Potential beneficial effect of hydrothermal treatment of starches from various sources on *in vitro* digestion

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ABSTRACT

Starches from various botanic origins (maize, quinoa, wheat, potato and rice) were studied. The thermal and pasting properties and their connection with enzyme digestibility were evaluated. Various hydrothermal treatments were applied, taking the starch physical parameters into account, in order to obtain partial and total gelatinisation of the starch structure and determine its influence on enzymatic action. Onset and pasting temperatures of the gelatinisation and pasting processes, respectively, followed the same order in the cereal starches (rice > maize > wheat > quinoa). These results were accompanied by an opposite trend in the percentage of raw starch hydrolysis, with quinoa reaching a level more than 2-fold higher than that of raw maize starch in *in vitro* digestion kinetics. Other technological parameters, such as high peak viscosity or low breakdown, also reflected modifications in the quinoa starch structure which were related to improved digestibility. However, starch from potato, the only tuber, displayed different characteristics from those of cereal starch, showing greater resistance to digestion. When the starches were pretreated, digestibility increased in all of them compared to their raw counterparts, with the pretreated quinoa and wheat starches showing greater susceptibility to modification of their structure. Although the hydrothermally pretreated maize and rice starches reached about 75% of the hydrolysis index of the corresponding gelatinised starches, raw quinoa had a similar hydrolysis index and quinoa obtained a higher value for total starch hydrolysed. Thus, quinoa starch could be potentially beneficial in the design of more digestible formulations for patients with metabolic disorders such as glycogen storage disease, among others.

Keywords: Glycogen storage disease, Maize starch, Thermal and pasting properties, *In vitro* digestion, Quinoa starch

1. Introduction

In recent years, glucose homeostasis has been an important focus of research owing to its physiological involvement in metabolic diseases such as diabetes, obesity and glycogen storage disease (GSD) (Ludwig, 2002; Weinstein, Steuerwald, De Souza & Derks, 2018). Consequently, several investigations have focused on studying the glycaemic index (GI) of foods and applying various strategies to modify starch digestibility and glucose release in order to manage glucose homeostasis and try to obtain optimal metabolic control (Li, Gidley & Dhital, 2019; Laparra & Haros, 2018).

The degree of starch gelatinisation is an important determinant for the rate of starch hydrolysis *in vitro* and for the metabolic response *in vivo* (Holm, Lundquist, Björck, Eliasson & Asp, 1988). Many food processing operations involve alteration of starch structure through thermal treatment, which leads to the starch becoming partially or completely gelatinised, depending on the final product (Delcour et al., 2010). The effects of thermal treatment on the morphological and crystalline structure of starch granules include important changes in physico-chemical properties (Ahmadi-Abhari et al., 2013). These changes in starch structure take place in pasting and gelatinisation processes, with swelling and gradual loss of crystallinity until there is total disruption of the starch granule (Horstmann, Lynch & Arendt, 2017). The nature of these structural changes depends on the starch source, composition, structure and isolation process, and therefore every starch has a different digestibility (Ratnayake & Jackson, 2007; Waigh, Gidley, Komanshek & Donald, 2000; Haros, Blaszczak, Perez, Sadowska & Rosell, 2006). However, techno-functional parameters can provide information about the crystalline structure of starch and its digestibility (Srichuwong, Sunarti, Mishima, Isono & Hisamatsu, 2005a).

The digestibility of starch is an important parameter that affects the severity and clinical manifestations of GSD and other diseases. GSD is a metabolic disorder that affects glycogen metabolism, in which the main clinical manifestation is fasting hypoglycaemia

(Weinstein et al., 2018). Since 1984, ingestion of uncooked maize starch (raw) has been used to prevent a fall in glucose concentration overnight in individuals with type I or III GSD (Chen, Cornblath & Sidbury, 1984). However, the relatively short duration of glucose availability from this dietary source still represents a major disadvantage with regard to the long-term outcome and quality of life of this special group. Also, raw maize starch intake is associated with injurious gastrointestinal symptoms such as abdominal cramps or bloating, which could be partly responsible for colonic fermentation of unused starch (Lee & Leonard, 1995). Some other starches (i.e., potato, rice, tapioca and arrowroot) have been tested in GSD patients, but these starches displayed significant differences, producing a worse glycaemic response than maize starch (Sidbury, Chen & Roe, 1986). In recent years, controlled heat-moisture processing of a high-amylopectin-containing maize starch was shown to be effective in improving maintenance of glucose concentrations, while gastrointestinal symptoms were reduced (Correia et al., 2008). However, not everyone can afford modified starch and many people depend on alternatives that are cheaper and that are easily available. In this connection, the inclusion of “ancient grains” (such as amaranth, quinoa or chia) in cereal bread formulations has been shown in the *in vitro* test to have an effect in delaying glucose release while extending its absorption (Brennan, Menard, Roudaut & Brennan, 2012; Laparra et al., 2018). Furthermore, these effects were accompanied by increased expression of the peroxisome proliferator-activated receptor (PPAR)-gamma, suggesting an improved insulin resistance that could lead to a significant decrease in glycolysis metabolism in an animal model (Laparra et al., 2018). Thus, starch from ancient grains could have a different digestibility that could help to maintain normoglycaemia longer than standard maize starch.

