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REVIEW

Characteristics of Potato Starch: Phosphorus Content, Physicochemical Properties, and Digestibility

Takahiro NODA*

Hokkaido Agricultural Research Center, National Agriculture and Food Research Organization, Memuro, Hokkaido, Japan

Abstract

Potato (*Solanum tuberosum* L.) is an important crop in Hokkaido, Japan, where starch is a common ingredient in many Japanese dishes. Potato starch differs from other starches in that it has a high concentration of phosphorus, which imparts unique functional properties such as high viscosity. This review article summarizes a series of approaches conducted at the Hokkaido Agricultural Research Center, National Agriculture and Food Research Organization, to investigate the characteristics of starches extracted from potatoes cultivated in Hokkaido, Japan. Rapid, nondestructive, and quantitative measurements of phosphorus content in potato starch were conducted using energy-dispersive X-ray fluorescence. Starches prepared from late-harvested potatoes had a higher peak viscosity and phosphorus content than those from early-harvested potatoes. Air classification of potato starch granules of different sizes revealed that peak viscosity decreased, but phosphorus content increased as granule size decreased. *In vitro* digestibility studies of raw starch from multiple samples of potato, sweet potato, cassava, and yam have suggested that higher phosphorus content reduces the rate of hydrolysis by amylolytic enzymes.

Discipline: Food
Additional key words: starch, potato, phosphorus, digestibility

Introduction

Potatoes, which belong to the genus *Solanum* in the family Solanaceae, are among the most widely produced crops worldwide, with *Solanum tuberosum* L. being the most cultivated species. The major potato producers are China, India, Russia, Ukraine, and the United States, with a combined annual global potato production exceeding 350 million tons. In 2023, Japan's total annual potato production was 2.245 million tons, with Hokkaido accounting for 81% of that total (Ministry of Agriculture, Forestry and Fisheries 2023). Potatoes are primarily used in food production through the commercial processing of fries, potato chips, and other potato-based products. Potato starch also has important applications in the food, pharmaceutical, and medical industries. Potato starch has become an important commercial product in Hokkaido, and local factories supply it as an ingredient for noodles and surimi products.

Starch, a storage carbohydrate ubiquitous in plants, constitutes more than 70% of the dry weight of potato tubers. Starch consists of 15%-25% amylose, a linear chain of glucose units, and 75%-85% amylopectin, a branched chain of glucose units. The minor non-carbohydrate constituents of starch include proteins, lipids, phosphorus-containing compounds, and minerals. The properties of starch molecules vary significantly among plant species. The physicochemical properties and *in vitro* digestibility of starch play important roles in determining the quality of potato-based foods. Starches from root and tuber crops contain esterified phosphate groups, primarily at the C-6 position of glucose units in amylopectin molecules (Hizukuri et al. 1970). Potato starch exhibits unique properties, including exceptionally high viscosity, which is attributed to its high phosphorus content (Hoover 2001, Srichuwong et al. 2005). Within

*Corresponding author: noda.takahiro263@naro.go.jp
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the same botanical origin, starch characteristics vary with differences in cultivar and environmental factors. For the past 20 years, our research group at the Hokkaido Agricultural Research Center, National Agriculture and Food Research Organization (HARC/NARO), has employed various approaches to elucidate the physicochemical and digestive properties of starches prepared from several potato cultivars grown under different environmental conditions in Hokkaido, Japan. This review summarizes recent studies regarding the characteristics of potato starch conducted at HARC/NARO.

