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Physicochemical Properties of Starches Isolated from New Potato Cultivars in Korea

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Abstract Physicochemical properties of starches isolated from 3 new potato cultivars developed by Potato Valley Ltd. were investigated and compared to those of starch isolated from 'Superior' being distributed prominently in Korea. Significant differences were observed in physicochemical properties such as granule size, amylose content, phosphorus content, water binding capacity, swelling power, solubility, and *in vitro* digestibility of starches from different potato cultivars. Thermal properties were evaluated using differential scanning calorimetry (DSC), and onset gelatinization temperatire (T_o), peak temperature (T_p), and enthalpies of gelatinization (ΔH) of different potato cultivars ranged as 58.0±0.3-61.7±0.4°C, 63.7±0.2-66.5±0.0°C, and 15.6±0.5-17.0±0.3 J/g, respectively. Pasting properties were evaluated using a rapid visco analyzer (RVA), and pasting temperature, peak viscosity, and final viscosity of different potato cultivars ranged as 65.0±0.1-68.9±0.1°C, 8,163.7±196.3-9,035.7±6.4 cp, and 4,397.7±166.7-7,025.0±271.3 cp, respectively. Especially, 'Gogu valley' starch showed the highest values in the amylose and phosphorus content among tested potato cultivars and higher water binding capacity, swelling power, and solubility than those of other tested starches. And it also showed high pasting temperature, peak viscosity, trough viscosity, and final viscosity as compared to other tested starches.

Keywords: new potato cultivar, starch, morphological, physicochemical, thermal, pasting

Introduction

Starch is considered as commercial importance due to its high industrial demands as an ingredient for a variety of processed foods. The most important properties to consider when determining starch uses in food systems and other industrial applications are physicochemical (e.g., gelatinization and retrogradation) and functional (e.g., solubility, swelling, water binding, syneresis, and rheological behaviour of pastes and gels) properties (1). Potato starch is an important raw material in the food industry because of its desirable properties of low gelatinization temperature, low tendency to retrograde, no residual proteineous material or soil residues, non-cereal flavor, high viscosity, high water-binding capacity, bland taste, translucent paste, and relatively good stability (2). Potato starch displays a normal distribution for granule size, but the range for size distribution is wide (3). Koo *et al*. (4) reported that the pasting properties of starch are highly dependent on the granule size as well as the degree of swelling of starch granules. Potato starch also contains a higher phosphorus content than other plant starches (about 0.08% in potato starch, about 0.02% in corn starch, about 0.01% in waxy maize starch, and about 0.01% in tapioca starch) (5). Thermal and pasting properties are the most important functional properties of starches. Among all commercial starches, potato starch has the highest swelling power and the highest viscosity of pasting properties (6). Therefore, potato starch is one of the most useful starches in food industry. Starch can be chemically modified by with various methods to enhance physicochemical and functional properties (7). The physicochemical properties of native starch play a significant role during starch modification (8). It has been suggested that native starches selected from suitable cultivars with unique properties may have the potential to replace chemically modified starches, and only minor modification may be required for use in food products (9).

The purpose of this study is to investigate the physicochemical properties of starches isolated from new potato cultivars developed by Potato Valley Ltd. in order to provide basic data for their use and applications in food industry. A systematic study of starches from different cultivars would be useful, as differences in physicochemical properties of starches between cultivars will affect the functional properties of the starch and thus its suitability for specific end use.

Materials and Methods

Materials Tubers of 3 new potato cultivars from Potato Valley Ltd., 'Gui valley', 'Bora valley', and 'Gogu valley' were procured from Pyeongchang, Gangwon, Korea. 'Superior' cultivar, being distributed prominently in Korea, was obtained in food market. Uniformly sized tubers were selected from each cultivar batch before starch isolation.

Starch isolation Potato starches were isolated according to the toluene method described by MacGregor (10). Potatoes were washed in water and peeled. The eyes and all bruises were pitted out. After peeling, potatoes were

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immediately cut into small pieces and soaked for 24 hr in 0.02 M acetate buffer (pH 6.5) containing 0.01 M mercuric chloride at 20°C. Pieces were homogenized in a blender and homogenized suspensions were passed through a sieve with 125 and 75-μm opening. The material left on the screen was again homogenized and passed through the sieve. The procedure was repeated 3 times to release the starch granules completely. The solids were then mixed with toluene and water (1:8, v/v) and shaken for 10 hr on a wrist shaker. The suspension was centrifuged at 5,000×g for 10 min. And the liquid, with the denatured protein at the water/toluene interface was discarded. Solids were again washed with the mixture of toluene and water, shaken for 15 min, and centrifuged. This was repeated 5 times. The isolated starch was washed with purified water, and dried at room temperature. Isolated starches were gently ground and passed through a 125-μm sieve.