In view of the above, this study aimed to analyse thermal and pasting properties of starches from various sources – maize, wheat, potato, rice and quinoa – and evaluated the effect of a controlled heat-moisture process – which took their physical parameters into account – on their *in vitro* digestibility. The results were compared with those of the raw (as negative control) and gelatinised (as positive control) starches with the purpose of developing foods/beverages with specific characteristics for people with glucose metabolism disorders.

2. Materials and methods

2.1. Materials and reagents

Commercial maize starch was provided by ACH Food Companies (Argo, USA). Potato starch (C*Gel 300) was purchased from Cargill (Minneapolis, USA). Wheat starch (Natilor) from Chamtor (Pomacle, France). Rice starch (S7260) from Sigma-Aldrich, Belgium. Red quinoa starch was obtained from real Bolivian quinoa (Organic red Quinoa Real©, ANAPQUI (La Paz, Bolivia) in the laboratory by wet-milling (Ballester-Sánchez, Gil, Fernández-Espinar & Haros, 2019). The amylose content of starches was determined using enzymatic assay kits and procedures outlined by Megazyme (Megazyme International Ireland Ltd., Wicklow, Ireland). Enzymes were purchased from Sigma-Aldrich: α-amylase (EC 3.2.1.1, A3176-1MU, USA, 16 U/mg), amyloglucosidase from *Aspergillus niger* (EC 3.2.1.3, 10115, Switzerland, 60.1 U/mg) and pepsin (EC 3.4.23.1, P7000, UK, 480 U/mg).

2.2. Pasting properties

To prepare the samples, 3.5 g of starches were weighted and 25 mL of distilled water was added. Pasting properties of the starches were measured using a Rapid Visco Analyser (RVA-4, Newport Scientific, Warriewood, Australia), according to AACC method 76-21.01 (1999). Pasting temperature (P_{temp}), peak time (P_{time}), peak viscosity (PV), hot paste viscosity (HPV), cool paste viscosity (CPV), breakdown (PV-HPV) and setback (CPV-HPV) were recorded. The experiments were performed in triplicate.

2.3. Thermal properties

Gelatinisation and retrogradation properties were determined using differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7, USA). Indium was used to calibrate the calorimeter (enthalpy of fusion 28.45 J/g, melting point 156.6 °C). The procedure followed was the method described by Haros et al. (2006), with slight modifications. Ten mg of starch was weighed out and distilled water was added to obtain a water:starch ratio of 3:1 for each sample. The calorimeter scan conditions used were: 25 °C for 1 min and then heating from 25 °C to 120 °C at 10 °C/min. Later, to analyse retrograded starch, the samples were stored in refrigeration for a week and were ran under the same conditions (1 min - 25 °C; from 25 to 120°C at 10°C/min). The parameters recorded were: onset temperature (T_o), peak temperature (T_p) conclusion temperature (T_c) and enthalpy of gelatinisation and retrogradation transition (ΔH_G and ΔH_R), respectively. The experiments were performed in triplicate.

2.4. Preparation of samples for digestion

Aliquots (100 mg) of the various starch samples were weighed into microcentrifuge tubes and 1 mL of water was added. Raw starches were kept in unheated water for 5 minutes and were considered the negative control. Pretreatment of the starches was chosen according to their pasting and thermal parameters: maize (70 °C – 2 min), quinoa (60 °C – 1 min), wheat (60 °C – 1 min), potato (70 °C – 1 min) and rice (75 °C – 2 min). The temperature selected for pretreatment depended on the T_p and T_c of the starch and was such as to achieve partial gelatinisation while avoiding loss of total crystallisation. The

P_{temp} and P_{time} values determined previously were taken into account to avoid the formation of paste. Gelatinised starches (GS) were kept in a water bath for 5 minutes at 100 °C as a positive control.

