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Characterization of new starches separated from several traditional Chinese medicines

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ABSTRACT

Starches were isolated from three traditional Chinese medicines (TCMs), *Angelica dahurica* (AD), *Trichosanthes kirilowii* (TK) and *Polygonum multiflorum* (PM), which were investigated for amylose content, morphological, thermal, crystal, swelling factor, and pasting properties. Amylose contents of AD, TK and PM were 20.8%, 30.3% and 31.8%, respectively. The granule lengths were in the size of 5–30 μm, 10–22.5 μm and 8.7–18.7 μm, respectively. The decomposition temperatures were similar at about 325 °C. The AD and PM starches showed the typical B-type, while TK starch was the C-type. The degrees of crystallinity for AD, PM and TK were 38.33%, 43.10% and 36.71%. In differential scanning calorimetry analysis of starches, the transition temperatures, transition range, and enthalpies of gelatinization (ΔH_{gel}) were determined. The pasting properties were also analyzed by using a Rapid Visco Analyzer. The dependence of swelling factor for three starches on temperature was tested at 10 °C intervals between 50 °C and 90 °C.

1. Introduction

Starch is a low cost, renewable and biodegradable carbohydrate polymer from a great variety of crops. Because of their ready availability and their extensive utilization in food and non-food application for several centuries, starches from wheat, corn, potato, and rice, have been researched extensively. Their physicochemical and functional properties are highly related to their sources, which determine the fine structure of the polysaccharide and the percentage distributions of amylose and amylopectin (Kaur, Singh, Sandhu, & Guraya, 2004).

Medicinal plants are the special kind of plant groups, which play a very good role in treatment of disease. Many traditional Chinese medicines (TCMs) contain a large number of starches in the bulb or roots. However, only active pharmaceutical ingredients are concerned on. When they are extracted from TCM, starch components are usually discarded. The extensive research on structure and functional properties of these novel starches from TCM will be necessary to widen their applications.

Angelica dahurica (AD) (Kang, Zhou, Sun, Han, & Guo, 2008), *Trichosanthes kirilowii* (TK) (Shin, Son, & Kang, 2008) and *Polygonum multiflorum* (PM) (Xu, Zheng, & Lee, 2006) are called *Bai-zhi*, *Tian-hua-fen* and *Ha-soo-Oh* in Chinese, which have been traditionally and widely prescribed in Chinese clinics. Starch is the main component in these three TCMs. In order to make good use of medicinal plant resources and widen their industrial application, we study the morphology, thermal stability, crystalline and swelling power of starch from these TCMs.

2. Materials and methods

2.1. Materials

A. dahurica (AD) and *P. multiflorum* (PM) were obtained from HeBei province, China. *T. kirilowii* (TK) was purchased from Shandong province, China.

2.2. Isolation of starch

Several starches were isolated according to the modified method of Simsek, Tulbek, Yao, and Schatz (2009) and Wang, Yu, Liu, and Chen (2008). The materials were washed, cut into small pieces and milled to pass through a 120 mesh sieve. The powders were steeped into water containing 0.02% NaOH for 12 h. After precipitation of starch, the supernatant was removed. The starch was washed three times in deionised water. The slurry containing starch was centrifuged in wide-mouthed cups at 3000 rpm for 5 min. The supernatant and upper non-white layer, which con-

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Table 1
Properties of starches for AD, TK and PM.

Starch	Amylose (%)	Gelatinization temperature (°C, DSC)				Enthalpy (J/g, DSC)	Relative crystallinity (%, X-ray)
		T_o	T_p	T_c	ΔT		
AD	20.8	50.3	56.2	66.7	16.4	7.89	38.33
TK	30.3	53.7	60.9	68.8	15.1	7.55	43.10
PM	31.8	58.2	65.8	73.1	14.9	8.42	36.71

T_o, onset temperature; T_p, peak temperature; T_c, completion temperature; $\Delta T = T_c - T_o$.

tained the skin and cell wall, were removed. The white layer (starch layer) was resuspended in distilled water and recentrifuged three times. Finally, the starch was washed with ethanol. The starch samples were collected and dried overnight at 30 °C.

2.3. Physicochemical properties of starch

2.3.1. Amylose content

Amylose content of the isolated starch was determined in triplicate by using the method of Wang et al. (2007) and Williams, Kuzina, and Hiynka (1970). The amyloses from AD, TK and PM were, respectively separated by alkali leaching, purified, and used as a standard.

