby	61.4	64.7	71.1	14.8
Red Andes	63.0	66.2	72.8	14.6
Shadow Queen	61.0	64.3	70.2	12.0
Cynthia	62.2	65.4	72.7	14.0
Dorothy	61.1	64.3	71.3	13.2
Sassy	60.9	63.7	69.3	14.2
Sherry	62.2	65.2	70.9	14.3
Kita-akari	63.9	66.8	72.5	13.5
Irish Cobbler	62.1	64.8	70.1	14.2

Mean values ($n = 2$).

Table 4 summarizes the pasting properties (pasting temperature, peak viscosity temperature, peak viscosity, breakdown and setback) of twelve starch samples, as determined by RVA. The pasting temperature ranged from 66.0°C in Sassy to 69.1°C in Kita-akari, and the difference between them was relatively small (3.1°C). The peak viscosity temperature differed widely among twelve starch samples; ranging from 77.8°C in Sassy to 95.0°C in Jaga Kids Purple. In addition to Jaga Kids Purple, Sherry and Kita-akari had higher peak viscosity temperatures compared to the other starch samples. These three kinds of starch had high amylose content (Table 1), and that acted on interrupting the swelling and the viscosity increase of the starch granules. Noda *et al.*³⁾ reported the same results.

There were major variations in peak viscosity and breakdown of twelve starch samples. The peak viscosity values ranged from 96 RVU in Cynthia to 241 RVU in Sassy. Similarly, the starch from Sassy had the highest breakdown value (132 RVU), Sherry had the lowest (34 RVU) and Cynthia had the second lowest (40 RVU). Noda *et al.*¹⁴⁾ indicated that the peak viscosity and breakdown of potato starch were greatly affected by starch granule size, although there was no significant correlation between the viscosity value and the granule size of the starches in this study. However, there was a negative correlation between the average granule size and the pasting temperature (Table 2, $p < 0.01$). Additionally, T_p was also negatively correlated with average granule size (Table 2, $p < 0.01$). We noticed consistently that the larger the average granule size, the lower the gelatinization temperature. So it was thought that the granule size of the potato starch had a significant influence on starch gelatinization properties.

Swelling power and solubility.

The results of the swelling power and the solubility of twelve starch samples are given in Table 5. The swelling power at 60°C exhibited minor differences among the cultivars, but there was a major difference between the highest and the lowest values of the swelling power among the cultivars at 70°C. The solubility was relatively low and showed minor differences among the different cultivars, ranging from 8.6% in Kita-akari to 14.5% in Shadow Queen at 70°C.

Lii *et al.*¹⁵⁾ and Karim *et al.*⁵⁾ explained about swelling and dissolution of starch as follows. The hydration and swelling

Table 4. Pasting properties by RVA of starches prepared from twelve potato cultivars.

	Pasting temperature (°C)	Peak viscosity temperature (°C)	Peak viscosity (RVU)	Breakdown (RVU)	Setback (RVU)
Inkanomezame	68.7	82.8	168	87	15
Jaga Kids Purple	68.2	95.0	158	55	20
Jaga Kids Red	68.0	87.6	210	110	21
Northern Ruby	66.6	81.2	175	96	16
Red Andes	68.7	89.1	163	75	18
Shadow Queen	66.1	78.1	148	81	16
Cynthia	67.4	80.2	96	40	11
Dorothy	66.4	79.3	177	98	15
Sassy	66.0	77.8	241	132	18
Sherry	68.1	90.9	103	34	16
Kita-akari	69.1	90.9	206	97	21
Irish Cobbler	66.7	78.0	201	112	17

Mean values ($n = 2$).

Table 5. Swelling power and solubility of starches prepared from twelve potato cultivars.

Starch	Swelling power		Solubility (%)	
	60°C	70°C	60°C	70°C
Inkanomezame	3.9	62.6	0.4	11.6
Jaga Kids Purple	4.5	42.6	0.4	10.9
Jaga Kids Red	4.2	53.0	0.5	9.3
Northern Ruby	4.6	71.8	1.0	10.2
Red Andes	3.6	53.5	0.5	10.7
Shadow Queen	6.9	66.3	1.0	14.5
Cynthia	3.2	53.9	0.6	11.5
Dorothy	9.1	79.5	0.7	10.5
Sassy	6.6	78.0	0.6	10.2
Sherry	3.5	47.9	0.6	13.6
Kita-akari	3.5	45.1	0.3	8.6
Irish Cobbler	5.6	87.2	0.3	9.3

Mean values ($n = 2$).

of the potato starch during heating reflected the magnitude of the interaction between the starch chains within the amorphous and crystalline domains. In addition, they explained that the extent of the interaction was affected by the amylose to amylopectin ratio and the molecular weight-distribution of amylose and amylopectin, resulting in a variation in the swelling power and solubility. In this study, the swelling power at 70°C of the starch granules from twelve potato cultivars was negatively correlated with the apparent amylose content (Table 2, $p < 0.05$). It is thought that the swelling of the starch was limited by the existence of amylose.

In addition to the amylose content, the swelling power at 70°C was negatively correlated with the pasting temperature (Table 2, $p < 0.01$), and positively correlated with the breakdown (Table 2, $p < 0.05$). It was considered that the starch that easily gelatinized had a greater tendency for swelling.

The solubility at 70°C was negatively correlated with the peak viscosity and the breakdown (Table 2, $p < 0.05$, respectively).

Digestibility and observation by FE-SEM.

The digestibility of twelve starch samples are presented in Fig. 3. It was ranged from 12.4% in Jaga Kids Red to 25.3% in Cynthia after 48 h exposure to pancreatin. The digestibility of the starch granules from Northern Ruby, Kita-akari and Irish Cobbler, after 48 h exposure to pancreatin, was also higher than that of the starch granules from other cultivars.