2.5. In vitro *starch digestion and GI estimation*

The rate of starch hydrolysis was evaluated according to the method described by Goñi, Garcia-Alonso and Saura-Calixto (1997), with modifications. Briefly, 10 mL of HCl-KCl buffer (pH 1.5) and 400 μL of a solution of pepsin in HCl-KCl buffer (0.1 g/mL) were added to the starches and the samples were placed in a shaking water bath at 37 °C for 1 hour. Afterwards, 19.6 mL of Tris-Maleate buffer (pH 6.9) and 1 mL of a solution containing α-amylase in Tris-Maleate buffer (0.01 g/mL) were added and the samples were incubated in the water bath for 2 hours. Aliquots were taken at intervals Aliquots were taken at intervals, from 0 to 120 min (0, 20, 40, 60, 90,120 min), and then the enzyme was thermally inactivated during 5 minutes at 100ºC. After centrifugation (10,000 rpm/10 min), 500 μL of the supernatant was taken from each sample. Then 1.5 mL of sodium acetate buffer (pH 4.75) and 60 μL of a solution of amyloglucosidase in sodium acetate buffer (88 mg/mL) were added and the samples were incubated at 60 °C for 45 min. Glucose, area under the curve (AUC) and hydrolysis index (HI) were determined according to Laparra et al. (2018). Finally, GI was calculated using the equation $GI = 39.71 + 0.549HI$ (Zabidi & Aziz, 2009). The hydrolysis kinetics was transformed from a cumulative curve into a linear curve by plotting the reciprocal values of [% starch hydrolysis] and time (Sanz-Penella, Laparra & Haros, 2014).

2.6. Statistical analysis

Multiple ANOVA and Fisher's least significant differences (LSD) were applied to establish statistically significant differences in thermal and pasting properties. The Tukey test was applied to analyse differences in the digestion values. The statistical analyses were performed with Statgraphics Centurion XVI software, and the significance level was established at $P < 0.05$.

3. Results and discussion

3.1. Pasting and thermal properties of starches

The determination of pasting parameters revealed differences between the starches, as was expected (**Table 1**). P_{temp} provides an indication of the minimum temperature required to cook the starch, which could be related to the degree of polymerisation (DP) of amylopectin (Li & Zhu, 2017; Srichuwong, Curti, Austin, King, Lamothe & Gloria-Hernandez, 2017; Srichuwong, Sunarti, Mishima, Isono & Hisamatsu, 2005b). This parameter decreased following this order: rice > maize > potato ~ wheat > quinoa. Quinoa and wheat are characterised by a higher proportion of short chains with a DP of 8–12, whereas maize, rice and potato have a high DP of 12–18 (Srichuwong et al., 2017; Srichuwong et al., 2005a). The higher proportion of shorter amylopectin chains could affect the crystalline structure (Srichuwong et al., 2017), resulting in a soluble molecule that can be easily digested as it has many end points onto which digestive enzymes can attach, which could have a positive effect on the digestibility of raw starches.

The peak viscosity (PV) parameter indicates the water-binding capacity of starch (Haros et al., 2006). The high PV of potato could possibly be explained, at least partly, by the high content of phosphate ester groups in the amylopectin in this tuber, resulting in repulsion between molecules (Waterschoot, Gomand, Fierens, & Delcour, 2015). Among the cereals, higher PV values were recorded for wheat and quinoa than for maize and rice. These results agree with the conclusions arrived at by Gomand, Lamberts, Visser and

Delcour (2010), who attributed an increase in swelling to short amylopectin chains, whereas long chains prevented this transition. The high viscosity value obtained during the heating process suggests a high water absorption capacity, which has been correlated with a lower resistance to enzymatic digestion (Reddy, Pramila & Haripriya, 2015). This behaviour could be interesting when formulating foods with specific glycaemic indexes. The breakdown parameter (PV–HPV) can give information about stability under heating conditions. Potato starch showed a very high value, displaying a structural fragility that could lead to easier destruction of the structure when it is cooked (Haros et al., 2006). Notably, the rice and quinoa starches exhibited a lower breakdown value than maize starch, which suggests a better preserved structure, favouring a lower peak glucose concentration and a slower rate of fall than with conventional maize starch.

During cooling, an important parameter to consider is retrogradation, which is the tendency to restructuration and can be measured through the setback parameter (CPV–HPV). Wheat and potato showed the highest setback viscosities, indicating a low resistance to retrogradation and, as a result, a higher rearrangement. The formation of double helices in this rapid process of restructuration is mainly attributed to amylose, which possesses a larger flexible structure than amylopectin (Van Soest et al., 1994). However, the lack of differences in the setback values of the maize and quinoa starches, despite the amylose content determined for maize (amylose 22%) and quinoa (amylose 7%) (data not shown), suggests that other starch characteristics are involved in the retrogradation process.