Rapid, nondestructive analysis of phosphorus content in potato starch

Starch-bound phosphate groups significantly influence the textural characteristics of potato starch. Altering the phosphorus content of potato starch can improve tuber quality, which is a significant objective in potato breeding. Therefore, a rapid, precise, and simple method for analyzing the phosphorus content of potato starch is essential for potato breeding programs. However, wet chemical analysis, the conventional approach for determining phosphorus in potato starch, is time-consuming and labor-intensive. Energy-dispersive X-ray fluorescence (ED-XRF) is a powerful technique for identifying elements and determining their concentrations. It has been widely applied to the rapid, simple analysis of various food materials, such as tea (Salvador et al. 2002) and milk powder (Alvarez & Mazo-Gray 1990). We developed a protocol for ED-XRF to rapidly determine phosphorus content in potato starch (Noda et al. 2006). The validity of ED-XRF as a rapid and reliable method for determining the phosphorus content of potato starch was confirmed. X-ray intensity counts (P-Kα, the characteristic X-ray for phosphorus) per second were measured using the ED-XRF method using 20 pelletized potato starch samples and compared with reference phosphorus values determined by wet chemical analysis. A second set of 15 pelletized potato starch samples was used to validate the results. Using ED-XRF, we investigated the phosphorus content of starches isolated from 535 potato samples grown during 2003 and 2004 in experimental fields at HARC/NARO in Memuro, Hokkaido (Noda et al. 2007). As shown in Figure 1, the phosphorus content ranged from 308 to 1,244 ppm, with mean and median values of 716 and 713 ppm, respectively.

Effects of the harvest period on the characteristics of potato starch

Previous studies on rice (Asaoka et al. 1985), maize (Inouchi et al. 1984), and sweet potato (Noda et al. 1997) have suggested that plant starch characteristics are generally determined during the developmental stage. Changes in starch quality during potato tuber development have also been investigated (Geddes et al. 1965, Christensen & Madsen 1996, Liu et al. 2003). Generally, seed tubers are planted between April and May and harvested between August and October in Hokkaido. We analyzed starch properties from six potato cultivars (Konafubuki, Benimaru, Sakurafubuki, Astarte, Early Starch, and Hokkai No. 87), which were harvested in late August (early harvest) and late September (late harvest) during the 2001 growing season from experimental fields at HARC/NARO (Noda et al.

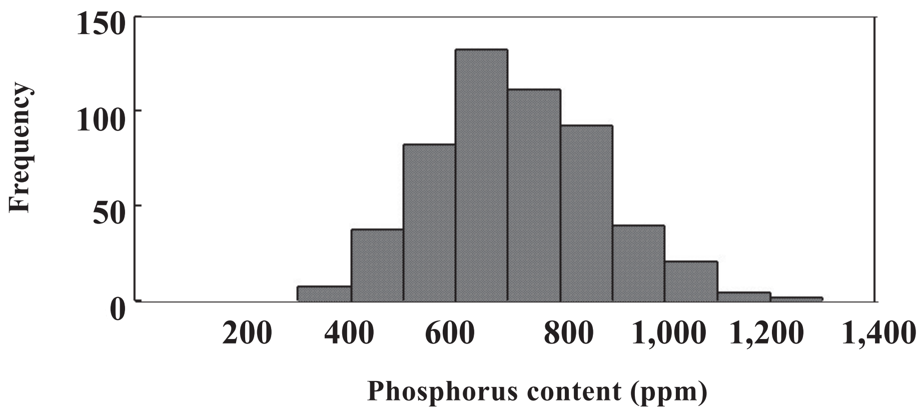

Fig. 1. Frequency distribution of the phosphorus content of 535 potato starch samples, analyzed by energy-dispersive X-ray fluorescence (ED-XRF) (Modified from Noda et al. 2007)

2004). The results are shown in Figure 2. Late harvest was associated with increased starch granule size and phosphorus content, as well as higher peak viscosity and breakdown values measured by a Rapid Visco-Analyzer (RVA). These results were consistent with previous findings (Christensen & Madsen 1996, Liu et al. 2003). It is widely accepted that the high phosphorus content of potato starch is a major factor contributing to its high peak viscosity, as phosphate groups are thought to enhance the hydration capacity of starch pastes (Wiesenborn et al. 1994). Therefore, the high peak viscosity observed in late-harvested samples was attributed to elevated phosphorus content. Late harvesting resulted in a slight reduction in the onset of gelatinization and peak temperature, as measured by differential scanning calorimetry (DSC), along with lower amylose content and a lower RVA pasting temperature. However, the harvest date had no significant effect on the DSC gelatinization enthalpy. Amylose content has been reported to remain constant during the late growth stage of potato tubers (Christensen & Madsen 1996, Liu et al. 2003). As with our findings on DSC gelatinization properties, Liu et al. (2003) observed that onset and peak temperatures for gelatinization tended to decrease and gelatinization enthalpy did not change essentially during potato growth. In summary, the choice of harvest date was identified as a key factor influencing potato starch characteristics, particularly starch granule size, phosphorus content, peak viscosity, and breakdown.

