## Characteristics of Java Taro Starches and Physical Properties of Acid- and Heat-treated Taro Starches

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Abstract: Characteristics of taro corm starches of four kinds were studied as follows: Java and Celebes were harvested in Indonesia; Uhan in China; Satoimo in Japan. In addition, effects of acid- and heat-treatments on physical properties of native Java starch were examined. The particle size of Java starch was in the range of  $3-17 \mu$ m with about 50% distribution of size of  $9-13 \mu$ m. From SEM observation, the size of starch granules for Java, Celebes, Uhan and Satoimo was 3.0-13.0, 1.0-4.8, 1.5-5.8 and  $0.5-3.4 \mu$ m, respectively. The native Java starch was mostly spherical, but some portions of the surface were square with a larger size than for other starch samples. The amylose content of the Java sample determined by the blue value method was 20.5% and number-average degree of polymerization was 880 and 2920 for amylose and amylopectin, respectively. The average chain length of amylose or amylopectin was 17 or 19, respectively. From the result of X-ray diffraction, the crystalline pattern of Java starch was A type. As for DSC results, Satoimo starch was gelatinized at a higher temperature, while the enthalpy was lower than those of other samples. In contrast, starch of Celebes or Uhan was gelatinized at lower temperature, as compared with native Java starch. The gelatinization enthalpy of heat-treated Java starch at  $50^{\circ}$ C showed the highest value among all samples. But, physical properties (DSC and SEM) of acid-treated Java starch were not distinctly different from those of native Java starch.

Key words: taro corm, starch, gelatinization, thermal property, scanning electron microscopy (SEM)

Taro corm, one of the root vegetables favored for the peculiar texture, has been used like potato tubers for boiled cuisine in Japan. Boiled taro corm shows various kinds of texture, such as the smooth mouth feel and stickiness, which are quite different from those of the potato tuber. These properties are considered to be caused by the mixture of viscous substances derived from polysaccharide and gelatinized starch after boiling. The degree of stickiness of taro corm is affected by the cooking conditions, such as additives, heating temperature and cooking methods.<sup>1)</sup> The peculiar sliminess of taro corm is quite similar to that of yam tuber, but the degree of enzyme digestion for taro corm starch is quite different from that of yam tuber starch.<sup>2,3)</sup> Characteristics of the starch of Japanese taro corms during different growing periods were determined from the viewpoints of the granule size, thermal properties, amylose contents and X-ray.<sup>3)</sup> Recently, taro corm has been imported from Asian countries as a peeled, freeze-dried material for the convenience of consumers. But, studies on the characteristics of imported taro corms have been rarely reported. In addition, many kinds of modified starch have been used in various fields in Japan. Among them, an acid-treated starch, which is called as Lintner starch or Nageli starch, contains some soluble starches with small molecular size and is used for gluing film or fiber and production of fried foods or sweets.<sup>4)</sup> On

the other hand, heat treatment of starch with warm water at lower temperature than that of gelatinization has been studied to change the thermal property and swelling or soluble power of starch granules.<sup>5)</sup> Therefore, it is important to make clear the characteristics of acid- and heattreated taro starches for practical application in the future. In this study, characteristics of starch in taro corms harvested in foreign countries were evaluated to compare them with Japanese taro corms, and the effects of acidand heat-treatments on the properties of taro starch were also studied.

### MATERIALS AND METHODS

*Taro corm.* Four kinds of taro corms cultivated in foreign countries and Japan were used to determine the characteristics of starch. Taro corm *Java* and *Celebes* were harvested in Indonesia; *Uhan* in China; and *Satoimo* in Japan.

**Preparation of starch granules.** Taro corms were washed to remove surface soil, and then peeled manually with a knife. The samples were cut into small pieces before cutting with an electric food processor equipped with a 0.1-cm ultra thin blade. Taro samples thus cut were suspended in 10-fold 0.1% NaOH aqueous solution for 48 h at 5 °C, then mixed for 2 h with a stirrer, and then the supernatant was removed by decantation. This alkaline washing procedure was repeated until the brown color of the supernatant disappeared. Starch granules thus precipi-

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tated were centrifuged at  $5000 \times g$  for 10 min at 4 °C and the starch samples were neutralized with 1 M HCl, followed by sieving through 125–400 meshes. The remaining starch samples on the sieve were collected and suspended in a mixture of deionized water and 1-pentanol (3: 1, v/v). The mixture was stirred for 2 h at 5 °C and allowed to stand for 2 h. The precipitate was collected by centrifugation (2800× g for 10 min at 4 °C) until the layer of 1-pentanol became clear. The starch sample was washed with ethanol and ether, dried at room temperature (RT) and stored in a desiccator.