Microstructure and granule size analysis Microstructure was observed using scanning electron microscopy (SEM, S-2380N; Hitachi Ltd., Tokyo, Japan). Isolated starches were mounted on aluminum stub using double-side adhesive tape. The samples were coated with gold-palladium. An accelerating potential of 20 kV was used during electron microscopy in this study. The mean diameter and granule size distributions of the starches were determined by the diffraction of laser light using a particle size analyzer (1064; CILAS, Orleans, France).

Amylose content Amylose content of the isolated starch was determined by using the method of Williams *et al.* (11). A starch sample (20 mg, w.b.) was taken and 10 mL of 0.5 N KOH was added to it. The suspension was thoroughly mixed. The dispersed sample was transferred to a 100-mL volumetric flask and diluted to the mark with distilled water. An aliquot of test starch solution (10 mL) was pipetted into a 50-mL volumetric flask and 5 mL of 0.1 N HCl was added followed by 0.5 mL of iodine reagent. The volume was diluted to 50 mL and the absorbance was measured at 625 nm.

Phosphorus content The phosphorus content of the starches was determined by inductively coupled plasma (ICP)-AES (JA38 PLUS; ISA Instrument S.A., Longjumeau, France). A 0.5 g of each starch sample was digested in capped polycarbonate tubes at 90°C for 60 min with a mixture of 2.5 mL nitric acid and 0.5 mL hydrochloric acid. Samples were cooled and diluted to a final volume of 50 mL with deionized water. Phosphorus was analyzed by ICP-AES at 213 nm using standards prepared in a mixture of 5%(v/v) nitric acid and 1%(v/v) hydrochloric acid.

Solubility, swelling power, and water binding capacity Solubility, swelling power, and water binding capacity at 80°C were determined using a modified method of Sathe and Salunkhe (12). Briefly, 40 mL of a 1%(w/v) starch suspension was prepared in a 50-mL centrifuge tube. A magnetic agitator was placed in the tube, and it was kept at 80°C in a water bath for 30 min. The suspension was then centrifuged at 2,500×g for 15 min, the supernatant decanted and the swollen granules weighed. From the supernatant, 10 mL were dried in an air oven adjusted at 120°C for 4 hr in a crucible to constant weight. Percentage solubility and swelling power were calculated using the following formulas:

% Solubility=dry weight at 120°C×(100/sample weight)

Swelling power=weight of swollen granules×(100/sample weight)×(100−% solubility)

Water binding capacity was measured using the same conditions as above, but was expressed as weight of the gel formed/sample, divided by treated sample weight.

Thermal properties Starch gelatinization was determined with differential scanning calorimetry (DSC-7; Perkin-Elmer Co., Waltham, MA, USA), using the technique described by Park *et al.* (13). The DSC device was calibrated with indium and the data were analyzed using the Pyris software program. Starch (2 mg, d.b.) were weighed into an aluminum pan and the moisture level was adjusted to 70% by adding deionized water. The pan was then hermetically sealed and left to equilibrate for 1 hr at room temperature. Samples were scanned at temperatures between 30 and 130°C at a rate of 10°C/min. Gelatinization temperature was determined by automatically computing onset temperature (T_o), maximum peak temperature (T_p), and gelatinization enthalpy (ΔH) from the resulting thermogram.

Pasting properties The pasting properties of potato starches were evaluated with a rapid visco analyzer (RVA-3D; Newport Sci., Sydney, Australia). Starch (3 g, d.b.) was weighed directly in the aluminum RVA sample canister, and deionized water was added to a final volume of 30 mL. The samples were held at 50°C for 1 min, heated at a rate of 6°C/min from 50 to 95°C, held at 95°C for 3 min and then cooled down to 50°C at a rate of 6°C/min. The pasting temperature, peak viscosity, trough viscosity, and final viscosity were recorded.