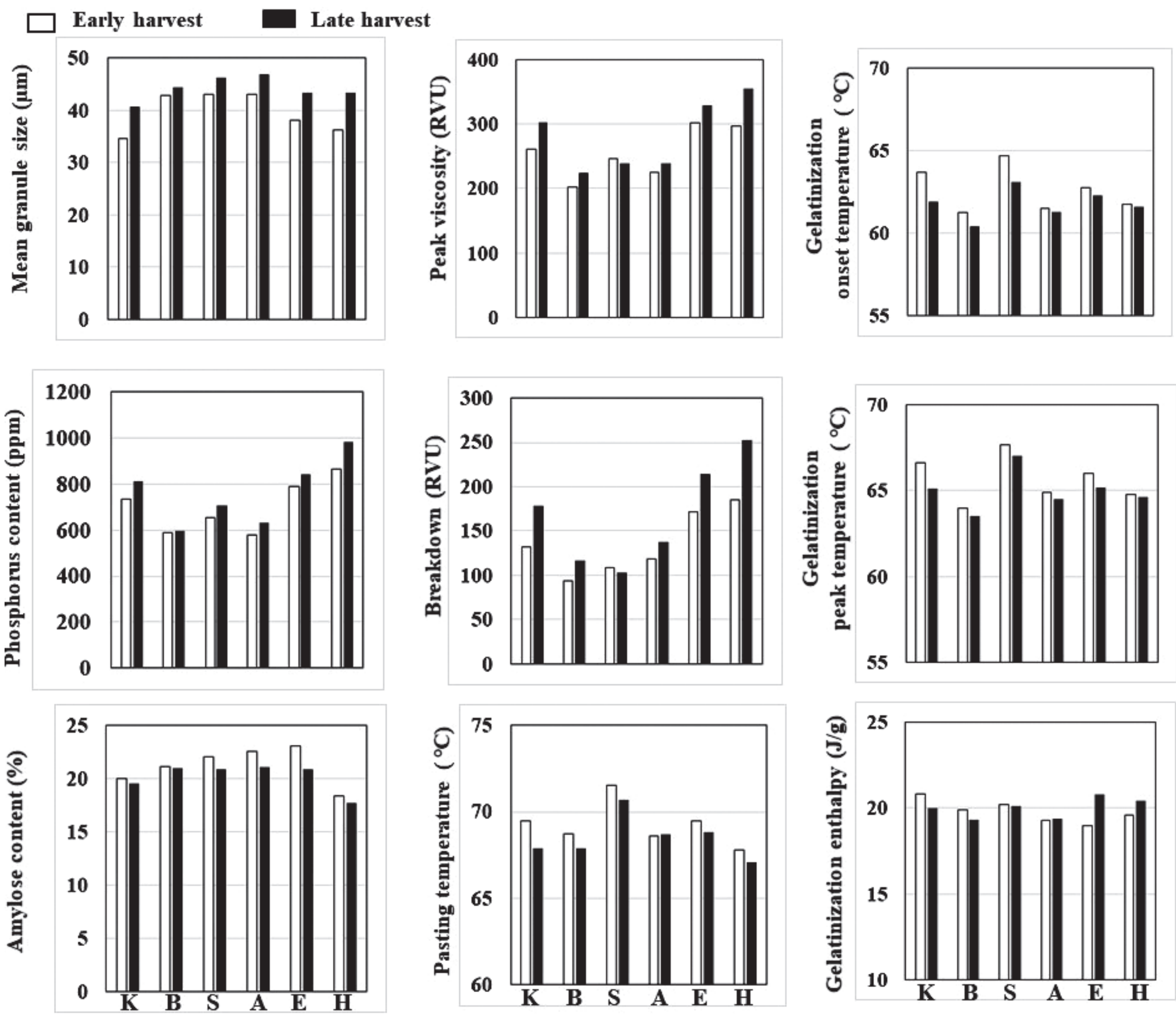

Fig. 2. Effect of harvest date on starch quality parameters in six potato cultivars (Modified from Noda et al. 2004)
K, Konafubuki; B, Benimaru; S, Sakurafubuki; A, Astarte; E, Early Starch; H, Hokkai No. 87

Effects of environmental temperature during potato tuber development on starch properties