2.3.2. Morphology

Scanning electron micrographs (SEM) were obtained with an environmental scanning electron microscope (ESEM, Philips XL-3), operating at an acceleration voltage of 20 kV. Starch samples were suspended in the ethanol. The suspension drops were drawn on the glass flake, dried for removing the ethanol, and then vacuum coated with gold for SEM.

2.3.3. Differential scanning calorimetry (DSC)

The temperature range of gelatinization was measured using a differential scanning calorimeter DSC204, HP (NETZSCH, Germany) equipped with a thermal analysis station. Starches (about 10 mg) were weighed in the aluminium pan, and deionised water was added on to achieve a starch–water suspension containing 70% water. The pan was hermetically sealed and held for 1 h at room temperature. The DSC analyzer was calibrated using indium and an empty aluminium pan was used as reference. Sample pans were heated at a rate of 10 °C/min from 20 °C to 120 °C. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy of gelatinization (ΔH_{gel}) were calculated.

2.3.4. Thermogravimetric analysis (TGA)

Thermal properties of starch powders were measured with a ZTY-ZP type thermal analyzer. Sample weight varied from 10 mg to 15 mg. Samples are heated from room temperature to 550 °C at a heating rate of 15 °C/min in a nitrogen atmosphere.

2.3.5. X-ray powder diffraction (XRD)

Starch powders were placed in a sample holder for XRD. XRD patterns were recorded in the reflection mode in angular range 4–30° (2θ) at the ambient temperature by a Panalytical X'Pert Pro diffractometer (PANalytical, Holland), operated at 45 kV and 30 mA with the Co Kα radiation, $k = 0.178901$ nm. The degree of crystallinity of samples was quantitatively estimated, following the method of Wang, Yu, and Yu (2008).

2.3.6. Characteristics of starch pastes

The pasting properties were analyzed using a Rapid Visco Analyzer (Newport Scientific, Sydney, Australia) according to AACC method 76-21 (Xie & Liu, 2004). 1.5 g of the powders was dispersed into a solution of distilled water (25 mL). The obtained starch slurry was held at 50 °C for 1 min, then heated to 95 °C at 12.2 °C/min and held at 95 °C for 2.5 min. It was then cooled to 50 °C (cooling rate of 11.8 °C/min) and held at 50 °C for 2 min. The paddle speed was 960 rpm for 10 s and then decreased to 160 rpm for the remainder of the experiment.

2.3.7. Swelling factor (SF)

The swelling factor was determined using a method described by Simsek et al. (2009). Starch slurries of each sample were made to contain 0.20 g starch and 10 mL deionised water. The starch slurries were heated and stirred. The slurries were equilibrated at 25 °C for 30 min before heating at 50 °C, 60 °C, 70 °C, 80 °C, or 90 °C for 60 min, and then cooled to 25 °C before centrifuging at 1000 × g for 20 min after the slurries were transferred into centrifuge tubes. Different starch slurry samples were used for each temperature treatment. The supernatant was removed and the swelling factor (SF) was calculated as: SF (mL/g dry starch) = (10 mL − supernatant volume)/0.2 g starch.

3. Results and discussion

3.1. Amylose content

Amylose contents of starches for AD, TK and PM are 20.8%, 30.3% and 31.8%, which are listed in Table 1. AD starch is obviously lower than TK and PM starches.

3.2. Morphology of starch granules

As shown in Fig. 1, three starches differed significantly in granule size and shape. Most of starch granules are spherical, even though round, oval and irregular shaped granules are also observed. AD starch shows the largest variation in terms of granule length from 5 μm to 30 μm. The lengths of TK and PM starches are 8.7–18.7 μm and 10–22.5 μm, respectively.

3.3. TGA

In TGA, the loss in mass due to volatilization of the degradation products is monitored as a function of temperature. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the starch powders were shown in Fig. 2. The mass loss of the powders is mainly ascribed to water loss before the initial decomposition temperature, T_{ini}, where the decomposition of starches appears at 267.3 °C, 268.6 °C and 273.6 °C for AD, TK and PM. T_{max}, the temperature at the maximum rate of mass loss is the peak temperature shown in DTG curves. The decomposition temperatures of AD, TK and PM are 324.9 °C, 326.3 °C and 326.3 °C, respectively. They exhibit similar thermal stability.

