

# Factors affecting the digestibility of raw and gelatinized potato starches

T. Noda<sup>a,\*</sup>, S. Takigawa<sup>a</sup>, C. Matsuura-Endo<sup>a</sup>, T. Suzuki<sup>a</sup>, N. Hashimoto<sup>a</sup>,  
N.S. Kottarachchi<sup>b</sup>, H. Yamauchi<sup>a</sup>, I.S.M. Zaidul<sup>a</sup>

<sup>a</sup> National Agricultural Research Center for Hokkaido Region, Shinsei, Memuro, Hokkaido 082-0071, Japan

<sup>b</sup> Obihiro University of Agriculture and Veterinary Medicine, Inada-cho, Obihiro, Hokkaido 080-8555, Japan

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## Abstract

The enzymatic digestibilities of raw and gelatinized starches in various potato starches, as well as sweet potato, cassava, and yam starches, were estimated, along with other starch properties, such as the phosphorus content, median granule size, and rapid visco analyzer (RVA) pasting properties. Furthermore, correlation coefficients were calculated between the hydrolysis rates (HR) by amylase and other starch quality parameters. A larger granule size was closely associated with a lower HR in raw starch, while the HR in gelatinized starch did not correlate with the median granule size. An increase in phosphorus content resulted in a definitely lower HR in raw starch and tended to decrease the HR in gelatinized starch for the composite of potato and other starches. In contrast, no correlation coefficients of the phosphorus content with the HRs in raw and gelatinized starches were observed within potato starches. Starches with higher peak viscosity and breakdown showed a lower HR in raw starch, while few or no effects of these RVA parameters on the HR in gelatinized starch were observed for the composite of potato and other starches or among potato starches, respectively.

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## 1. Introduction

Starch is the major source of available energy-producing carbohydrate in the human diet. Starch that avoids hydrolysis by amylolytic enzymes in the small intestine and passes to the large bowel for fermentation is defined as resistant starch (RS) (Thompson, 2000). RS is thought to be desirable in human health, as it has functional properties similar to fermentable dietary fibres. The content of RS is related to the rate of starch digestion by amylolytic enzymes. Starch digestibility is largely ascribed to the plant source and is dependent on the physicochemical properties of the starch. Furthermore, it is also influenced by processing and storage conditions. As most starchy foods are cooked before consumption, the enzymatic digestibility of gelatinized starch is a critical property in the food industry.

Additionally, raw or nearly raw starch is sometimes utilized in food processing. Therefore, estimating the digestibility of raw starch is also meaningful when making value-added food products. The potato is an important starch crop in Japan. In 2004, 38% of the total net production was utilized for starch production. It is generally accepted that investigation of the enzymatic digestibility of potato starches has led to their high utilization in the food industry. In potato starch, raw starch granules have a larger granule size and typical B-crystalline structure, as studied by X-ray diffraction. Tests of in vitro hydrolysis by amylolytic enzymes have indicated extremely low digestibility of raw potato starch (Englyst, Kingman, & Cummings, 1992; Fuwa, Nakajima, & Hamada, 1977; Kingman & Englyst, 1994; Sandstedt, Strahan, Ueda, & Abbot, 1962). Compared to other starches, potato starch has a manifestly higher concentration of covalently bound phosphate (Hizukuri, Tabata, & Nikuni, 1970). Starch phosphate has a large impact on the starch pasting

\* Corresponding author. Tel.: +81 155 62 9278; fax: +81 155 62 2926.  
E-mail address: [noda@affrc.go.jp](mailto:noda@affrc.go.jp) (T. Noda).

characteristics. Particularly, higher phosphorus in potato starch is associated with higher peak viscosity (Noda et al., 2004a,b, 2006; Wiesenborn, Orr, Casper, & Tacke, 1994). As amylolytic enzymes are incapable of bypassing the phosphorylated glucosyl residue, phosphoryl-oligosaccharides are released from the digestion of potato starch with amylase (Abe, Takeda, & Hizukuri, 1982; Kamasaka et al., 1995; Takeda, Hizukuri, Ozono, & Suetake, 1983). It is likely that higher phosphorus content in potato starch might reduce the enzymatic digestibility of gelatinized starch, as well as raw starch. Potato starch properties, including the granule size, phosphorus content and pasting properties, differ to some extent according to cultivars and environmental factors (Noda et al., 2004a,b, 2006; Wiesenborn et al., 1994). However, experimental data on starch digestibility are not available for many types of potato starches.