Thitisaksakul et al. (2012) reported that environmental factors, in addition to cultivar, influence starch properties. Several studies have shown that environmental temperature influences starch properties in many crops, including rice (Hizukuri 1969, Asaoka et al. 1984), wheat (Matsuki et al. 2003), sweet potato (Hizukuri 1969, Noda et al. 2001), and potato (Hizukuri 1969, Tester et al. 1999). These investigations were conducted using starch isolated from crops grown in temperature-controlled growth chambers. We previously examined the impact of annual fluctuations in environmental temperature on starch properties during potato tuber development (Noda et al. 2012). Starches were prepared from 12 potato cultivars grown between 2001 and 2010 in experimental fields at HARC/NARO, Memuro, Hokkaido, and several quality parameters of these starches were determined. Daily temperature data at Memuro were obtained from the Japan Meteorological Agency. We analyzed the relationships between environmental temperature during potato tuber development (July to September) and all measured starch quality parameters. The phosphorus content of potato starch exhibited a significant negative correlation with accumulated temperature in all cultivars (Fig. 3). A significant positive correlation was observed between pasting temperature and accumulated temperature. In contrast, the accumulated temperature did not significantly influence other pasting parameters, such as peak viscosity, breakdown, or median granule size (data not shown; see Noda et al. 2012). Hizukuri (1969) and Tester et al. (1999) reported a reduction in the phosphorus content of potato starch as environmental temperature increased within an experimental range of 10°C-25°C. The pasting temperature of starch has been reported to increase markedly with rising environmental temperature in rice (Hizukuri 1969), sweet potato (Hizukuri 1969, Noda et al. 2001), and potato (Hizukuri 1969).

Different-sized potato starches

Potato starch is distinguished from other commercially available starches by its larger granule size. It exhibits a wide granule size distribution, ranging from 5 to 100 µm. Factories in Hokkaido have used air classification and sedimentation techniques to separate potato starches of different sizes. Previous studies on barley (Kang et al. 1985), wheat (Peng et al. 1999), and potato (Kainuma et al. 1978) have reported considerable variations in the characteristics of starch granules of varied sizes. Therefore, we determined the physicochemical properties of potato starches of different sizes: large, small, and extremely small (Table 1), which were obtained by air classification in a local potato starch manufacturing factory over three consecutive years (2001-2003) (Noda et al. 2005). The median granule size ranged from 39.9 µm-43.7 µm, 20.3 µm-23.4 µm, and 13.2 µm-14.0 µm for large, small, and extremely small potato starches, respectively. The highest mean phosphorus content was detected in the extremely small potato starch fraction (1,114 ppm); the small-granule fraction (979 ppm) showed intermediate phosphorus

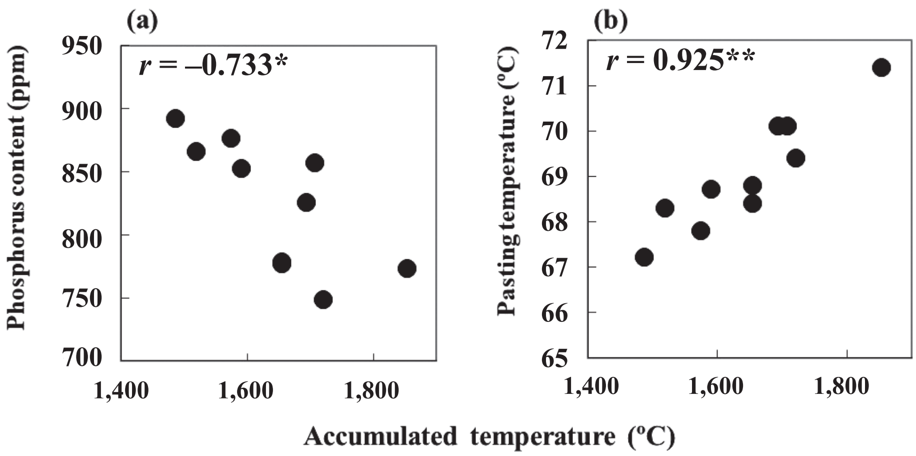

Fig. 3. Scatter plots showing the relationships between accumulated temperature from July to September and (a) starch phosphorus content and (b) starch pasting temperature, using the average of all potato cultivars (Modified from Noda et al. 2012)