It was reported that the digestibility of starch granules by amylase was correlated with several factors, such as granule size,^{16–18)} amylose content,^{19–20)} phosphorus content¹⁹⁾ and gelatinization properties.^{19,21)}

It was reported that small starch granules from several kinds of potato cultivars and sweet potato cultivars were found to be digested faster than large starch granules.^{16,21)} Kainuma *et al.*¹⁶⁾ explained that with respect to the average granule size of many kinds of starch granules isolated from the same plant species, the surface areas of the starch granules per unit weight increased with a reduction in the starch granule size, making it easier for amylase to attack the starch granules. In this study, the starch granules from Northern Ruby, Cynthia and Kita-akari, having a relatively

Fig. 3. Time courses for digestion by pancreatin of starches prepared from twelve potato cultivars.

After the reaction time (3, 24 or 48 h), the total carbohydrate content of the reaction mixture supernatants was determined by the phenol-sulfuric acid method. Reaction duration: ■, 3 h; ■, 24 h; □, 48 h.

small granular size at 75% on the frequency distribution of the granule size, had a higher digestibility than those from other cultivars.

With respect to the apparent amylose content, these starches from Northern Ruby and Irish Cobbler had a relatively low apparent amylose content (16.4–19.7%) and relatively high digestibility. In contrast, those from Jaga Kids Purple, Jaga Kids Red and Sherry had a relatively high apparent amylose content (21.0–23.5%) and low digestibility.

It was reported that the phosphate-bound sites of potato amylopectin were preferentially digested by alpha-amylase.²²⁾ Furthermore, it was reported that the extremely small potato starch granules contained 1.5 times the phosphate of the large granules.¹⁴⁾ These reports confirm the aforementioned description about the relationship between starch granule size and digestibility. In this study, these starches from Inkanomezame and Kita-akari which had relatively small granule size had high phosphorus content, but the granules size and phosphorus content were not correlate with digestibility.

Juliano and Perez *et al.*¹⁹⁾ observed a negative correlation between digestibility and photometrically determined gelatinization temperature of rice starch. Moreover, Noda *et al.*²¹⁾ found that ΔH had an influence on the digestibility of thirty kinds of sweet potato starch, although T_0 had no effect. They demonstrated that the higher the crystalline structure content, the lower the amylase digestibility of the sweet potato starch. We found similar results in this study, in that the digestibility of the potato starches was negatively correlated with the starch gelatinization temperature (T_p and pasting temperature) (Table 2, $p < 0.05$ and $p < 0.01$), and positively correlated with the swelling power (70°C) (Table 2, $p < 0.01$).

Fig. 4. Continued on next page.

Fig. 4. Scanning electron micrographs of raw potato starch granules and their digested residue by pancreatin for 48 h.

The samples were coated with evaporated osmium (coating thickness 10 nm) and observed at 2.0 kV of accelerating voltage and 10 μA of electrical current. Magnification and % degradation: (a), Irish Cobbler (raw starch), $\times 1,000$; (b), Inkanomezame, $\times 1,100$, 15.0%; (c), Northern Ruby, $\times 10,000$, 20.4%; (c)-1, enlarged view of (c), Northern Ruby, $\times 50,000$; (d), Cynthia, $\times 30,000$, 25.3%; (d)-2, enlarged view of (d), Cynthia, $\times 100,000$; (e), Kita-akari, $\times 5,000$, 21.9%; (e)-3, enlarged view of (e), Kita-akari, $\times 50,000$; (f), Jaga Kids Red, $\times 6,000$, 12.4%; (g), Northern Ruby, $\times 5,000$, 20.4%; (h), Jaga Kids Red, $\times 5,000$, 12.4%; (h)-4, enlarged view of (h), Jaga Kids Red, $\times 50,000$; (i), Jaga Kids Red, $\times 5,000$, 12.4%; (i)-5, enlarged view of (i), Jaga Kids Red, $\times 20,000$; (j), Sherry, $\times 5,000$, 15.3%; (j)-6, enlarged view of (j), Sherry, $\times 15,000$.

Figure 4 shows electron micrographs of the raw potato starch granules and their digested residue, respectively. It was not found the particular differences in twelve kinds of potato starches, and the differences were inconsistent with the cultivars.

The raw potato starch granules had a smooth surface and showed unique shapes in general (Fig. 4(a)). After digestion for 48 h, the starch granules showed surface erosion; the small granules were particularly affected (Fig. 4(b)). The starch granules attacked by pancreatin were relatively rough, with fine wrinkles on the surfaces. It was thought that these wrinkles developed sharp canals, which enlarged and merged on the surface (Figs. 4(c) and (f)). The areas circled by canals were eroded and sunken (Figs. 4(d), (h) and (i)). These holes of endo-corrosion sunken into the granules were made up of numerous concentric terraces (Figs. 4(g), (h), (h)-4, (i)-5, (j) and (j)-6). These layered structures appeared to be structures of stacked crystalline hard shells and semi-crystalline soft shells in layers as described by Gallant *et al.*²³⁾ Furthermore, structures with spherical roughness were observed at high magnification (Figs. 4(c)-1, (d)-2, (e)-3 and (h)-4). They were also very similar to the blocklet structures of residual potato starch granules digested by alpha-amylase demonstrated by Gallant *et al.*²³⁾ We got the similar results to our previous report¹⁾ on the other ten kinds of potato starches. These results of our research are thought that they will help further research to elucidate the structure of potato starch granules.

This article revealed the physicochemical and structural properties of starch isolated from twelve cultivars of potato which are becoming increasingly popular in Japan. These results of this study point to the need for similar research in the future on other potato cultivars cultivated under identical conditions to expand our understanding of characteristics of potato starches.

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