The objective of this study was to assess the variation in the enzymatic digestibility of different potato starches. Isolated potato starches, which vary widely in granule size, phosphorus content and RVA pasting properties, as well as other representative tuber and root starches, were selected for the evaluation of the enzymatic digestibility of gelatinized and raw starches. Additionally, the effects of starch quality parameters, median granule size, phosphorus content and RVA pasting properties on enzymatic digestibility were determined.

## 2. Materials and methods

### 2.1. Starch samples

Details about the profiles of tuber and root starches examined in this study are given in Table 1. Fifteen potato samples, consisting of 14 cultivars, were grown at the experimental farm at the National Agricultural Research Center for the Hokkaido Region (NARCH) at Memuro, Hokkaido. Starches were isolated from these potato samples by a previously reported method (Noda et al., 2004b). Seven potato starch samples, which were derived from four cultivars and were produced by the Jinnno Starch Co., Sarabetsu, Hokkaido, were purchased and also used for this experiment. Four differently sized potato starch samples, which were produced by air classification at the Nakashari Starch Factory, Shari Agricultural Cooperative Association, Shari, Hokkaido, Japan, were used in this study. Two different cultivars of sweet potato samples were grown at the experimental farm at the National Institute of Crop Science (NICS), Tsukuba, Ibaraki. Starches were isolated from these sweet potato samples using a previously described method (Noda, Takahata, Nagata, & Monma, 1992). One sweet potato starch was purchased from Haraigawa Starch Factory, Kimotsuki Agricultural Cooperative Association, Kanoya, Kagoshima, Japan. Cassava starch, isolated from cassava tubers grown in Thailand, was obtained from Nippon Starch Chemical Co., Ltd., Osaka, Japan. Yam starch was isolated from fresh yam tubers obtained from Kawani-

Table 1  
Profiles of tuber and root starches examined

No.	Botanical source	Cultivar	Year	Origin
1	Potato	Konafubuki	2005	NARCH
2	Potato	Setoyutaka	2005	NARCH
3	Potato	Shadow Queen	2005	NARCH
4	Potato	Oojiro	2005	NARCH
5	Potato	Kitamurasaki	2005	NARCH
6	Potato	Hokkaikogane	2005	NARCH
7	Potato	Benimaru	2005	NARCH
8	Potato	Nothern Ruby	2005	NARCH
9	Potato	Touya	2005	NARCH
10	Potato	Benimaru	2004	NARCH
11	Potato	May Queen	2004	NARCH
12	Potato	Touya	2004	NARCH
13	Potato	Inca-no-mezone	2004	NARCH
14	Potato	Norin No. 1	2004	NARCH
15	Potato	Toyoshiro	2004	NARCH
16	Potato	Hokkaikogane	2005	Jinnno Starch Co.
17	Potato	Norin No. 1	2005	Jinnno Starch Co.
18	Potato	Benimaru	2005	Jinnno Starch Co.
19	Potato	Hokkaikogane	2004	Jinnno Starch Co.
20	Potato	Eniwa	2004	Jinnno Starch Co.
21	Potato	Norin No. 1	2004	Jinnno Starch Co.
22	Potato	Benimaru	2004	Jinnno Starch Co.
23	Potato	Unknown	2005	Nakashari Starch Factory
24	Potato	Unknown	2005	Nakashari Starch Factory
25	Potato	Unknown	2005	Nakashari Starch Factory
26	Potato	Unknown	2004	Nakashari Starch Factory
27	Sweet potato	Purple sweet road	2002	NICS
28	Sweet potato	Healthy red	2002	NICS
29	Sweet potato	Unknown	2004	Haraigawa Starch Factory
30	Cassava	Unknown	2005	Nippon Starch Chemical Co., Ltd.
31	Yam	Unknown	2005	Kawanishi Agricultural Cooperative Association

shi Agricultural Cooperative Association, Obihiro, Hokkaido, Japan, as reported previously (Zaidul, Norulaini, Omar, Yamauchi, & Noda, 2007).