***In vitro* digestibility** Starch digestibility was analyzed according to the method described by Chung *et al.* (14) Porcine pancreatic α-amylase (No. P7545; Sigma-Aldrich, St. Louis, MO, USA) (6 g) was dispersed in water (40 mL) by magnetic stirring for 10 min. The dispersion was then centrifuged for 10 min at 30,000×g, and a portion of the supernatant (32 mL) was transferred to a beaker. Amyloglucosidase (No. A9913; Sigma-Aldrich) (2 mL) and deionized water (3 mL) were added to the enzyme solution. The solution was freshly prepared for the digestion analysis. Aliquots of guar gum solution (10 mL, 5 g/L in 0.05 M HCl) and sodium acetate solution (5 mL, 0.5 M) were added to the starch samples (500 mg in 10 mL of distilled water) in test tubes. Seven glass balls (10-mm diameter) and 10 mL of the enzyme solution were then added to each tube, followed by incubation in a water bath (37°C) with agitation. Aliquots (0.5 mL) were taken at intervals and mixed with 4 mL of 80% ethanol, and the glucose contents in the mixture were measured using glucose oxidase and peroxidase assay kits (Megazyme International Ireland Ltd., Bray, Ireland). The starch classification based on its digestibility was; rapidly digestible starch (RDS) as the starch that was hydrolysed within 20 min of incubation, resistant starch (RS) as the starch not hydrolysed within 120 min, and slowly digestible starch (SDS) as the starch digested during the period between 20 and 120 min.

Statistical analysis All analyses were carried out in triplicate and data were expressed as mean±standard deviation (SD). Analysis of variance (ANOVA) was performed to calculate significant differences in treatment means, and Duncan's multiple test range was used to separate means using the Statistical Analysis System, (version 8.2, SAS Institute Ind, Cary, NC, USA) statistical software.

Results and Discussion

Morphological properties Scanning electron microscopys of starches from different potato cultivars are shown in Fig. 1. Starches consisted of small (10-20 μm), medium (20-40 μm), and large (40-70 μm) granules. The small granules were mainly spherical or oval while the medium and large granules were ellipsoid to polygonal or irregular in shape. 'Superior', 'Gui valley', and 'Bora valley' starches contained a relatively high percentage of large granules. Especially, 'Bora valley' starch showed distribution of the larger granule size than the others. On the other hand, 'Gogu valley' starch had relatively low percentage of large granules and relatively high percentage of small granules. Hoover (15) revealed that granule sizes of potato starches ranged widely from a few microns in diameter for small granules to 110 μm for large granules. The full granule size distribution of starches were shown in Table 1. Mean diameters of starch granules from 'Superior', 'Gui valley', 'Bora valley' and 'Gogu valley' were 34.1±0.1, 34.3±0.0, 37.1±0.0, and 29.1±0.1 μm, respectively. 'Bora valley' showed the largest granule size, while 'Gogu valley' showed the smallest granule size, which was consisted with the result from Fig. 1.

It has been reported that granule size of starches made greatly effect on the physicochemical properties of starches. Singh and Kaur (16) reported that large and small granule starches from potatoes had different gelatinization temperature regimes. Small granules fractionated from potato starches have been reported to have higher phosphorus content than large granules (2). Percent light transmittance, amylose content, swelling power, and water binding capacity also are significantly correlated with the average granule size of starches isolated from different plant sources (17). Since enzyme hydrolysis took place first on the surface of starch granules, the morphology of starch could be one of important factors influencing starch functionality such as *in vitro* digestibility (18).

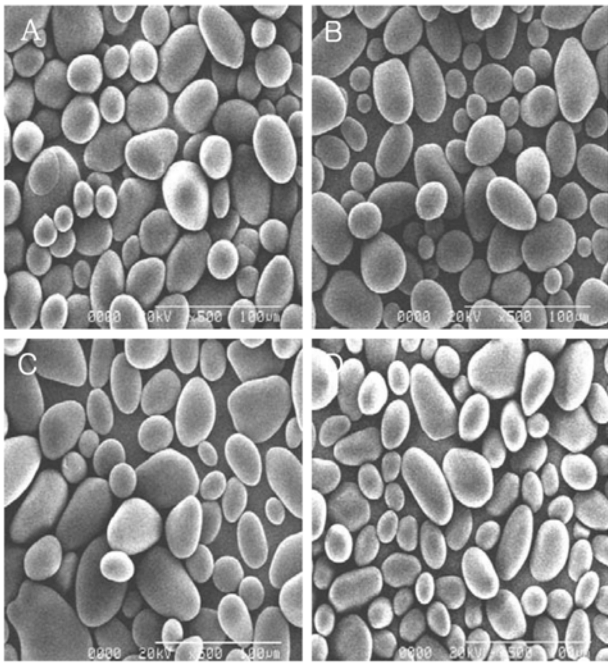

Fig. 1. Scanning electron microscopy of starches from different potato cultivars. A, 'Superior'; B, 'Gui valley'; C, 'Bora valley'; D, 'Gogu valley'.