content, whereas the large-granule fraction (756 ppm) had the lowest. The lowest mean values of RVA peak viscosity and breakdown were observed in the extremely small potato starch fraction, whereas the highest values occurred in the large fraction. Therefore, as granule size decreases, RVA peak viscosity and breakdown decrease, whereas phosphorus content increases. These findings are consistent with those of Kainuma et al. (1978), who used amylography to study potato starches of different sizes. Potato starch with higher phosphorus content has been reported to exhibit greater viscosity (Wiesenborn et al. 1994, Blennow et al. 2003). This finding is consistent with our research, which demonstrated that high phosphorus content in potato starch positively affects peak viscosity and breakdown (Noda et al. 2004, 2007, 2012). However, these studies used non-fractionated starches from different potato cultivars. No positive correlation was observed between phosphorus content and either peak viscosity or breakdown when size-fractionated small starch granules were analyzed. Neither the DSC gelatinization properties (onset and peak temperatures, and gelatinization enthalpy) nor the amylose content varied substantially with granule size. Kainuma et al. (1978) also reported that potato starches of different sizes had similar amylose contents. Similar to our findings, Kang et al. (1985) and Peng et al. (1999) observed no or only slight differences in gelatinization onset and peak temperatures among differently sized starch granules in barley and wheat, respectively. In contrast, they reported that A type (large) starch granules contained more amylose and exhibited higher enthalpy than B type (small) granules in barley and wheat. No differences in the molecular structures of amylopectins were observed among potato starches of different sizes (data not shown; see Noda et al. 2005). Consistent with these observations, the distributions of amylopectin unit chains in size-fractionated starches were reported to be similar in potato (Kainuma et al. 1978) and barley (Kang et al. 1985). Potato starch exhibits a unimodal size distribution, whereas wheat and barley starches display a bimodal size distribution. Notably, the biosynthetic mechanisms responsible for starch granules of different sizes in potatoes are assumed to differ fundamentally from those in wheat and barley.

Phosphorus content and *in vitro* digestibility

It has long been known that amylolytic enzymes cannot bypass the phosphorylated glucosyl residues of potato starch (Posternak 1951). The actions of sweet potato β-amylase (Takeda & Hizukuri 1981), *Aspergillus niger* glucoamylase (Takeda et al. 1983), and α-amylases from porcine pancreas and *Bacillus subtilis* (Takeda et al. 1983) on glucosyl residues with phosphate groups have been studied in detail. When potato starch is thoroughly digested by amylase, phosphoryl oligosaccharides are

Table 1. Starch quality parameters of potato starch granules of different sizes produced in 2001, 2002, and 2003 (Modified from Noda et al. 2005)

				RVA pasting properties		DSC gelatinization properties		
	Median granule size (μm)	Phosphorus content (ppm)	Amylose content (%)	Peak viscosity (RVU)	Breakdown (RVU)	Onset temperature (°C)	Peak temperature (°C)	Enthalpy (J/g)
Large-2001	43.7	764	20.5	321	215	61.5	65.6	19.2
Large-2002	43.2	790	21.5	322	223	60.9	65.3	19.2
Large-2003	39.9	715	20.2	306	208	60.2	64.4	20.0
Large-mean (n=3)[a]	42.3a	756c	20.7a	316a	215a	60.9a	65.1b	19.5a
Small-2001	23.4	990	20.6	283	165	61.0	66.2	20.3
Small-2002	21.2	1011	19.9	277	158	60.9	66.0	19.1
Small-2003	20.3	935	19.4	265	150	60.5	65.2	20.1
Small-mean (n=3)[a]	21.6b	979b	20.0a	275b	158b	60.8a	65.8b	19.8a
Extremely small-2001	14.0	1128	19.6	225	104	59.7	67.0	19.4
Extremely small-2002	13.5	1090	22.5	217	92	59.9	66.7	20.9
Extremely small-2003	13.2	1125	18.5	220	93	60.7	66.8	20.3
Extremely small-mean (n=3)[a]	13.6c	1114a	20.2a	221c	96c	60.1a	66.8a	20.2a

[a] Values followed by the same letter in the same row within the same parameter are not significantly different ($P < 0.05$).

generated as by-products, which have attracted increasing attention because of their functional properties (Kamasaka et al. 1995). Therefore, the phosphorus content of potato starch influences its *in vitro* digestibility.