### 2.2. Starch analysis

Several starch characteristics, namely, the phosphorus content, granule size distribution, and RVA paste viscosity at 4% starch suspension, were determined, as previously reported (Noda et al., 2004b). The hydrolysis rate (HR) was determined by the modified method of Englyst et al. (1992). For the HR analysis in raw starch, starch granules (0.4 g) were weighed in 50 ml screw-cap tubes and suspended in 20 ml of a 0.1 M acetate buffer (pH5.2). Then, 5.0 ml of an enzyme solution containing 633 mg of pancreatin from porcine pancreas (P-1500, Sigma Chemical, St. Louis, MO), 2.86 mg of amyloglucosidase from *Rhizopus* (A-0273, Sigma Chemical, St. Louis, MO), and 2.64 mg of invertase, grade VII, from bakers' yeast (14504) were

added, thoroughly mixed, and kept at 37 °C with stirring. After 2 h of incubation, 0.5 ml samples of the reaction mixture were taken and placed into 20 ml of 66% ethanol to terminate the enzyme reaction. After centrifugation at 1500g for 2 min, the glucose content in the supernatant was measured using a glucose oxidase peroxidase assay. The HR was calculated from the released glucose after 2 h of incubation. For the trial in gelatinized starch, before adding pancreatin, amyloglucosidase, and invertase, the tube containing the starch suspension was kept at 80 °C for 20 min with stirring, heated in a boiling-water bath for 15 min, and then incubated at 37 °C. Other procedures were similar to those used in the starch gelatinization trial.

### 2.3. Statistical analysis

The phosphorus content, granule size distribution, RVA analysis and enzymatic digestibility were determined in duplicate. Each value was the mean of duplicate measurements. The correlation coefficients between the enzymatic digestibility and three parameters of other properties were calculated in 26 potato starches, as well as in 31 tuber and root starches.

## 3. Results

The starch quality parameters, phosphorus content, and median granule size, as well as the peak viscosity and breakdown, as determined by RVA, in potato, sweet potato, cassava, and yam starches, are provided in Table 2. The phosphorus content ranged from 416 to 1118 ppm in 26 potato starches, the average value being 770 ppm, while manifestly small values (97–231 ppm) were observed in other tuber and root starches. The data of the median granule size reflected a large difference (14.0–44.7 µm) among potato starches and a small difference (15.7–22.8 µm) among other tuber and root starches. As expected, lower values were observed for three small-sized potato starches (14.0–22.5 µm; obtained by air classification) than for other potato starches (29.7–44.7 µm). The results of RVA at 4.0% starch concentration indicated that all potato starches exhibited manifestly higher peak viscosity (157–423 RVU) than did other tuber and root starches (40–87 RVU). Similarly, a definitely higher breakdown was observed in all potato starches (63–295 RVU) than in other tuber and root starches (2–12 RVU). The HR was calculated from the extent of digestion after 2 h at 37 °C by amyolytic enzymes using raw and gelatinized starches prepared from potato, sweet potato, cassava and yam, and the results are shown in Fig. 1. In general, the HR in raw potato starches was lower, ranging from 0.9% to 9.8%. A relatively higher HR (7.2–9.8%) was found in three small-sized potato starches. Raw yam starch also had a lower HR (3.9%), while sweet potato raw starches had higher HRs (16.8–24.5%). Among the raw starch samples used, the highest HR (36.2%) was found in cassava

Table 2

Phosphorus content, median granule size, peak viscosity and breakdown of tuber and root starches

No.	Phosphorus content (ppm)	Median granule size (µm)	Peak viscosity (RVU)	Breakdown (RVU)
1	753	39.1	320	174
2	533	33.8	279	147
3	812	31.6	354	207
4	538	33.0	257	133
5	954	38.3	374	238
6	918	39.0	423	295
7	501	39.5	281	157
8	850	39.0	348	219
9	986	29.8	401	265
10	669	43.1	287	156
11	649	39.1	306	185
12	1118	29.7	391	246
13	894	31.2	310	174
14	670	32.7	240	89
15	779	31.9	341	198
16	840	39.7	285	161
17	541	34.1	193	84
18	599	44.4	241	140
19	947	39.0	270	157
20	841	38.0	302	199
21	416	34.4	157	63
22	625	44.7	233	133
23	656	41.5	312	199
24	900	22.5	263	141
25	992	14.4	206	74
26	1050	14.0	215	79
27	138	16.0	45	2
28	113	16.3	48	2
29	231	19.4	40	6
30	97	15.7	45	12
31	166	22.8	87	4