The gelatinisation parameters were determined by DSC analysis (**Table 2**). Onset temperature (T_o) showed the same trend as P_{temp}: rice > maize > potato > wheat > quinoa, as was expected. This relationship between gelatinisation and pasting temperatures was also confirmed previously by other researchers (Li, Wang & Zhu, 2016). Low values in starch gelatinisation and pasting processes might suggest a less crystalline structure, which could result in higher enzymatic susceptibility (Lin, Zhang, Zhang & Wei, 2017;

Srichuwong et al., 2017). The gelatinisation enthalpy (ΔH_G) varied from 10 to 12 J/g, except in the case of potato, which had a value of 16 J/g, demonstrating that higher energy was required to disrupt the crystalline structure. The resistance produced by potato may be interpreted as high crystallinity, which could interfere with the accessibility of the enzyme (Shi, Gao & Liu, 2018). Retrogradation parameters were measured after 7 days at 4 °C, and quinoa starch presented the highest resistance to retrogradation of amylopectin (Table 2). In long-term retrogradation, amylopectin is mainly responsible for reorganisation of structure (Van Soest et al., 1994). The presence of short chains in quinoa might contribute to a less compacted starch structure, leading to a starch with low retrogradation, which could be displayed as better digestibility (Lin et al., 2017; Srichuwong et al., 2017). On the other hand, the consumption of retrograded starches may be beneficial for health, owing to the lower depletion of total digestible starch than gelatinised starch (Chung, Lim & Lim, 2006). Moreover, rearrangement of the crystalline structure could hinder α-amylase action and trigger a slow rate of intestinal digestion, which could be reflected in a lower glucose concentration peak *in vivo*.

3.2. In vitro *starch digestion and GI estimation*

In this study, the hydrolysis percentages of various common starches were compared with that of raw maize starch (**Table 3**). The digestion method used has been proved suitable for establishing variations in susceptibility to enzyme interaction depending on structural differences between the samples considered (Rosin, Lajolo & Menezes, 2002; Sanz-Penella et al., 2014).

Significant differences ($p < 0.05$) were found in the total (%) starch hydrolysed (TSH_{120}) as a function of the sample considered. Native potato presented the lowest value compared to any other raw starch studied. This is supported by previous studies, which indicate that the lack of peripheral channels in potato starch granules inhibits the penetration of α-amylase, whereas the presence of superficial pores, such as in maize starch, could enable enzymatic action (Dhital, Shrestha & Gidley, 2010; Lehmann & Robin, 2007). Moreover, the smaller specific surface area of large granules in potato starch compared to the others cereals may difficult the access and attachment of enzyme (Lehmann et al., 2007; Srichuwong et al., 2005a). As indicated at Fig 1, rice and maize starches had similar hydrolysis, wheat achieved greater hydrolysis and quinoa presented the highest hydrolysis value, reaching around 70% hydrolysis, which is curious, considering that it was uncooked starch. These results are in good agreement with Srichuwong et al., (2017), who investigated starches obtained by various isolation processes and reported a similar trend in hydrolysis relating to short amylopectin chains, but without giving other digestion parameters. It is highlighted that the amylose content in cereals is generally about 15-30 % (Waterschoot et al., 2015) which is corroborated by our cereals starches (maize, 22%; rice, 21%; wheat, 25%). Nevertheless, quinoa presented only about 7% of amylose which could influence in the high digestibility displayed. The lower presence of amylose reported could favour the digestibility due to a higher amylose content has been associated with reduced susceptibility to enzymatic hydrolysis (Chung, Liu, Lee, & Wei, 2011).

In order to determine whether the various sources of starch released the same amount of glucose during digestion, the area under the curve (AUC) and hydrolysis index (HI) were calculated (Table 3). The analyses revealed that the raw starches obtained from quinoa and wheat had significantly higher AUC values than the raw starch obtained from maize. It is important to remember here that major differences would be determined by the structural fragility and short amylopectin proportion, as indicated above. When the various raw starches were tested after thermal processing at 100 °C (GS), there were no significant differences in GI values except for potato GS, which continued to have the lowest GI, owing to the lack of digestibility, as was also observed previously (Shi et al., 2018).