3.4. X-ray diffractograms

The X-ray diffractograms of the starches are presented in Fig. 3. The X-ray diffraction patterns are compared with reported standard diffraction patterns of different crystalline types (Gernat, Rodosta, & Anger, 1993). The AD and PM starches show the highly similar X-ray diffraction patterns, the typical B-type. They give the strongest

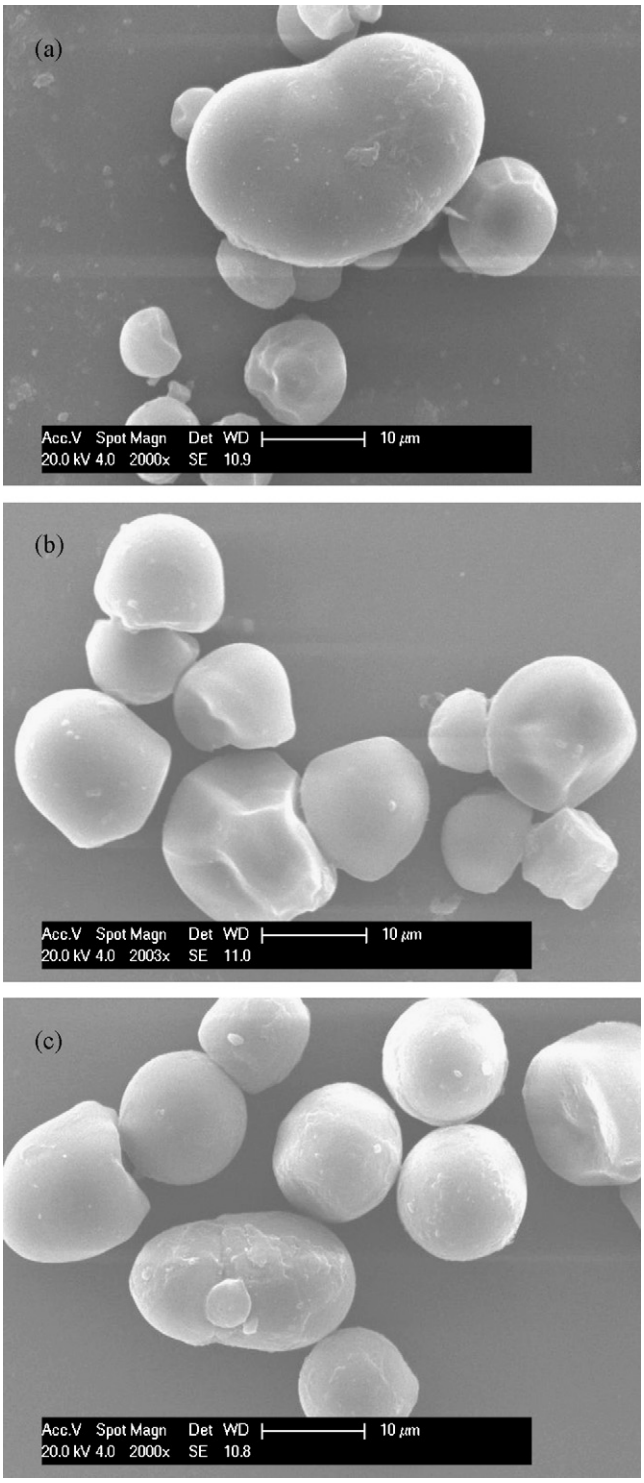

Fig. 1. SEM micrograph of granular starches for AD (a), TK (b) and PM (c).

diffraction peaks at 17° 2θ and a few small peaks at around 2θ values of 15°, 22° and 24°. A representative peak appears at 5.6° 2θ, which is characteristic of B-type starch (Wang, Yu, Liu, et al., 2008). The crystalline structure in TK starch is different from that in AD and PM starches. Crystals in TK starch are C-type, which shows the peaks at 14.8°, 16.9° and 23.1° 2θ. As shown in Table 1, the relative crystallinity of TK starch (43.10%) is higher than those of AD (38.33%) and PM (36.71%) starches.