starch. With the gelatinization process, the HR increased dramatically in all starch samples used. Gelatinized potato, cassava, and yam starches contained HRs of 53.3–67.4%, 60.6% and 61.6%, respectively, whereas slightly higher HRs (66.3–74.9%) were recorded for gelatinized sweet potato starches. The correlation coefficients were calculated, to examine the relationship between the starch quality parameters, such as median granule size, phosphorus content and RVA pasting properties, and the HR in 31 tuber and root starches (Table 3). The results of the HR of both raw and gelatinized starches were included. The HR in raw starch was significantly and negatively correlated with all starch quality parameters, phosphorus content ( $r = 0.650$ ,  $P < 0.01$ ), median granule size ( $r = 0.697$ ,  $P < 0.01$ ), peak viscosity ( $r = 0.791$ ,  $P < 0.01$ ) and breakdown ( $r = 0.705$ ,  $P < 0.01$ ). When gelatinized starch was used, the HR correlated negatively but weakly with the phosphorus content ( $r = 0.398$ ,  $P < 0.05$ ), peak viscosity ( $r = 0.450$ ,  $P < 0.05$ ) and breakdown ( $r = 0.401$ ,  $P < 0.05$ ). However, the HR in gelatinized starch did not correlate with the median granule size. Next, the correlation coefficients were recalculated using a total of 26 potato starches. The HR in raw starch correlated signifi-

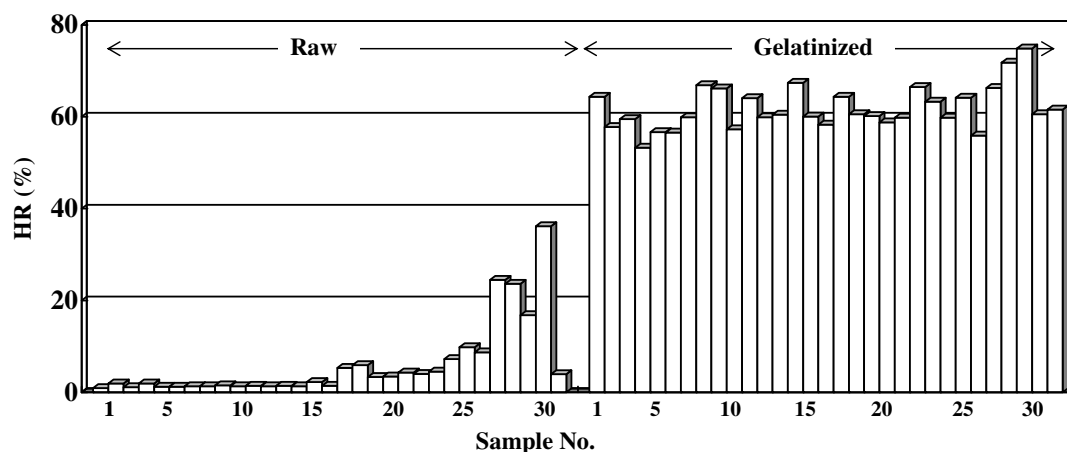


Fig. 1. Enzymatic digestibility in raw and gelatinized starches prepared from tuber and root crops.

Table 3

Correlation coefficients between HR and starch quality parameters, phosphorus content, median granule size, peak viscosity and breakdown

	HR in raw starch		HR in gelatinized starch	
	All ( <i>n</i> = 31)	Only potato ( <i>n</i> = 26)	All ( <i>n</i> = 31)	Only potato ( <i>n</i> = 26)
Phosphorus content	−0.650**	0.121	−0.398*	−0.053
Median granule size	−0.697**	−0.589**	−0.267	0.099
Peak viscosity	−0.791**	−0.633**	−0.450*	−0.069
Breakdown	−0.705**	−0.606**	−0.401*	−0.071

\* and \*\**P* < 0.05 and 0.01, respectively.

cantly and negatively with the median granule size ( $r = 0.589$ ,  $P < 0.01$ ), peak viscosity ( $r = 0.633$ ,  $P < 0.01$ ) and breakdown ( $r = 0.606$ ,  $P < 0.01$ ), while no correlation of the phosphorus content with the HR in raw starch was found. In the case of gelatinized starch, no correlation coefficients were found between the HR and all starch quality parameters.

