



Amylolysis of native and annealed potato starches following progressive gelatinisation



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ABSTRACT

The extent of α -amylase hydrolysis of normal potato starches, extracted from different varieties grown under the same conditions in the same season, is regulated more by gelatinisation than the composition or structure of the granules. This is evident for native and annealed starches gelatinised and then hydrolysed with α -amylase. With similar gelatinisation peak (T_p) temperatures (62.5–66.1 and 70.2–72.3 °C respectively) and enthalpies (15.1–17.8 and 15.8–19.5 Jg⁻¹ respectively) for the native and annealed starches, increasing the temperature exposure in excess water (to cause progressive gelatinisation) by 10 °C increments creates progressively more hydrolysis reflecting the (similar) gelatinisation transition. Overall, therefore, processing has a greater potential impact on the glycaemic index (GI) of potato starches than any variety specific variations.

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1. Introduction

Potato starches provide a good model by which variety specific variations in starch properties can be tested, using tubers grown at the same site and at the same time (or indeed different sites). The properties of potato starches are quite different from other starches (Singh, Singh, Kaur, Sodhi, & Gill, 2003). A study on some physico-chemical properties of ten potato varieties grown at the same site at the same time have been discussed elsewhere (Alvani, Qi, Tester, & Snape, 2011). Subtle physical differences related to the structure of the α -glucans and their architectural associations have been identified. These data support previous data reported by Yusuph, Tester, Ansell, and Snape (2003). Other groups have reported varietal and seasonal influences on potato starch α -glucan composition/structures and starch properties (Alvani, Qi, & Tester, 2012; Hemar et al., 2007; Karim et al., 2007; Kaur, Singh, Ezekiel & Guraya, 2007; Kaur, Singh, McCarthy, & Singh, 2007; Kaur, Singh, & Sodhi, 2002; Liu, Tarn, Lynch, & Skjodt, 2007; Liu, Weber, Currie, & Yada, 2003; Lu et al., 2011; Pycia, Juszczak, Galkowska, & Witzczak, 2012; Singh, Kaur, & Singh, 2004; Singh, Isono, Srichuwong, Noda, & Nishinari, 2008; Svegmarm et al., 2002; Zaidul et al., 2007).

Relatively large granule sizes such as those found in potato starches reduce the amount/extent of hydrolysis of native granules

with enzymes (including α -amylase) although post gelatinisation this 'resistance' is lost (Noda et al., 2008). The work of these authors' has indicated, however, that the role of starch phosphorylation with respect to amylase susceptibility was less clear. Starch granule composition and architecture affects α -amylase hydrolysis of sweet potato starches extracted from different varieties grown under the same conditions (Zhang & Oates, 1999). Amyloglucosidase shows similar (sweet potato) variety specific hydrolysis patterns (Noda, Takahata, Nagata, & Monma, 1992).

Treatment of partially swollen/gelatinised potato starches with α -amylase (and amyloglucosidase) has shown that although starch phosphorylation could restrict enzyme hydrolysis, granule size and amylose content were less significant factors (Absar et al., 2009). Similar effects have been reported for sweet potato (and tapioca) starches (Shariffa, Karim, Fazilah, & Zaidul, 2009). The enhancement of α -amylase hydrolysis by partial gelatinisation of potato starch (*in vitro*) should reflect hydrolysis *in vivo* and hence Glycaemic index (GI, Parada & Aguilera, 2009).

Heat-moisture treatments applied to potato starch can influence the physical properties (Eerlingen, Jacobs, Block, & Delcour, 1997) and digestibility (rate) *in vivo* by digestive α -amylase (Lee, Kim, Choi, & Moon, 2012). Annealing of potato starches also affects their physico-chemical properties – with a relationship between (native and modified) physical properties and the extent of phosphorylation (Muhrbeck & Svensson, 1996). Annealing increases the gelatinisation temperatures of potato starches where the magnitude of change depends on the initial gelatinisation temperatures of the starches (Alvani et al., 2012). The susceptibility of potato

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Table 1
Amylose and phosphorus content of ten potato starches.

Cultivar	Amylose (α -glucan basis, %)	Phosphorus (mg/100 g, db)
Brodick	29.05 \pm 0.13	57.38 \pm 0.59
Desiree	25.51 \pm 0.05	52.90 \pm 0.26
Inca Sun	26.23 \pm 0.19	52.59 \pm 0.32
Kara	27.04 \pm 0.20	64.50 \pm 0.46
Maris Piper	27.06 \pm 0.20	58.04 \pm 0.29
Mayan Gold	25.23 \pm 0.18	66.20 \pm 0.45
Pentland Crown	26.91 \pm 0.10	59.48 \pm 0.25
Pentland Dell	26.54 \pm 0.06	62.05 \pm 0.25
Pentland Javelin	27.97 \pm 0.12	65.76 \pm 0.34
Record	28.10 \pm 0.06	65.02 \pm 0.33

Adapted from Alvani et al. (2011).

starches to acid or enzymatic hydrolysis decreases upon annealing (Hoover & Vasanthan, 1993). Cooking methods can affect the amount and profile of resistant starch in potato starches and hence the Glycaemic index in food systems (Gracia-Alonso & Goñi, 2000; Kingman & Englyst, 1994; Mishra, Monro, & Hedderley, 2008).

The glycaemic index of foods has become a very popular nutritional aspect to define in recent years and has been used to define the 'healthiness' (less pronounced glucose response). Sometimes the underlying reasons for differences in the glycaemic indices of foods are overlooked. Potatoes are usually considered to have a high glycaemic index when cooked – although cooking methods vary and the relationship between the amount of starch present and the extent of gelatinisation is often not considered.

