Physicochemical Properties of Hydroxypropylated Apios Starches

Mi Hye Park¹ and Meera Kim¹,²

¹Department of Food Science and Nutrition and ²Center for Beautiful Aging, Kyungpook National University, Daegu 41566, Korea

ABSTRACT: Apios (Apios americana Medikus), also called the potato bean, Indian potato, or groundnut, belongs to the legume family, and is widely distributed across eastern North America. Apios starch was hydroxypropylated, and its physicochemical and structural characteristics were investigated in this study. The starch was extracted by alkali precipitation method, and hydroxypropylated apios starch (HPAS) was prepared using propylene oxide at concentrations of 2.5, 5, 7.5, and 10% (v/w). X-ray diffraction of native apios starch and HPAS revealed the presence of the typical ‘A’ type of cereal starch. Additionally, the hydroxypropylation affects the relative crystallinity of the starch. The swelling power and solubility of apios starch increased after hydroxypropylation. Gelatinization parameters were obtained using differential scanning calorimetry. The gelatinization temperature of native starch is 69°C, whereas that of HPAS-10% is 52.94°C. This suggests that HPAS is suitable for preparing food items requiring enhanced gelatinization.

Keywords: apios, DSC, FT-IR, hydroxypropylation, starch

INTRODUCTION

Starch is a storage carbohydrate that is distributed in seeds, roots, and/or stems of plants; grains, bulbs, and tubers are rich in starch. It is the main source of calories for people, and is also used as a gel-forming agent, stabilizer, moisturizer, and thickening material in the food industry because of its distinct physicochemical properties. However, its usability is limited due to insolubility and syneresis. Thus, physical, chemical, and enzymatic methods that enhance its properties are used to create modified starch (Fleche, 1985). Hydroxypropylation is a modification method that reduces the number of hydroxyl groups in a molecule, to weaken the hydrogen combinations between molecules. In other words, the concentration, clarity, and freeze-thaw stability of paste increases with the increase in the level of hydroxypropylation (Tuschhoff, 1988). There are precedent studies on the physiological characteristics of hydroxypropylated starch made from several sources such as rice starch (Yamamoto et al., 1973; Seow and Thevamalar, 1993), maize starch (Wootton and Manatsathit, 1983), potato starch (Singh and Singh, 2003), and wheat starch (Hung and Morita, 2005). Properties of starch differ based on its source and hence, a study on the structure and physicochemical properties of starch from different sources is required. A scientific name of apios is Apios americana Medikus, and it is also known as groundnut, earthnut, or potato bean. The place of origin of apios is North America, and it is an edible tuberous plant which belongs to the family legumin (Wilson et al., 1987). The major organizing ingredients of apios are water, starch, and protein. Apios contains three times more crude protein than other tuber crops (Wilson et al., 1987), and is rich in glutamic acid and aspartic acid, and can thus be used as a good source of protein (Ogasawara et al., 2006). Furthermore, apios tubers contain plenty of special ingredients such as saponin, calcium, iron, fiber, and isoflavone-genistein (Okubo et al., 1994), and is reported to be effective against skin diseases (i.e. atopy) (Krishnan, 1998), cardiac disorder, and diabetes (Iwai and Matsue, 2007). Some studies on the functional characteristics and physicochemical properties of apios starch were performed (Kikuta et al., 2012; Yangcheng et al., 2016) but there is not much research on the physicochemical properties of modified apios starch. In this study, starch was extracted from apios and chemically modified to create hydroxypropylated apios starch (HPAS), and its physicochemical properties were examined.
MATERIALS AND METHODS

Raw materials
Apios was obtained from a farm in Yangpyung, Korea. Native apios starch was isolated by the procedure described by Yamamoto et al. (1973). Peeled apios was washed and cut into small pieces. It was ground with 0.2% NaOH (two-fold the volume of apios) for 2 min using a blender (HMF-595, Hanil Electric, Seoul, Korea). It was stored at 4°C for 12 h and after passing the solution through a sieve (100 and 400 mesh) to silt out the lumps, the supernatant was removed. The residue was then mixed with 0.2% NaOH, and the supernatant was removed, after which the residue was homogenized in a refrigerator (4°C). This process was repeated until the supernatant was clear. A washing process using emulsion was performed, and the mixture was allowed to settle. This process was repeated until the suspension was clear and the pH was 6.8–7.4. The collected starch was dried at room temperature, filtered through a 100-mesh sieve, and stored under sealed conditions at low temperatures.