In this study, we investigated the relationship between phosphorus content and the digestion of raw and gelatinized starches using amylolytic enzymes (Noda et al. 2008). We measured the phosphorus content of 26 starch samples isolated from potatoes grown in Hokkaido, along with other tuber and root starches (sweet potato, cassava, and yam). The phosphorus content of potato starches ranged from 416 to 1,118 ppm, which was higher than that of other tuber and root starches (97-231 ppm). We then determined the digestion percentage of the raw and gelatinized starches after 2 h of incubation at 37°C using an enzyme solution containing porcine pancreatic α-amylase and *Rhizopus* glucoamylase. Generally, lower hydrolysis ratios were observed in raw potato starches (0.9%-9.8%) than in raw other tuber and root starches (3.9%-36.2%). Three small-sized potato starches had relatively high hydrolysis ratios (7.2%-9.8%). Raw cassava starch showed the highest hydrolysis ratio (36.2%), followed by sweet potato (16.8%-24.5%) and yam (3.9%). Marked increases in the hydrolysis ratio occurred during starch gelatinization. The hydrolysis ratios of gelatinized sweet potato starch were slightly higher (66.3%-74.9%) than those of gelatinized potato (53.3%-67.4%), cassava (60.6%), and yam (61.6%). Thus, increased phosphorus content led to a clear reduction in the hydrolysis ratio of raw starch (Fig. 4) and tended to lower the hydrolysis ratio of gelatinized starch in multiple samples of potato, sweet potato, cassava, and yam. Previous studies have also reported negative correlations between phosphorus content and the enzymatic digestibility of gelatinized starches for tubers and roots, including potato starch (Absar et al. 2009), and of raw potato starches with large variations in phosphorus content (Wickramasinghe et al. 2009).

Starch can be classified into rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) according to its *in vitro* digestibility (Englyst et al. 1992). Unlike RDS and SDS, RS escapes amylase digestion in the small intestine. RS reaches the large intestine, where it is fermented by colonic bacteria, producing short-chain fatty acids such as acetate, propionate, and butyrate (Topping & Clifton 2001). RS can be further classified into RS1, RS2, RS3, RS4, and RS5 based on its physicochemical and structural characteristics (Birt et al. 2013). RS1 is a physically inaccessible starch entrapped within plant cells and is mainly found in legumes, partially milled grains, and cereals. RS2 is a non-gelatinized starch with highly crystalline structures and occurs in high-amylose maize starch and raw potato starch. RS3 is a retrograded or recrystallized starch with high thermal stability, formed after starch gelatinization and cooling. RS4 refers to chemically modified starches such as etherified, esterified, and cross-linked starches to enhance their functionality as food additives (Chung et al. 2008). RS5 comprises starch-lipid complexes that form helical

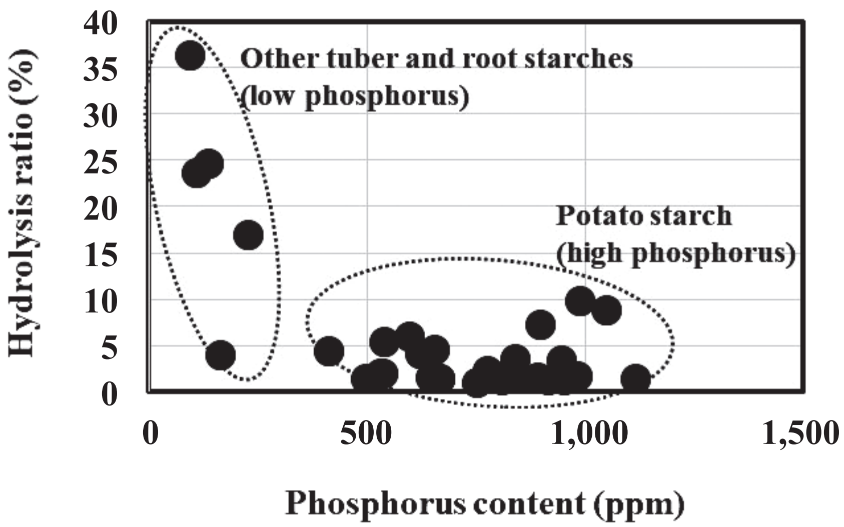

Fig. 4. Effect of phosphorus content on the hydrolysis ratio of raw starch in multiple samples of potato, sweet potato, cassava, and yam starches (Modified from Noda et al. 2008)

