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Effects of storage temperatures and annealing conditions on the structure and properties of potato (*Solanum tuberosum*) starch

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Abstract

Starches were extracted from freshly harvested potatoes (12 cultivars, grown in Perthshire) and the properties of the starches of six cultivars were compared with starches extracted from the same samples but stored at 5, 25 or 55 °C for 7 days before extraction. The amylose (total) content of the freshly extracted starches from tubers stored at 5, 25 or 55 °C was on average 27.9 ± 2.3, 28.3 ± 1.7, 29.2 ± 2.2 and 28.8 ± 1.5%, respectively, with corresponding phosphorus representing 60 ± 16, 64 ± 9, 61 ± 5 and 63 ± 9 mg 100 g^{-1}. The unit chain distribution by chromatography of the amylopectin molecules from the starches extracted from the different conditions was very similar with an average degree of polymerisation (DP) of 26 ± 2 where the two major fractions (F1 and F2) represented 54 ± 2 and 19 ± 1, respectively. Peak gelatinisation temperatures (T_p) and enthalpies (ΔH) for the freshly extracted starches and from tubers stored at 5 or 25 °C were very similar (63.3 ± 1.5 °C and 18.6 ± 0.8 J g^{-1}; 63.1 ± 1.0 °C and 17.7 ± 1.5 J g^{-1} and; 62.9 ± 0.7 °C and 18.7 ± 1.1 J g^{-1}, respectively) although starches stored at 55 °C were annealed, where T_p represented 71.1 ± 1.1 °C and ΔH 18.1 ± 1.4 J g^{-1}. These in situ-annealed starches were comparable in terms of gelatinisation characteristics to annealed freshly extracted starches where on average, T_p represented 72.7 ± 1.0 °C and ΔH 20.8 ± 1.0 J g^{-1}. Annealing of tubers in situ prior to processing might be beneficial with respect to developing new potato-based products.

Keywords: Potatoes starch; Amylose; Gelatinisation temperature; Annealing condition

1. Introduction

Annealing processes (and comparisons with 'heat–moisture treatments') with respect to starch (especially potato) structure and properties have been discussed in detail and reviewed by others elsewhere [1–16]. Annealing of starch involves heating granules below their onset of gelatinisation (T_o) for a period of time (many hours/few days) in excess water, whereupon crystalline order within starch granules is improved and the gelatinisation endotherm is 'sharpened'. The annealing effect is maximised the closer the temperature is set to (T_o) (which is well above the glass transition temperature (T_g) in excess water [13]), when water is not limiting and when there is a long duration (days not hours). This reorganisation tends to be associated with a slight increase in the proportion of double helical material (due to improvement of helical length but not the formation of new helices) and hence a slight increase of the enthalpy of gelatinisation. The gelatinisation temperatures (especially T_o and the peak temperature, T_p, but less so the conclusion temperature, T_c) increase whilst the gelatinisation range ($T_c - T_o$) is reduced (endotherm 'sharpened'). This is due to an increase in helical lengths and restriction of granule hydration caused by the more ordered granule crystallites (with perhaps more 'rigid' interspersed amorphous regions) which are analogous to the effects of (elevated) growth temperature on starch properties and crystalline lamellae lengths [17–25]. Enhanced ordering

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(registration) causes a requirement for higher temperatures to 'drive' double helix hydration and dissociation accordingly. At equilibrium the enthalpy (ΔH) = the temperature (T) multiplied by the difference in entropy (ΔS) [$\Delta H = T\,\Delta S$]. If ΔH increases post-annealing (reflecting more hydrogen-bonded double helices) the parameter $T\,\Delta S$ must increase—with a greater magnitude of ΔS at a constant T. Small increases in helical length would exert an increase in ΔH. Recent work on starch crystallite dimensions pre- and post-annealing has confirmed that there tends to be a small increase in their radial lengths due to this form of thermal processing [28–30].