Chemicals
For hydroxypropylation, propylene oxide reagent was purchased from Kanto Chem Co. (Tokyo, Japan). Also, sodium hydroxide, sodium sulphate, and ninhydrin were purchased from Samchun Chemicals (Seoul, Korea). Propylene glycol was purchased from Sigma Chemical Co. (St. Louis, MO, USA).

Preparation of HPAS
Apios starch was converted into a range of hydroxypropyl derivatives according to the procedure of Wootton and Manatsathit (1983). Propylene oxide was added to the solution at concentrations of 2.5, 5, 7.5, and 10% (w/v), and the vessels were sealed with lids. The suspension was allowed to react in a closed vessel for 40 h at 40°C, and then passed through a 100-mesh sieve. Hydroxypropylation of HPAS was confirmed according to ninhydrin reaction proposed by Johnson (1969). The content of hydroxypropyl groups (HPs) in the starch was calculated from the standard curve using propylene glycol standard solution. The degree of substitution (DS) was calculated by converting the HP results (Johnson, 1969; Fu et al., 2019).

Fourier-transform infrared spectroscopy (FT-IR) spectroscopy
The structural changes of HPAS were determined. FT-IR spectra were recorded with a FT-IR Spectroscope (Spectrum GX & AutolImage, Perkin-Elmer, Shelton, CT, USA). Spectra were recorded from 400 to 4,000 cm⁻¹ using a mercury-cadmium-teluride detector cooled with liquid nitrogen. The starch were blended with KBr and pressed into pellets before measurement.

X-ray diffractometry
X-ray diffractogram analysis was performed using an X-ray diffractometer (Quantera SXM, ULVAC-PHI, Inc., Chigasaki, Japan). The analysis parameters were as follows: 45 kV, 35 mA, and Cu-Kα radiation. The sample was scanned through the 20 range from 5° to 45°.

Scanning electron microscopy
The surface of apios starch granules was visualized using a scanning electron microscope (SEM; S-570, Hitachi, Tokyo, Japan). The morphologies of native apios starch and HPAS were examined. The samples were then coated with gold and examined under a scanning electron microscope working at magnifications of 1,500 times, and an accelerating voltage of 15 kV.

Swelling power and solubility
The swelling power and solubility were measured by the method of Schoch (1964). 0.5 g of starch was put in a tube and 20 mL of distilled water was added. The tube was placed in a water bath at 70°C for 10 min, and then heated in boiling water for 10 min. The tube was then cooled in a cold water bath for 5 min, and centrifuged at 3,000 g for 40 min.

Light transmittance
Light transmittance was measured by the method described by Wilson et al. (1943). An aqueous suspension of starch (1%) was heated in a water bath at 35, 45, 55, 65, 75, 85, and 95°C for 5 min, with constant stirring. The absorbance of the suspension was measured at 635 nm using a UV/Visible spectrophotometer (DU 800, Beckman Coulter, Inc., Fullerton, CA, USA).

Differential scanning calorimetry (DSC)
Thermal properties were investigated using differential scanning with a Thermal Analyzer System (Q2000, TA Instruments, New Castle, DE, USA). Starch samples (1.5 mg) and 3 mg of water were put into a differential scanning calorimeter aluminum pan and after sealing, the pan was left for 1 h to equilibrate (Donovan, 1979). The temperature range for scanning was 30–100°C, and the heating rate was 10°C/min. The differential scanning calorimetric parameters recorded were as follows: difference in onset temperature (Tₒ), peak temperature (Tₚ), conclusion temperature (Tₚ₋ₕ), and enthalpy (AH).

Statistical analysis
Statistical analysis was performed with SPSS ver. 10 package program (SPSS Inc., Chicago, IL, USA). A difference in the variables among different concentrations was analyzed using one-way analysis of variance (ANOVA) fol-
RESULTS AND DISCUSSION