Physicochemical properties Amylose and phosphorus content of starches from different potato cultivars are shown in Table 2. The amylose content of starches ranged between 23.3±0.4 and 30.6±0.1%, the lowest was observed for 'Bora valley' and the highest for 'Gogu valley'. The phosphorus content of starches ranged between 70.1±0.4 and 83.7±0.4 mg%, the lowest was observed for 'Bora

Table 1. Particle size of starches from different potato cultivars

Potato cultivar	Cumulative particle distribution (μm)			Mean diameter (μm)
	Diameter at 10%	Diameter at 50%	Diameter at 90%	
Superior	16.7±0.4[b1)]	33.9±0.1[b]	53.8±0.4[c]	34.1±0.1[b]
Gui valley	16.3±0.6[b]	33.8±0.0[b]	54.9±0.1[b]	34.3±0.0[b]
Bora valley	19.2±0.1[a]	37.3±0.1[a]	57.4±0.1[a]	37.1±0.0[a]
Gogu valley	4.4±0.4[c]	29.4±0.1[c]	44.9±0.2[d]	29.1±0.1[c]

[1)]Each value represents mean±SD (n=3); Values with the different letter in the same column are significantly different (p<0.05).

Table 2. Amylose and phosphorus contents of starches from different potato cultivars

	Superior	Gui valley	Bora valley	Gogu valley
Amylose (%)	23.7±0.0[c1)]	27.1±0.2[b]	23.3±0.4[c]	30.6±0.1[a]
Phosphrous (mg%)	71.1±0.3[b]	80.6±0.2[a]	70.1±0.4[b]	83.7±0.4[a]

[1)]Each value represents mean±SD (n=3); Values with the same letter in the same row are not significantly different (p<0.05).

Table 3. Water binding capacity, swelling power, and solubility of starches from different potato cultivars heated at 80°C for 30 min

	Superior	Gui valley	Bora valley	Gogu valley
Water binding capacity (g water/g starch)	50.9±0.3[c1)]	51.5±0.6[c]	61.2±0.6[b]	66.2±1.7[a]
Swelling power (g water/g starch)	55.3±0.0[c]	55.6±0.2[c]	68.3±0.5[b]	74.5±0.6[a]
Solubility (%)	7.9±0.5[ab]	6.8±1.5[b]	9.0±0.5[ab]	11.1±1.5[a]

[1)]Each value represents mean±SD (n=3); Values with the different letter in the same row are significantly different (p<0.05).

Table 4. Thermal properties of starches from different potato cultivars

Parameter	Superior	Gui valley	Bora valley	Gogu valley
Onset temperature (T_o, °C)	58.0±0.3[b1),2)]	59.9±0.4[ab]	58.2±0.2[b]	61.7±0.4[a]
Maximum peak temperature (T_p, °C)	63.7±0.2[b]	66.2±0.1[a]	63.9±0.1[b]	66.5±0.0[a]
Gelatinization enthalpy (ΔH, J/g)	16.3±0.6[b]	17.0±0.3[a]	15.6±0.5[c]	16.1±0.3[b]

[1)]Each value represents mean±SD (n=3); Values with the different letter in the same row are significantly different (p<0.05).

valley' and the highest for 'Gogu valley'. In potato starch, phosphorus is mainly present as phosphate monoesters, which are covalently bound to amylopectin fraction of starch (19).