Recently [29,30] research has been conducted on the gelatinisation and retrogradation properties of potato starch in situ. This is an interesting approach which might be adopted to produce novel potato-based products. The work discussed in this paper presents a comparison between annealing-based changes to starch structures within potatoes (in situ) and starches extracted from the native tubers. The aim was to identify if the physico-chemical properties of the tubers (starches) could be modified prior to processing by annealing and reveal potentially new processing opportunities. The research presents an extension of work undertaken on these starches which is discussed elsewhere [30].

2. Experimental

2.1. Materials

Potato tubers were grown and starches were extracted as described previously [30]. The extracted starches were annealed by heating samples containing 80% moisture (by weight on a dry starch basis) within sealed 10 ml Sovirel screw cap tubes (containing 10 μl of toluene as a bacteriostatic agent) at 55 °C for 7 days.

Whole tubers were annealed at different temperatures within incubators for 7 days. For incubations at 5 and 25 °C, the tubers were simply placed in incubators at the pre-set temperatures. For treatment at 55 °C, however, the tubers were washed and then soaked in 1% sodium metabisulphite before incubation to prevent spoilage. After the incubation, the tubers were peeled, liquidised in cold 1% sodium metabisulphite and the starches were extracted as previously described [30].

2.2. Methods

2.2.1. Analytical

Compositional analysis of the native starches have been described previously [30] using established protocols [31–34]. Starch susceptibility to 2 M HCl hydrolysis was determined in triplicate 100 mg starch samples incubated at 35 °C for 9 days in sealed 1 ml Sovirel tubes containing 10 ml of acid. The tubes were mixed daily (repeated inversion by hand) during the period of hydrolysis. After the incubation period, the tubes were centrifuged at 2000 × g for 5 min whereupon aliquots (0.1 ml) were removed by pipette and transferred to clean 10 ml tubes. The contents were neutralised (0.1 ml KOH) whereupon the α-glucan content was determined ([31], omitting the α-amylase hydrolysis step and adding 0.9 ml of distilled water before hydrolysis with amyloglucosidase).

2.2.2. Chromatography

In common with the native starches [30] the annealed starches were debranched with *iso*-amylase and the linear fractions were separated by gel permeation chromatography [35].

2.2.3. Physical properties

Starch gelatinisation parameters were determined by differential scanning calorimetry (DSC), the proportion of double helices by ^{13}C cross polarisation magic angle spinning nuclear magnetic resonance (^{13}C CP-MAS/NMR) and the amount of crystallinity by wide angle X-ray scattering (WAXS) as discussed previously [30].

2.2.4. Analytical variation

Analytical variation was typically with a coefficient variation (cv) of 1% or better although the determination of gelatinisation enthalpy , crystallinity (X-ray diffraction) and proportion of double helices (NMR) was <5%.

3. Results and discussion

It is apparent from Table 1 that the field grown potato starches [30] could be readily annealed with increases in gelatinisation temperatures ($\Delta T_o > \Delta T_p > \Delta T_c$), a reduction in the gelatinisation range $\Delta(T_c - T_o)$, and a small increase in the gelatinisation enthalpy (ΔH). Specifically for the 12 tuber starches investigated, annealing in excess water (in vitro) at 55 °C for 7 days increased T_o, T_p and T_c by 11.2, 9.6 and 8.1 °C with the difference $\Delta(T_c - T_o)$ of −3.0 °C on average. The gelatinisation enthalpy (ΔH) increased by 2.0 and 5.3 J g^{-1} on a starch and amylopectin basis, respectively, as a consequence of annealing.

The increase with respect to gelatinisation temperatures is classical in terms of annealing effects on starches [1–16] where crystalline registration in the annealed starches is enhanced. It probably reflects restriction of hydration caused by the perfected crystalline structures whilst the small increase in gelatinisation enthalpy (a measure of intra-helical hydrogen bonds) reflects small elongation of imperfect helical lengths (ends) [1,12–14,16,36]. The increase with respect to gelatinisation temperatures (and relatively small increase in enthalpy) was associated generally with a decrease in the amount of acid soluble material (−4.4 percentage units, Table 1). This is to be expected if the crystalline domains became less accessible to the acid as a consequence of improving the crystalline register and