DS

The DS for HPAS at different concentrations of propylene oxide (2.5, 5, 7.5, and 10% v/w) are presented in Table 1. The DS of 0.025~0.275 increased as the concentration of propylene oxide added to the reaction mixture increased \( (r^2=0.95) \). As the DS of HPAS is higher than that of propylene oxide-hydroxypropylated potato starch (Bae et al., 1997) or finger millet starch (Lawal, 2009), it seems that the substitution of modified apios starch is comparatively easier. Hoover et al. (1988) reported that the DS for a modified starch was proportional to the amylose content in starch. Therefore, it seems that the substitution of modified apios starch with relatively high amylose content (33.2%) was comparatively easier. Shi and BeMiller (2000) reported that the degree of hydroxypropyl substitution of amylose was 0.109 and 0.225 when the DS of hydroxypropylated corn starch was 0.096 and 0.186, respectively. It means that the DS for hydroxypropylation of starch is mainly affected by the DS for hydroxypropylation of amylose. This research also reported that substitution of hydroxypropylated corn starch occurred on the starch amylose region. The property of modified starch varies according to the starch source and degree of modification (Hoover et al., 1988). The HPs and DS of the hydroxypropylation process, in particular, are altered by parameters such as reagent concentration, water-starch ratio, tolerance response, and alkali concentration. Amylose-amylopectin ratio and disposition in particles affect HPs and DS as well (Wootton and Manatsathit, 1983).

FT-IR spectroscopy

FT-IR spectra of native apios starch and HPAS are shown in Fig. 1. Native apios starch has peaks at 3,419 cm\(^{-1}\) (OH stretching vibration), 2,932 cm\(^{-1}\) (CH stretching vibration), 1,646 cm\(^{-1}\) (OH bending of water), 1,150 cm\(^{-1}\) (C-O+C-C stretching vibration), 1,082 cm\(^{-1}\) (CH stretching vibration), and 1,016 cm\(^{-1}\) (C-O stretching+C-OH bending), which is a typical starch absorption spectrum. The peaks at 1,082 and 2,932 cm\(^{-1}\) increased and the peak at 1,646 cm\(^{-1}\) slightly increased along with the degree of hydroxypropylation substitution. This is a phenomenon resulting from increased hydroxyl group concentrations in starch molecules. On the other hand, the weakened peak at 1,016 cm\(^{-1}\) is due to a decrease of crystallizability (Hoover et al., 1988), which is caused by hydroxypropylation. The changes in peaks show that native apios starch has reacted well with propyleneoxide, and that the hydroxypropylation process has been accomplished.

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Table 1. Hydroxypropyl group content and degree of substitution in hydroxypropylated apios starches (HPAS)

| Sample     | Optical density | Propylene oxide concentration (%) | Content of hydroxypropyl groups (%) | Degree of substitution |
|------------|----------------|-----------------------------------|-------------------------------------|------------------------|
| Native     | 0              | 8.52                              | 0.000                               | 0.000                  |
| HPAS-2.5%  | 0.0055         | 1.15                              | 0.893                               | 0.025                  |
| HPAS-5%    | 0.0160         | 3.33                              | 2.585                               | 0.074                  |
| HPAS-7.5%  | 0.0385         | 11.33                             | 8.795                               | 0.269                  |
| HPAS-10%   | 0.0555         | 11.56                             | 8.974                               | 0.275                  |

Fig. 1. FT-IR spectra of native starch and hydroxypropylated starch (HPAS) between 400 and 4,000 cm\(^{-1}\).

Fig. 2. X-ray diffractogram of native and hydroxypropylated apios starches (HPAS).
X-ray diffraction (XRD) pattern
The X-ray patterns are shown in Fig. 2, and the relative crystallinity (amorphous region area is divided by crystalline region area) is shown in Table 2. XRD pattern is used to examine the crystallinity of starch. A-type grain starch shows the peaks at 15° and 23°, and two strong peaks at 18° diffraction angles. B-type tuberous plant, fruit, and stem starch shows the peaks at 5°, 17°, and 22°-24° diffraction angles, and C-type (a combination of the A and B types) sweet potato, mung bean, and green pea starch shows the peaks at both the A-type and B-type peak angles. This peak difference in starch sources is due to the difference of the molecular structure in the crystal lattice of starch (Zobel, 1964). Native apios starch shows a typical A-type X-ray pattern, in which the peaks are present at 2θ values of 15.1°, 17.1°, 17.9°, and 23.2° (Fuwa et al., 1997). The relative crystallinity of native apios starch was 21.99% and relative crystallinities of HPAS-2.5%, HPAS-5%, HPAS-7.5%, and HPAS-10% were 21.37%, 21.28%, 21.03%, and 20.97%, respectively (Table 2). This result implies that the relative crystallinity was reduced as the hydroxypropylation level increased. It coincides with the results obtained by Yook et al. (1991), in which the crystallinity of hydroxypropylated corn starch was found to be lower than that of native corn starch. They reported that the hydroxypropyl group might affect the crystalline area because of its large molecular size.