#### 4. Discussion

This investigation revealed that the enzymatic digestibility in both raw and gelatinized starches varied when 26 potato starches, three sweet potato starches, one cassava starch, and one yam starch were used. Potato starch granules having B-type crystallites are well known to be resistant to digestion by amylase (Englyst et al., 1992; Fuwa et al., 1977; Kingman & Englyst, 1994; Sandstedt et al., 1962). We also found extremely low values of HR in raw starch for the potato starches used in this investigation. Similarly, a clearly lower HR was shown in raw yam starch. Fuwa et al. (1977) reported that the relative order of the hydrolysis rate of raw starch was potato < yam < sweet potato. According to the report of Srichuwong, Sunarti, Mishima, Isono, and Hisamatsu

(2005), on the digestibility of tuber and root starch granules by porcine pancreatic  $\alpha$ -amylase, the starch granules of one yam (water yam) were difficult to digest, having similar digestibility to potato starch granules, while those of another yam (lesser yam) showed definitely higher digestibility than did potato starch granules. To assess the factors determining enzymatic digestibility, we calculated the correlation coefficients between HR and other starch quality parameters, median granule size, phosphorus content and RVA pasting properties. The starch granule size is an important factor affecting the digestibility of raw starch by amylase. Large starch granules have a smaller surface area than have smaller ones, and the smaller surface area of the substrate in the larger starch granules reduces the chance for amylase to absorb. Thus, several results, including ours, have shown that large starch granules are digested more slowly than smaller granules (Cottrell, Duffus, Paterson, & Mackay, 1995; MacGregor & Balance, 1980; Noda et al., 2005; Kang, Sugimoto, Kato, Sakamoto, & Fuwa, 1985). In support of these results, we proved that a larger starch granule was associated with a lower HR in raw starch. In addition, we demonstrated with the use of gelatinized starches, that there is no relationship between the HR and the median size of the starch granule. Differences in the digestibility of starch have been attributed to the compositional characteristics of starch. For example, high-amylose starch showed manifestly lower digestibility by amylase than did normal-amylose starch in maize (Fuwa et al., 1977; Sandstedt et al., 1962) and potato (Karlsson, Leeman, Björck, & Eliasson, 2007). It is well known that amylase action is prevented by the esterified phosphate groups attached to the glucosyl residues of starch (Abe et al., 1982; Takeda et al., 1983). Therefore, the complete hydrolysis of starches with phosphate groups yields phosphoryl-oligosaccharides. Theoretically, starches rich in phosphate groups display lower enzymatic digestibility. According to the report of Abe et al. (1982), on the degree of hydrolysis of three potato starches differing in phosphorus content with purified glucoamylase, the

higher the phosphorus content, the lower was the HR. In the present report, we determined the relationship between starch digestibility and starch phosphorus content using many starch samples with a large range of phosphorus contents. The influence of the phosphorus content on the enzymatic digestibilities of raw and gelatinized starches could be confirmed for the composite of potato and other starches, while such trends were not found within potato starches. One explanation for these results may be that the range of phosphorus contents for potato starches is narrower (416–1118 ppm) than that for the composite of potato and other starches (97–1118 ppm). Another explanation is that the condition for amylase hydrolysis used in the study is not particularly severe. There is limited information about the effects of starch pasting properties on starch digestibility. Using several rice cultivars, Hu, Zao, Duan, Linlin, and Wu (2004) reported that the starch with the lowest peak viscosity obviously showed low enzymatic digestibility of gelatinized starch. Contrary to this, our data provided evidence that the peak viscosity and breakdown reduced the enzymatic digestibility in raw starch and tended to decrease the enzymatic digestibility in gelatinized starch. Thus, the contribution of the starch pasting properties to enzymatic digestibility needs further investigation. In food processing, starch is generally gelatinized. However, gelatinization is incomplete when excess water is not used for the manufacture of food. The structure of the starch that is incompletely gelatinized is a combination of raw starch and gelatinized starch. Information regarding the enzymatic digestibility of raw and gelatinized starches is meaningful to the food industry, especially, for those divisions that make use of potato starch.

## 5. Conclusions

In this investigation, we found factors affecting the enzymatic digestibility of raw and gelatinized starch using 26 potato starches, three sweet potato starches, one cassava starch, and one yam starch. Larger median granule size resulted in lower digestibility of raw starch, whereas no relationship of median granule size to the digestibility of gelatinized starch was observed. Higher values of phosphorus content, peak viscosity and breakdown were generally associated with lower digestibility in raw and gelatinized starches. Our data provide useful information for the food industries that make use of potato starch.

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