After analysing the raw starches (as negative controls) and the gelatinised starches (as positive controls), the effect of the hydrothermal treatment was investigated, taking into account the effect of the pasting and thermal properties on the enzymatic hydrolysis of starch, in order to develop food with specific characteristics. The degree of gelatinisation has been reported as one of the main rate-limiting factors in the binding of enzymes to starch for digestion of starches (Wang et al., 2019). The treatment was applied to attain partial gelatinisation of starch in order to evaluate to what extent alterations in starch structure caused by heat-moisture processing affect its digestibility. The pretreatment temperature was selected on the basis of the parameters shown in Tables 1 and 2. The thermal pretreatment of maize and rice starches led to a higher hydrolysis rate than in the case of their raw counterparts, as was observed by Chung et al. (2006) in waxy rice starch subjected to various thermal treatments. Pretreatment of the maize and rice starches, consisting of the application of 70 °C (maize) and 75 °C (rice) for 2 minutes, led to an HI that was approximately 75% of the HI of the corresponding gelatinised starches. However, the pretreated maize did not hydrolyse totally and did not exceed the hydrolysis values of the raw quinoa. A similar tendency was observed by Ahmadi-Abhari et al. (2013), who reported that wheat starch began to lose crystallinity, and consequently starch digestibility improved, but total hydrolysis was not achieved. In the current investigation, pretreated wheat starch began to lose crystallinity and thus improved its digestibility and reached HI values similar to those obtained for pretreated quinoa starch. The higher hydrolysis observed in the pretreatment of wheat and quinoa in comparison with maize and rice could be due to their low T_p and high PV values, which suggest greater susceptibility to disintegration of their structure (Li et al., 2016).

Data from the hydrolysis parameters were transformed according to Lineweaver-Burk's model in order to obtain approximate values of the kinetic parameters of starch digestion, helping to gain insight into the potential physiological effects (Sanz-Penella et al., 2014). Although the raw quinoa and wheat starches had higher slopes (Table 3), they were accompanied by high hydrolysis, which means that a lower dose would be required. This would help to reduce the digestive inconveniences resulting from the consumption of high amounts of raw maize starch. Furthermore, although the slope values calculated for both raw and gelatinised quinoa starch were similar, the values for gelatinised maize were significantly higher than those of the raw counterpart.

Collectively, these structural changes in quinoa starch may help to maintain glucose concentrations for a longer time and lead to a less rapid rate of fall than in the case of maize starch. Notably, although there are many studies on differences in the techno-functional characteristics of starches and their digestibility, it is not clear how these differences would relate to the rate or efficiency of hydrolysis by pancreatic amylase.

4. Conclusions

To sum up, from this study it can be concluded that it may be possible to modify digestibility by controlling starch properties through variations in temperature or cooking time, which could be useful when designing GI-specific formulations for impaired glucose metabolism. Maize and rice starches showed similar technological characteristics, which were concordant with the lack of differences in digestion. Potato starch showed high resistance to digestibility, whereas quinoa and wheat were more susceptible to enzymatic attack. Furthermore, pasting and thermal parameters for quinoa starch indicated structural changes at granule and molecular level that were reflected in its digestibility. Raw maize starch has been used for years by patients with glycogen storage disease despite the short duration of its effect and the gastrointestinal problems associated with it. Raw quinoa starch could offer a promising potential for extending normoglycaemia in these patients. The results indicate the starches and their pretreatment, taking into account their physico-chemical characteristics, could be a potential useful dietary source for patients who have an altered glucose metabolism. Knowing these parameters and how enzymatic susceptibility is affected is essential to a better understanding of the changes in starch structure which could be applied to develop specific formulations. This proposal gives information in order to develop simple formulations with cereals/pseudcereals/tubers flours to control the starch digestibility. Taking into account their behaviour according the source, composition, grade of crystallinity and/or structure in the food matrices to control the glucose homeostasis. However, this is a preliminary study which could open the door to future investigations designed to attain a better understanding of the physiological effects *in vivo*.

Acknowledgements

This work was financially supported by grants QuiSalhis-Food (AGL2016-75687-C2-1-R) from the Ministry of Science, Innovation and Universities (MICIU) and CYTED, LA ValSe-Food (119RT0S67). The contract given to R. Selma-Gracia as part of LINCE (PROMETEO/2017/189) by the Generalitat Valenciana (Spain) is gratefully acknowledged.

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Figure caption

Figure 1: Hydrolysis of raw starches. Symbols: - - -, maize starch; ——, quinoa starch; ——, wheat starch; - - -, rice starch; ......, potato starch.