structures resistant to degradation by amylolytic enzymes. We previously reported a lower hydrolysis rate for raw potato starch, supporting the assumption that it contains a substantial proportion of RS2 (Raigond et al. 2015). Blennow et al. (2002) suggested that phosphorylation is the only naturally occurring covalent modification of starch. Hoover & Sosulski (1985) observed that acetylation decreased legume starch hydrolysis by α-amylase from porcine pancreas. Similarly, hydroxypropylation reduces the *in vitro* digestibility of pea (Hoover et al. 1988) and wheat (Wootton & Chaudhry 1981) starches. Our previous studies suggested that, similar to acetylated and hydroxypropylated starches (RS4), phosphorus content negatively affects the digestion degree of both raw and gelatinized starches by amylolytic enzymes (Noda et al. 2008, Absar et al. 2009, Wickramasinghe et al. 2009). Notably, using potato starch with high phosphorus content as a source of resistant starch instead of chemically modified alternatives is more environmentally friendly to consumers.

Divalent cation substitution

Several divalent cations have been reported to promote human health. Calcium and magnesium play important roles in reducing the risk of type 2 diabetes (Villegas et al. 2009) and osteoporosis (Nieves et al. 2005). Iron is essential for hemoglobin synthesis in red blood cells, and approximately two billion people worldwide are iron-deficient (Zimmermann & Hurrell 2007). Potato starch contains metal cations bound to esterified phosphate groups through ionic binding. It is well known that metal cations influence the pasting characteristics of potato starch. For example, potato starch containing a high level of divalent cations such as calcium and magnesium exhibits reduced peak viscosity and breakdown, implying improved viscosity stability due to ionically cross-linked starch phosphate esters (Kainuma et al. 1976, Bergthaller et al. 1999, Fortuna et al. 2013). We found that potato starch produced in Hokkaido factories has a high potassium content, low level of divalent cations, and poor viscosity stability (Noda et al. 2005, 2019; Zaidul et al. 2007). Therefore, modifying the metal cation composition of potato starch produced in Hokkaido factories is essential for improving its nutritional properties and viscosity stability. We focused on developing a method to prepare divalent cation-substituted potato starch using starch with high potassium content. Calcium- and magnesium-substituted potato starches were prepared by treating the starches with solutions containing $CaCl_2$ and $MgCl_2$, respectively (Noda et al. 2014). Iron-substituted potato starch was prepared by immersing the starch in a solution containing $FeSO_4$ (Noda et al. 2018). Additionally, immersing potato starch in natural mineral water with high calcium levels enabled the preparation of calcium-substituted potato starch without using food additives such as $CaCl_2$ (Noda et al. 2015). All divalent cation-substituted potato starches exhibited lower peak viscosity and breakdown values, indicating improved viscosity stability. Kainuma et al. (1978), Bergthaller et al. (1999), and Fortuna et al. (2013) suggested that this phenomenon could be ascribed to cross-linking between phosphate esters and divalent cations. However, divalent cation substitution had little or no effect on gelatinization temperature or enthalpy as determined by DSC and on the *in vitro* digestibility of raw starch. Our study suggests that divalent cation-substituted potato starch is a value-added food ingredient with improved nutritional value and viscosity (Noda et al. 2014, 2015, 2018).

Conclusions

Potatoes are an important crop in Hokkaido, and their starch serves as a valuable raw material for the production of various food products. In this review, we discussed the characteristics of potato starch produced under different conditions, emphasizing starch phosphate content and its *in vitro* digestibility by amylolytic enzymes. Late harvesting increased the phosphorus content of starch in six potato cultivars. The small-granule fraction of potato starch obtained by air classification exhibited higher phosphorus content than large granules. Increased phosphorus content resulted in a clear reduction in the ratio of raw starch digestion across potato, sweet potato, cassava, and yam samples. Immersing starch in solutions containing divalent cations enabled the preparation of potato starch substituted with these cations, which were bound to esterified phosphate groups. In conclusion, the results herein open the door to a new generation of potato starch applications in value-added food production.

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