*Separation of amylose and amylopectin.* Amylose and amylopectin were fractionated using the procedure as reported by Takeda *et al.*<sup>6</sup> Taro starch (10 g dry weight) prepared as described above was used for the separation. The precipitate was used for the following preparation of amylose, and the supernatant for amylopectin.

The precipitate was collected by centrifugation (10,000  $\times$  g for 20 min, 4°C, named high-speed centrifugation), then the precipitate was suspended in 400 mL of deionized water at 70-80°C for 10 min, and 100 mL of 1butanol and 500 mL of deionized water were added. The suspension was refluxed by heating for 1 h, cooled to RT, and stored at 4°C overnight. The precipitate (crude amylose) obtained by high-speed centrifugation was suspended in deionized water (480 mL) at 70-80°C for 10 min. Then the suspension was immediately centrifuged at  $100,000 \times$ g for 1 h at 45°C. To the supernatant were added 1butanol (100 mL) and deionized water (500 mL) for refluxed heating under nitrogen bubbling for 10 min, and then it was filtered through a glass filter (G-5). The filtrate was added to the 1-butanol (100 mL) and boiled again under reflux conditions for 5 min, and then cooled at 4°C overnight. After high-speed centrifugation of the suspension, the precipitate was dissolved in 400 mL of deionized water at 70-80°C for 10 min, and refluxed again for 10 min in 1-butanol (100 mL) and deionized water (500 mL). These procedures were repeated twice. The amylose-1-butanol complex was collected by highspeed centrifugation. The precipitate was washed with ethanol, then filtered through a glass filter (G-2), washed with ether, and then dried in vacuo at RT.

As for the separation of amylopectin, three-fold mixtures of deionized water, 1-butanol and 3-methyl-1butanol (18:1:1, v/v/v) were added to the amount of supernatant as mentioned above. After addition of 3-fold ethanol to the mixture, the solution was kept at 5°C overnight. The precipitate was collected by high-speed centrifugation, and then the precipitate was passed through a glass filter under reduced pressure, washed with ethanol and ether, and stored in a desiccator.

**Particle size distribution of starch granules.** The particle size distribution of native Java taro starch granules was examined by a particle-size analyzer (Horiba, LA-700).<sup>7</sup>

Determination of blue value (BV) for starch, amylose and amylopectin.<sup>8)</sup> Ten milligrams of starch, amylose and amylopectin obtained from *Java* taro corm was completely dissolved in 2.0 mL of 0.5 M NaOH aqueous solution. After neutralization with 1.0 M HCl and distillation with deionized water, amylose content (AC) was calculated according to the following formula:<sup>8)</sup>

$$AC = \{BV (starch) - BV (amylopectin)\} \\ / \{BV (amylose) - BV (amylopectin)\} \\ \times 100 (\%)$$

Number-average degree of polymerization (DPn) and average chain length (CL) of amylose and amylopectin.

Number-average degree of polymerization (DPn) and average chain length (CL) of amylose or amylopectin were determined by the modified Park-Johnson<sup>9)</sup> and rapid Smith degradation methods,<sup>10)</sup> respectively.

*X-ray diffraction of starch granules.* X-ray diffraction was performed with an X-ray diffractometer, the Rint-2000 (Rigaku Denki, Tokyo), according to the same methods as reported.<sup>7,11)</sup>

Acid- and heat-treatments of native taro corm starch.

The starch granules prepared from Java variety were modified by acid- and heat-treatments as follows. Prior to the treatments, starch samples (20 g) were suspended in 0.075 M NaOH aqueous solution (250 mL). After vigorous shaking of the suspension at room temperature to obtain homogeneously swelled and dispersed starch granules, the suspension was neutralized with 0.5 M HCl and filled up to make 350 mL with distilled water. To the suspension was added an equal volume of 0.15 M HCl. Then an aliquot (100 mL) of the suspension was acid-treated at 25, 30, 40 and 50°C for 5 h. After the acid-treatment, each suspension was neutralized with NaOH, and filtered through a glass filter (G-4). The residual starch granules were repeatedly washed with distilled water, and then the starch granules were dried at room temperature and stored in a desiccator over silica gel. As for the preparation of heat-treated starch granules, an aliquot (about 100 mL each) of the neutralized starch suspension above was treated at 30, 40 and 50°C for 2 h. After the heattreatment, the suspension was filtered through the glass filter and the starch granules were stored in a desiccator as described above. These dried starch samples were used for the following experiments.