The aim of this study was to investigate if starches extracted from different potato varieties grown at the same site and the same time, were more or less susceptible to (fungal) α -amylase hydrolysis in (i) their native form, (ii) after annealing and (iii) when partially gelatinised. This work has implications with respect to predicting and controlling the glycaemic index of the potato tubers.

2. Materials and methods

2.1. Potatoes

Ten potato cultivars (Brodick, Kara, Desiree, Inca Sun, Maris Piper, Mayan Gold, Pentland Crown, Pentland Dell, Pentland Javelin

and Record) were grown at the same time and under the same conditions in Perthshire at the Scottish Crop Research Institute (SCRI), Dundee, UK as reported elsewhere (Alvani et al., 2011; 2012).

2.2. Reagents and enzymes

All chemicals, reagents and solvents were of Merck Analar quality or better.

2.3. Chemical characterisation

This proximate composition has been reported elsewhere (Alvani et al., 2011).

2.4. Hydrolysis with fungal α -amylase

The general method used to determine the extent of starch hydrolysis was according to Karkalas, Tester, and Morrison (1992). However, the fungal α -amylase (E.C. 3.2.11, Sigma A-62211 from *Aspergillus oryzae*, 150–250 U mg^{-1}) concentration was a factor of five times more than utilised in the general method.

2.5. Pre-swelling starch

Starches (25 mg ml $^{-1}$) were incubated from 25 to 80 °C (shaking water bath, approximately 60 cycles s $^{-1}$) for 30 min and then cooled to room temperature. Within 15 min of reaching room temperature, the extent of hydrolysis (2.4) was determined.

2.6. Annealing

Starches were annealed according to Alvani et al. (2012). Starch samples (2 g) were weighed into 100 ml conical flasks to which 100 ml deionised water (containing 0.02% sodium azide) was added by pipette. The flasks were shaken at approximately 60 cycles s $^{-1}$ in a water bath at 50 °C for 14 days.

Table 2
Gelatinisation properties (DSC) of native and annealed potato starches.

Cultivar		Gelatinisation temperatures (°C)			Enthalpy (ΔH , Jg $^{-1}$)	T _c –T _o (°C)
		T _{Onset}	T _{Peak}	T _{Conclusion}		
Brodick	Native	61.01 \pm 0.10	64.82 \pm 0.38	70.69 \pm 0.54	16.41 \pm 0.13	9.68 \pm 0.54
	Annealed	68.36 \pm 0.23	71.21 \pm 0.03	77.00 \pm 0.47	18.20 \pm 0.31	8.64 \pm 0.62
Desiree	Native	59.20 \pm 0.19	63.55 \pm 0.21	69.83 \pm 0.30	17.78 \pm 0.31	10.64 \pm 0.48
	Annealed	67.83 \pm 0.29	70.96 \pm 0.02	76.30 \pm 0.44	18.08 \pm 0.15	8.47 \pm 0.31
Inca Sun	Native	60.37 \pm 0.30	62.96 \pm 0.09	70.47 \pm 0.37	17.49 \pm 0.15	10.10 \pm 0.40
	Annealed	69.04 \pm 0.14	71.23 \pm 0.09	76.80 \pm 0.37	17.90 \pm 0.77	7.75 \pm 0.49
Kara	Native	62.45 \pm 0.09	66.05 \pm 0.22	71.86 \pm 0.26	15.83 \pm 0.11	9.41 \pm 0.25
	Annealed	69.12 \pm 0.10	71.87 \pm 0.11	76.86 \pm 0.07	15.76 \pm 0.30	7.74 \pm 0.11
Maris Piper	Native	59.89 \pm 0.48	63.72 \pm 0.35	69.59 \pm 0.05	17.40 \pm 0.10	9.71 \pm 0.43
	Annealed	68.04 \pm 0.10	70.82 \pm 0.10	76.34 \pm 0.48	19.54 \pm 0.23	8.30 \pm 0.47
Mayan Gold	Native	61.20 \pm 0.08	65.90 \pm 0.63	72.27 \pm 0.58	15.13 \pm 0.04	11.08 \pm 0.62
	Annealed	68.83 \pm 0.10	72.30 \pm 0.11	77.37 \pm 0.16	17.57 \pm 0.34	8.54 \pm 0.17
Pentland Crown	Native	60.95 \pm 0.38	64.46 \pm 0.57	69.58 \pm 0.44	17.11 \pm 0.35	8.63 \pm 0.53
	Annealed	68.38 \pm 0.13	71.34 \pm 0.13	76.77 \pm 0.14	17.72 \pm 0.77	8.39 \pm 0.25
Pentland Dell	Native	59.56 \pm 0.14	63.71 \pm 0.68	69.52 \pm 0.21	15.37 \pm 0.19	9.96 \pm 0.09
	Annealed	66.75 \pm 0.12	70.22 \pm 0.45	76.23 \pm 0.64	17.90 \pm 0.25	9.48 \pm 0.33
Pentland Javelin	Native	58.71 \pm 0.22	62.52 \pm 0.27	68.67 \pm 0.22	15.40 \pm 0.31	9.96 \pm 0.41
	Annealed	66.15 \pm 0.13	71.13 \pm 0.13	76.21 \pm 0.25	16.00 \pm 0.27	10.06 \pm 0.54
Record	Native	61.18 \pm 0.02	65.88 \pm 0.59	72.09 \pm 0.47	17.76 \pm 0.12	10.91 \pm 0.36
	Annealed	68.21 \pm 0.15	70.85 \pm 0.00	76.90 \pm 0.15	18.73 \pm 0.43	8.69 \pm 0.22

Adapted from Alvani et al. (2012).

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