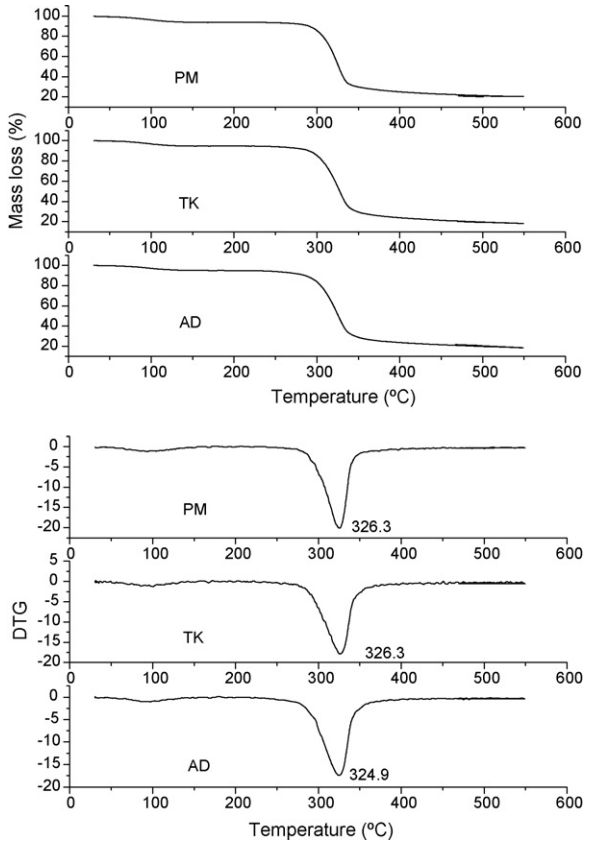

Fig. 2. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of starches for AD, TK and PM.

3.5. Differential scanning calorimetry (DSC)

In DSC analysis of starches, the transition temperatures (T_o, T_p and T_c), range (T_c–T_o), and enthalpies of gelatinization (ΔH_{gel}) are summarized in Table 1. Starch gelatinization is the transition from an order to disorder phase. Starch granule begins to swell and intermolecular hydrogen bonds of starch molecules breakdown in the presence of sufficient water and elevated temperature. At higher temperatures, the granule is completely disrupted and gelatinization is finished (Ratnayake, Hoover, & Warkentin, 2002). PM starch exhibits the highest ΔH_{gel} of 8.42 J/g, while TK starch shows the

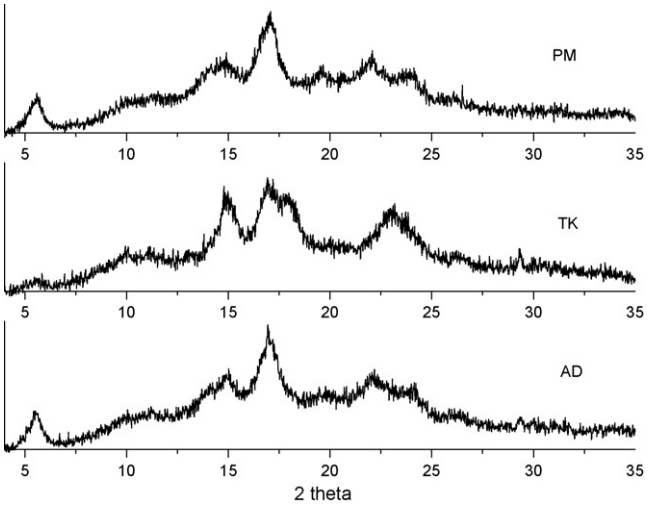

Fig. 3. X-ray diffraction patterns of starches for AD, TK and PM.

Table 2
Pasting characteristics of starches for AD, TK and PM determined by RVA.

Starch	Pasting temperature (°C)	PT (min)	PV (cP)	HV (cP)	FV (cP)	BKD (cP)	STB (cP)
AD	68.5	5.17	858	774	1084	84	310
TK	69.7	4.27	1050	718	904	332	186
PM	71.1	3.9	739	551	915	188	364

RVA, Rapid Visco Analyzer; PT, peak time; PV, peak viscosity; HV, holding viscosity; FV, final viscosity; BKD (breakdown = PV − HV); STB (setback = FV − HV).

lowest ΔH_{gel} of 7.55 J/g. According to Tester and Morrison (1990), ΔH_{gel} is an indicator of the loss of molecular order within the granules. In Table 1, X-ray diffraction data of starches reveals that ΔH_{gel} value increases with the decreasing of the crystallinity of starches for AD, TK and PM.

In views of the transition temperatures (T_o, T_p and T_c), PM starch shows the highest values, followed by TK, whereas it is the lowest for AD. The differences in gelatinization temperature may be attributed to the differences in amylose content, size, form and distribution of starch granules, and to the internal arrangement of starch fractions within the granule. Noda et al. (1998) have postulated that T_o, T_p and T_c are influenced by the molecular architecture of the crystalline region, which corresponds to the distribution of short chain amylopectin.

3.6. Pasting properties

As shown in Fig. 4, the pasting profiles of three starches are similar. The results are listed in Table 2. Pasting properties are reported to be influenced by granule size, amylose/amylopectin ratio, starch molecular characteristics, and the condition of the thermal process employed to induce gelatinization (Simi & Abraham, 2008).