SEM analysis
SEM of the granules for native apios starch and HPAS is presented in Fig. 3. The native apios starch granules (Fig. 3A) are in an oval shape with various diameter sizes ranging from about 3 μm to 20 μm. Ogasawara et al. (2006) states that the starch particle in apios tuber is oval in shape with a diameter of 5-10 μm, and its average size is 10.6 μm. Starch particles of similar shapes and sizes were also observed in this study. Native apios starch has a smooth surface, but the surface becomes slightly rougher for HPAS-2.5% and HPAS-5% with no change in the starch shape. Apios starch granules treated with 7% and 10% propylene oxide have irregular granule morphologies. It showed that hydroxypropylation could cause the shape change or structure destruction of the starch. This result is consistent with that obtained from a study by Kaur et al. (2004), which states that 10% propylene oxide-treated potato starch has a different shape than native starch. Kim et al. (1992) demonstrated that hydroxypropylation brings about spalling of starch granules and

Table 2. Physicochemical properties of hydroxypropylated apios starch (HPAS)

| Sample          | Native       | HPAS-2.5%    | HPAS-5%      | HPAS-7.5%    | HPAS-10%     |
|-----------------|--------------|--------------|--------------|--------------|--------------|
| Relative crystallinity (%) | 21.99±0.08<sup>a</sup> | 21.37±0.12<sup>ab</sup> | 21.28±0.07<sup>ab</sup> | 21.03±0.09<sup>b</sup> | 20.97±0.13<sup>b</sup> |
| Solubility (%)  | 29.16±1.88<sup>d</sup> | 40.90±0.25<sup>c</sup> | 49.51±1.91<sup>b</sup> | 51.42±1.81<sup>b</sup> | 58.42±0.79<sup>a</sup> |
| Swelling power  | 10.62±0.48<sup>d</sup> | 11.98±0.31<sup>c</sup> | 13.25±1.13<sup>c</sup> | 15.45±0.89<sup>b</sup> | 16.17±0.54<sup>c</sup> |
| Water-binding capacity (%) | 161.89±0.68<sup>e</sup> | 171.87±0.13<sup>d</sup> | 180.52±0.42<sup>c</sup> | 183.54±0.46<sup>b</sup> | 187.95±0.06<sup>a</sup> |

The same letters (a-e) are not significantly different within each row (P<0.05).

Fig. 3. Shape and size of hydroxypropylated apios starch (HPAS) granules shown by a scanning electron microscope (×1,500). (A) Native, (B) HPAS-2.5%, (C) HPAS-5%, (D) HPAS-7.5%, and (E) HPAS-10%.
results in a change in the starch shape, as the center of the starch particle tissue becomes relatively loose. This study also confirms that starch molecules are being dented towards their centers as the degree of hydroxypropyl substitution increases. Therefore, this study demonstrated that the morphology of starch particles was changed by hydroxypropylation and the relative crystallinity of the starch was reduced. This result supposed that high level hydroxylation can affect not only the amorphous region of starch but also the crystal region.

**Solubility and swelling power**

Solubility and swelling power of native starch and HPAS are shown in Table 2. Solubilities of native apios starch and HPAS-10% starch were 29.16 and 58.42, respectively, and their swelling powers were 10.62 and 16.17, respectively, which implies that hydroxypropylation increases both swelling power and solubility. Swelling and elution occur when starch is heated in water. Swelling power and solubility are known as to be affected by many factors including heat treatment, particle structure, and type of starch (Leach et al., 1959). Swelling power is the ability to become hydrated and it is closely related to solubility, clarity, and viscosity. Swelling property of starch is largely affected by the intensity and property of micelle structure; solubility is influenced to a larger extent than swelling power (Gunaratne and Corke, 2007). Furthermore, Gunaratne and Corke (2007) have reported that hydrogen bonds in starch collapse because of hydroxypropylation, and moisture then permeates into the loosened starch structure, which results in an increase in swelling power. Both swelling power and solubility appeared to increase in this study as hydroxypropylation loosens the starch structure. A study by Kaur et al. (2004) also shows a similar result; both swelling power and solubility of potato starch increased with an increase in the degree of hydroxypropyl substitution.