*Thermal properties of starch granules.* Thermal properties of starch granules prepared from taro corms were determined using differential scanning calorimetry (DSC). DSC was done with a Shimadzu DSC instrument (Model DSC-50, Tokyo) as reported previously.<sup>12,13)</sup>

*Scanning electron microscopy (SEM).* The appearance and average particle size of starch granules of taro corms were observed by SEM (Hitachi Model S-800) after osmium fixation. The SEM procedures were the same as those as reported previously<sup>13,14)</sup> and the granular size was determined from 10 observations for each starch sample.

## **RESULTS AND DISCUSSION**

# Characteristics of taro corm starch produced in Indonesia.

Appearance of starch granules of Java taro was not constant and the granular size of Java starch was in the range of  $3-17 \ \mu m$  with about 50% distribution of size of  $9-13 \ \mu m$ , as shown in Fig. 1. As the average particle size of starch granules prepared from two kinds of Japanese taro corm was reported to be  $1.4-2.0 \ \mu m$  having about



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Fig. 1. Distribution of diameter of starch granules prepared from native *Java* taro corm.

(A) distribution of starch granules, (B) light-microscopic observation of taro starches.

40-50% distribution of size of 1-2  $\mu$ m,<sup>15</sup> the starch granules of Java taro were larger than those of Japanese taro. When the starch granules became more susceptible to enzyme digestion (hog pancreatin), the blue value of starches fell.<sup>15)</sup> As the blue values of starch prepared from Japanese taro corms were 0.250-0.292,<sup>15)</sup> and the blue value of Java taro corms in the present study was higher than that of Japanese taro corms, the Java starch might be more difficult to decompose with the enzyme, as compared with Japanese taro corm starch. The amylose content of the Java sample was 20.5% and the degree of polymerization was 880 and 2920 for amylose and amylopectin, respectively. The average chain lengths of amylose and amylopectin were 17 and 19, respectively (Table 1). X-ray diffraction of Java starch showed major peaks at d-spacing of 0.58, 0.51 and 0.38 nm (Fig. 2), and these peaks were characteristic of the A-type crystal pattern as reported.<sup>16)</sup> The X-ray diffraction pattern was similar to that of Japanese taro corm (Takenokoimo) as reported by Sugimoto et al.<sup>15)</sup>

#### DSC results.

The gelatinization temperatures and enthalpies of starch of various taro corms were measured using DSC (Table 2). *Satoimo* starch of Japan was gelatinized at higher temperature, while the enthalpy was lower than for that pro-



Fig. 2. X-ray diffraction of native Java starch.

 Table 1.
 Characteristics of starch, amylose and amylopectin of native Java taro corm produced in Indonesia.

Sample	Starch	Amylose	Amylopectin
Blue value	0.324	1.230	0.090
Amylose content (%)	20.5	_	—
DPn	_	880	2920
CL	_	17	19
NC	—	52	155

DPn, number-average degrees of polymerization; CL, average chain length; NC, average number of chains per molecule. The value of NC was calculated from (DPn/CL-1).

Table 2. DSC data for various taro corm starches.

Sample	Ti	Tp	Tr	$\Delta H$
		(°C)		(J/g)
Java (Native)	73.5	75.9	79.9	15.4
AT (25)	72.5	74.9	79.4	13.6
AT (30)	72.7	75.1	79.8	14.3
AT (40)	72.4	74.8	79.5	14.4
AT (50)	72.6	74.9	79.4	14.3
HT (30)	72.5	75.1	79.5	14.9
HT (40)	72.4	74.9	79.6	14.7
HT (50)	72.8	75.3	80.2	17.1
Celebes	69.7	73.3	78.7	15.1
Uhan	68.9	72.5	76.8	13.0
Satoimo	78.0	80.8	85.2	12.4

*T*<sub>i</sub>, initial temp.; *T*<sub>P</sub>, peak temp.; *T*<sub>r</sub>, recovery temp.;  $\Delta H$ , enthalpy. AT and HT are acid- and heat-treatments, respectively. The numbers in parenthesis are temperatures for treatments.

duced in Indonesia, irrespective of the kinds of taro species. This result agreed with the results of the thermal properties of Japanese taro corm (*Takenokoimo*) as reported by Sugimoto *et al.*<sup>15)</sup> Starch of *Celebes* or *Uhan* showed different gelatinization properties from native *Java* starch. In brief, starch of *Celebes* or *Uhan* was gelatinized at lower temperature, as compared with native *Java* starch. In particular, *Uhan* showed the lowest initial, peak and recovery temperatures of all samples. The initial, peak and recovery temperatures for gelatinization of acidtreated *Java* starch were not distinctly different from those of native *Java* starch, irrespective of the treatment temperature. However, the gelatinization enthalpy ( $\Delta H$ ) of heat-treated *Java* starch at 50°C showed the highest value among all samples. Regarding the gelatinization



A, Java; B, Celebes; C, Uhan; D, Satoimo.