The pasting temperatures of AD, TK and PM starch are 68.5 °C, 69.7 °C and 71.1 °C, which are close to the gelatinization temperature obtained by DSC analysis. The peak time (PK) of AD is much more than those of TK and PM. It can be related to the granules in the large size, the complete disruption of which cost more time. TK and PM, respectively exhibit the highest peak viscosity value (1050 cP) and final viscosity (1084 cP). The breakdown viscosity is regarded as a measure of the paste stability. AD starch showed higher paste stability. The setback viscosity of PM is higher than AD and TK. The setback is the viscosity increase resulting from the rearrangement of amylose molecules. The setback is generally used as a measure of the gelling ability or retrogradation tendency of the starch (Simi & Abraham, 2008).

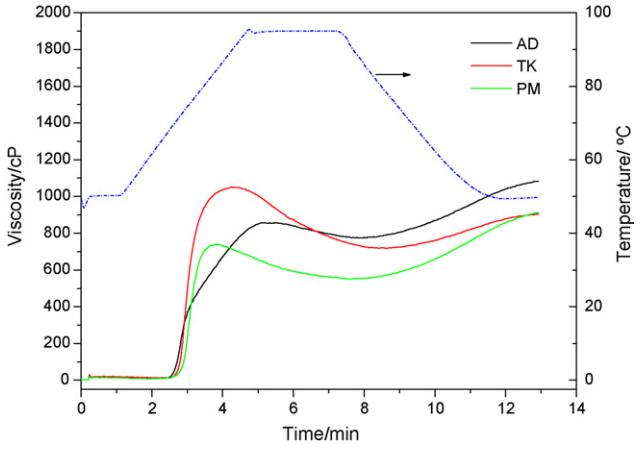

Fig. 4. Pasting curves of starches for AD, TK and PM. The top curve (dash dot line) is the temperature profile.

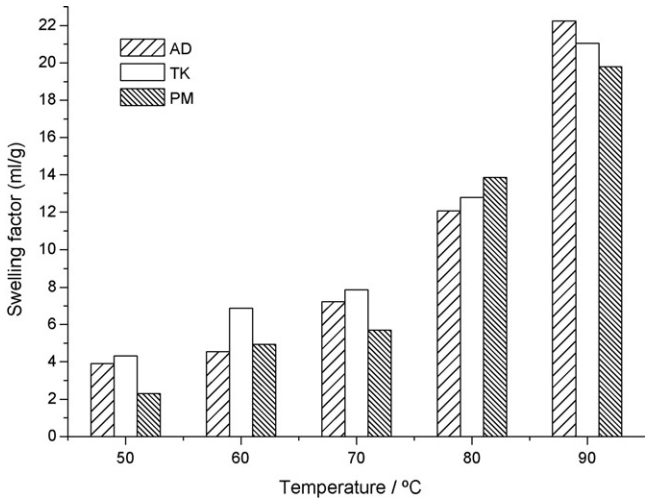

Fig. 5. Swelling factor analysis of starches for AD, TK and PM.

3.7. Swelling factor (SF)

With the increasing of the temperature, water gradually swells the granules of starch and disrupts some of intermolecular and intramolecular hydrogen bonds among starch molecules (Ma, Jian, Chang, & Yu, 2008). At this time, the crystalline structure is destroyed instead of an amorphous structure. Exposed hydroxyl groups of starch form hydrogen bonds with water molecules. On the other hand, the original interactions among starch still retain the structural association originated from the granular structure. The equilibrium between granule swelling and retaining governs the swelling factor (Simsek et al., 2009).

The dependence of swelling factor on temperature is tested at 10 intervals between 50 °C and 90 °C with continuous mixing (Fig. 5). The rapid increase in the swelling factor was detected between 70 °C and 90 °C, while the swelling factor increased slightly from 50 °C to 70 °C, where TK has the highest swelling factor. The higher swelling factor at 90 °C indicates that more amylopectin chains can form more strongly associated in AD starch than TK and PM starches (Hoover, Li, Hynes, & Senanayake, 1997).

4. Conclusions

Three starches are isolated from TCMs. Compared to starches from TK and PM, AD exhibits lower amylose content, wider particle size distribution and B-type crystalline structure. There are no obvious difference among three starches in term of thermal stability, the degree of crystallinity, the transition temperature range (T_c–T_o), enthalpies of gelatinization and swelling factors. The results of this study will provide the basic knowledge on the starch structure of AD, TK and PM. And it will extend the application (such as thermoplastic starch, porous starch, raw materials for starch derivatives and so on) of these starches, which are ever regarded as the waste of TCM extraction. Acid modification of starch will be carried out to further understand the inner structure of starch granules (Wang, Yu, & Yu, 2008).

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