Water binding capacity, swelling power, and solubility of potato starches are shown in Table 3. Water binding capacity of starches ranged between 50.9±0.3 and 66.2±1.7 g water/g starch at 80°C. The difference in the degree of availability of water binding sites among starches may have contributed to the variation in water binding capacity among different starches (20). 'Superior' starch showed the lowest (55.3±0.0 g water/g starch) swelling power whereas 'Gogu valley' starch showed the highest (74.5±0.6 g water/g starch) swelling power at 80°C. The difference in swelling power among starches indicates variation in the strength of associative bonding forces with granules (21). The solubility (%) ranged between 6.8±1.5 and 11.1±1.5% at 80°C, the lowest was observed for 'Gui valley' and the highest for 'Gogu valley'. The higher water binding capacity, swelling power, and solubility of starches are probably due to higher content of phosphate groups on adjacent chains, which increase hydration by weakening the extent of bonding within the crystalline domain (22). Lii *et al*. (23) have reported that amylose content is inversely proportional to granule swelling. The swelling power and solubility provide measures of the magnitude of interaction between starch chains within the amorphous and crystalline domains. The extent of this interaction is influenced by the amylose to amylopectin ratio and phosphorus content and by the characteristics of the amylose and amylopectin in terms of molecular weight/ distribution, degree of branching, and branch length and conformation (15,16). Noda *et al*. (3) have reported that small granules have higher phosphorus content than large granules, which may also be responsible for the higher swelling power of the small granule fractions in this study. The repulsion between adjacent starch molecules caused by negatively charged phosphate groups in small granules can apparently reduced interchain associations and give increased levels of hydrated molecules (24).

Thermal properties The results of the DSC analysis of potato starches are shown in Table 4. The onset gelatinization temperature (T_o), peak temperature (T_p), and enthalpies of gelatinization (ΔH) of starches ranged as 58.0±0.3-61.7±0.4°C, 63.7±0.2-66.5±0.0°C, and 15.6±0.5-17.0±0.3 J/g, respectively. The lowest T_o and T_p were observed for 'Superior' and the highest for 'Gogu valley'. The lowest ΔH was observed for 'Bora valley' and the highest for 'Gui valley'. These values are in accordance with the values for potato starches reported in the literature (17,25). The difference in transition temperature between starches was also due to the difference in the degree of crystallinity. High transition temperatures have been reported to result from a high degree of crystallinity, which provides structural stability and makes the granule more resistant to gelatinization (26). Enthalpy of gelatinization (ΔH) gives an overall measure of crystallinity and is an indicator of the loss of molecular order within the granule that occurs on gelatinization (27,28). Variation in the thermal properties of potato starches may be attributed to differences in starch phosphorus and amylose contents. Wischmann *et al*. (29) reported that the starches with higher amylose content showed higher gelatinization temperatures, and this study also revealed that 'Gui valley' and 'Gogu valley' starches with higher amylose contents showed higher gelatinization temperatures than 'Superior' and 'Bora valley' starches with lower amylose contents. Noda *et al*. (30) reported that gelatinization temperatures increased significantly with the increase of phosphorus contents in potato starches, which was in consistent with results of this study.

Pasting properties The results of the RVA analysis of starches from different potato cultivars are shown in Table 5. Pasting temperatures of starches ranged between 65.0±0.1 and 68.9±0.1°C, the lowest for 'Superior' and the highest for 'Gogu valley'. This is consistent with the results of the transition temperatures measured using DSC. A range between 64.9 and 71.5°C for pasting temperature in potato starches has been reported earlier (31). Peak viscosity of starches ranged between 8,163.7±196.3 and 9,035.7±6.4 cp. 'Superior' showed lower peak viscosity as compared to 'Gui valley', 'Bora valley', and 'Gogu valley'. Trough viscosity was found to be the lowest for 'Superior' (3,743.7±186.6 cp) and the highest for 'Gogu valley' (6,033.7±145.5 cp). Final viscosity of starches ranged between 4,397.7±166.7 and 7,025.0±271.3 cp, the lowest for 'Superior' and the highest for 'Gogu valley'.

Table 5. Pasting properties of starches from different potato cultivars

Parameter	Superior	Gui valley	Bora valley	Gogu valley
Pasting temperature (°C)	65.0±0.1[b1)]	68.8±1.0[a]	65.8±0.1[b]	68.9±0.1[a]
Peak viscosity (cp)	8,163.7±196.3[b]	9,024.0±3.6[a]	9,035.7±6.4[a]	8,941.0±25.1[a]
Trough viscosity (cp)	3,743.7±186.6[c]	4,963.3±796.5[b]	4,948.0±293.7[b]	6,033.7±145.5[a]
Final viscosity (cp)	4,397.7±166.7[d]	5,950.7±373.7[b]	5,343.3±318.4[c]	7,025.0±271.3[a]

[1)]Each value represents mean±SD (n=3); Values with the different letter in the same row are significantly different (p<0.05).