**Fig. 4.** SEM images of acid- and heat-treated *Java* starches. E, acid-treated *Java* starch; F, heat-treated *Java* starch. Treatment temperature of E and F: 50°C.

temperature of starch, the initial temperature for gelatinization of potato starch was lower when the temperature for the cultivation was lower, and the thermal properties of starch were controlled by the cultivation temperature.<sup>17)</sup> Therefore, the different thermal properties of taro corm starches of the present four kinds were assumed to be dependant on differences in the cultivation conditions.

## SEM results.

Appearance or shapes of starch granules of various taro species were observed by SEM (Figs. 3 and 4). The native *Java* starch was mostly spherical, but some portions of the surface of the taro starch were square (Fig. 3A). The granular size of native Java starch  $(3.0-13.0 \ \mu m)$  was larger than those of Celebes  $(1.0-4.8 \ \mu m)$ , Uhan  $(1.5-5.8 \ \mu m)$  and Satoimo starches  $(0.5-3.4 \ \mu m)$  (Fig. 3B, C and D). Furthermore, the shape of starch granules for these taro corms was not round, and many wrinkled or square surfaces of starch granules were observed. The appearance was quite different from that of native Java starch. After acid-treatment at 50°C, the size of starch granules tended to increase slightly, as compared with the native Java starch granules. But, distinct difference in the shape of granules could not be observed from

SEM (Fig. 4E). The appearances of starch granules treated with heat were similar to those without heating, and the starch granules still contained somewhat square granules, like native or acid-treated *Java* starch (Fig. 4F).

Amylose content of potato starch increased more in the case of larger starch granules than the smaller ones.<sup>18)</sup> In addition, moisture sorption of starch, which was obtained from waxy barley flour, showed negative correlation to the granular size, and the gelatinization enthalpy of starch and DPn of amylopectins also decreased in the order of large, medium and small granules.7,19) Moreover, characteristics (amylose content, DPn, CL and gelatinization temperature or enthalpy) of starch in non-waxy barley flour varied or differed with the size of granules.<sup>20)</sup> These facts suggest that the differences in the shape or size of starch granules affect the characteristics of starch. Although there were no clear differences in properties between the acid- or heat-treated starch and native starch, the distinct differences in particle size or shape of Java starch from other taro corms might affect the thermal properties. Therefore, more detailed studies on the characteristics of these native taro corms and also on effective treatments before cooking or processing are required to improve the quality of frozen foods made from taro corms.

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## ジャワ産サトイモ澱粉の特性と酸および 熱処理澱粉の物性について

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国内産 (Satoimo), 外国産 (インドネシアの Java, Celebes, 中国の Uhan) の4種のサトイモ澱粉の特性につ いて調べた.また、Java 澱粉には熱処理と酸処理を行い、 澱粉の熱特性に及ぼす影響についても検討した. Java 澱 粉の粒径分布範囲は 3-17μm となり最多粒は 9-13μm で 50%の分布率であった. また SEM 観察の結果, Java, Celebes, Uhan および Satoimo 澱粉の粒径は、それぞれ、 3.0-13.0, 1.0-4.8, 1.5-5.8 および 0.5-3.4µm であった. Java 澱粉の形状はほぼ球形であったが、一部凹凸のある 表面も観察され、他の澱粉試料よりも大きかった.また、 青価によるアミロース含量は20.5%であり、アミロース とアミロペクチンの重合度はそれぞれ,880と2920,ま た、その平均鎖長はそれぞれ17と19,X線結晶図形はA 型であった.澱粉の糊化温度は,Satoimo 澱粉は他の澱粉 よりも高温かつ低熱量で, Celebes および Uhan 澱粉は Java 粉より低温で糊化する傾向を示した.一方,50℃で 熱処理を行った Java 澱粉の糊化熱量は全ての澱粉試料の 中で最も高い値を示した.しかしながら,酸処理を行っ た Java 澱粉の DSC と SEM による物性結果は、未処理の Java 澱粉の場合とほぼ同様であり、両者に顕著な差はみ られなかった.