**Water-binding capacity**

The water-binding capacities of native apios starch and HPAS are shown in Table 2. As the degree of hydroxypropyl substitution increases, the water-binding capacity increased from 161.89 to 187.95. This result was consistent with that of a study by Bae et al. (1997), which stated that the water-binding capacity of potato starch is increased by hydroxypropylation. Water-binding capacity represents the affinity between moisture and the starch. Bonded water is absorbed into the starch particles or onto their surfaces (Lee et al., 2000). Water-binding capacity is determined by the ratio of the crystalline region and amorphous region on the starch particle; a larger amorphous region results in higher water binding capacity (Lee and Shin, 1991).

**Light transmittance**

Light transmittance of native starch and HPAS is shown in Fig. 4. Light transmittance values of native apios starch and HPAS-2.5% did not change significantly up to 65°C, but dramatically increased from 70°C. In the case of HPAS-5%, HPAS-7.5%, and HPAS-10%, light transmittance increased from 65°C. Madamba et al. (1975) reported that in spite of slight differences between the different starch species, most of them have gelatinization temperatures between 63.6 and 70.7°C, which corresponds to that of apios starch. Additionally, light transmittance of hydroxypropylated starch was higher than that of native starch, regardless of the temperature; light transmittance of the starch slurry became higher with the increase in the degree of hydroxypropyl substitution. Such an increment in light transmittance is caused by the hydroxypropyl substitution that weakens the retentivity of particles and loosens their structures. Swelling and gelatinization is thus easier when heated (Tuschhoff, 1988). Furthermore, Liu et al. (1999) reported that the bonding in hydroxypropylated starch is disturbed; this enhances starch clarity during gelatinization. Clarity of food is an important organoleptic property in the production of jellies, sauces, or fruit pie fillings. Thus, HPAS, which has an enhanced clarity, can be considered as suitable materials for preparing these foods.

**Thermal analysis**

The gelatinization temperatures (T<sub>G</sub>, T<sub>p</sub>, and T<sub>c</sub>) and ∆H from native apios starch and HPAS were measured by differential scanning calorimetric analysis (Table 3). ∆H of native apios starch was 4.845 J/g, whereas that of HPAS-2.5% was 4.161 J/g, which implies that ∆H decreases with an increase in the degree of hydroxypropylation. T<sub>G</sub>, T<sub>p</sub>, and T<sub>c</sub> values for HPAS also decreased, compared to native apios starch. This result is consistent with the results obtained from hydroxypropylated potato starch, rice starch, pea starch, and maize starch (Wootton...
and Manatsathit, 1983; Hoover et al., 1988; Seow and Thevamalar, 1993; Kaur et al., 2004). The results from this study are also consistent with the fact that gelatinization temperature decreases as substitution increases in the previous studies. Perera and Hoover (1999) demonstrated the reason for the decrease of gelatinization temperature of hydroxypropylated starch. They reported that the hydroxypropylation process weakens hydrogen bonds in the amorphous regions, and then collapses the double helices, which consequently attenuates the crystalline regions. As a result, a smaller amount of energy is required for gelatinization of hydroxypropylated starch. Furthermore, hydroxypropylation in the crystalline region causes the swelling phenomenon, which results in the process of starch particle fracture and recombination of amylpectin double helices (Bemiller, 1997). Similarly, in this study, it was thought that the weakening of hydrogen bonds by hydroxypropylation can facilitate swelling of apios starch, and thus, easier gelatinization can be allowed. In addition, hydroxypropylation can cause a decrease in gelatinization temperature and facilitate the gelatinization process.

**AUTHOR DISCLOSURE STATEMENT**

The authors declare no conflict of interest.

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Table 3. DSC characteristics of hydroxypropylated apios starch (HPAS)

| Sample     | T₀ (°C) | Tp (°C) | TC (°C) | ∆H (J/g) |
|------------|---------|---------|---------|----------|
| Native     | 69.06   | 75.08   | 89.74   | 4.845    |
| HPAS-2.5%  | 65.24   | 70.08   | 79.89   | 4.161    |
| HPAS-5%    | 63.94   | 68.53   | 78.72   | 1.746    |
| HPAS-7.5%  | 61.44   | 67.48   | 74.12   | 1.257    |
| HPAS-10%   | 60.20   | 65.84   | 71.35   | 0.586    |

T₀, onset temperature; Tp, peak temperature; TC, completion temperature; ∆H, enthalpy.
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