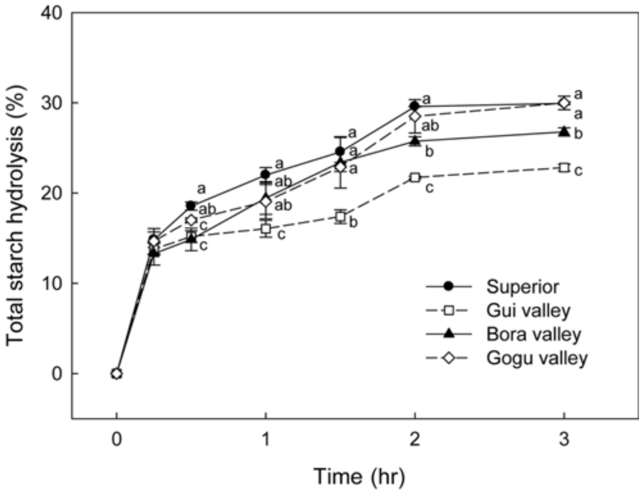

Fig. 2. Enzymatic digestion of starches from different potato cultivars.

Physicochemical characteristics such as amylose content, phosphorus content and granule size distribution are the main determinants of the pasting and rheological properties of potato starches (32-34). The difference in peak viscosity was very small among the 'Gui valley', 'Bora valley', and 'Gogu valley'. The higher peak viscosities of the 'Gui valley' and 'Gogu valley' may be attributed to its higher phosphorus contents. Lower peak viscosities of potato starches having low phosphorus content have been reported earlier (33). And the highest final viscosity of 'Gogu valley' may be attributed to its highest apparent amylose content. Miles *et al.* (35) reported that increase in final viscosity might be due to the aggregation of the amylose molecules. The increased viscosity with increasing temperature has been attributed to the removal of water from the exuded amylose by granules on the swelling of starches (36).

***In vitro* digestibility** Differences in the digestibility of native starches among species have been attributed to interplay of many factors, such as starch source, granule size, amylose/amylopectin ratio, degree of crystallinity, and type of crystalline polymorphic forms (14,37,38). Size of starch granules may affect digestibility, as the relationship between surface area and starch volume decreases with increasing of granule size (39). *In vitro* digestibility of starches from different potato cultivars are shown in Fig. 2. RDS content of starches ranged between 14.9 and 18.6%, the lowest for 'Bora valley' and the highest for 'Superior'. RDS is associated with greater and more rapid elevation of postprandial plasma glucose and insulin, and is linked to diabetes, coronary heart disease, and with the aging process (40). SDS content of starches ranged between 6.5 and 11.5%, the lowest for 'Gui valley' and the highest for 'Gogu valley'. SDS is completely but more slowly digested in the small intestine, and has an attenuated influence on postprandial plasma glucose and insulin levels, and is nutritionally the more desirable form of starch (41). RS content of starches ranged between 70.3 and 78.3%, the lowest for 'Superior' and the highest for 'Gui valley'. Total digestibility of starches (RDS+SDS) varied from 21.7 to 29.7%, the lowest for 'Gui valley' and the highest for 'Superior' was observed. It was assumed that lower digestibility of 'Gui valley' and 'Bora valley' compared to 'Superior' and 'Gogu valley' was resulted from higher degree of crystallinity in 'Gui valley' (Table 4) and large granule size in 'Bora valley' (Table 1). Englyst *et al.* (40) reported that potato starch showed the highest RS content (about 75%) among various starches, which was similar to result of this study.

Starches isolated from 'Superior' and 3 new potato cultivars, 'Gui valley', 'Bora valley', and 'Gogu valley', showed significant differences in morphological, physicochemical, thermal, pasting properties and digestibility. Starches from new potato cultivars had higher amylose and phosphorus contents than 'Superior' starch, and showed significantly higher water binding capacity, swelling power and solubility. Among them, 'Gogu valley' starch showed the highest values, which might be resulted from its high amylose and phosphorus contents. 'Gogu valley' starch also had thermostable paste with high transition temperatures, enthalpy of gelatinization and low breakdown. And this starch also showed high pasting temperature, peak viscosity, trough viscosity, and final viscosity compared to other starches.

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