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Relationships between starch pasting properties, free fatty acids and amylose content in barley

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ABSTRACT

Relatively few studies have examined the influence of lipids or fatty acids on starch pasting properties in barley. The aim of this study was to evaluate the use of the Rapid Visco Analyser (RVA) as a tool to examine changes in starch functionality related with free fatty acids (FFAs) and amylose content in barley flour samples. Changes in RVA parameters such as setback (STB) and final viscosity (FV) were related to differences in both FFA (oleic and palmitic acids) and amylose contents due to the diverse barley genotypes analysed. The magnitude of the RVA profile values derived from samples having high a concentration of palmitic acid (3900 mg/g) was lower compared with that having the lower concentration of the same FFA (2470 mg/g), displaying low FV (5666 vs 4166 cP) and low STB (1625 vs 1174 cP) values. Similar trends were observed for the other FFA measured. These results showed that pasting properties of barley measured using RVA are determined by a complexity of parameters, where the combination of lipids (FFA) and amylose might determine the characteristics of the material and its final use (e.g. malting).

1. Introduction

Most cereal grains are low in lipid and fatty acid content (less than 6% w/w), however their composition influences lipid stability, their functionality properties during processing and storage as well as other biophysical characteristics (e.g. water uptake) (Debet & Gidley, 2006; Kaukovirta-Norja, Peinikainen, Olkku, & Laakso, 1997; Liu, 2011; Morrison, 1995; Patindo, Mendez-Montealvo, & Wang, 2012; Srichuwong and Jane, 2007; Seefeldt, Larsen, & Viereck, 2011). kIt has been suggested that cereal lipids associated with starch, influence the gelatinization temperature, leaching of soluble polysaccharides, and contribute to the swelling of starch granules (Morrison, 1995; Morrison, Tester, Snape, Law, & Gidley, 1993; Tester & Morrison, 1990; Tester, South, Morrison, & Ellis, 1991; Tester et al., 1995). Starch can also form complex added lipids under some conditions, and in particular amylose–lipid complexes have been studied with reference to the behaviour of starch in the baking industry and dough making, as well as in determining important functional interactions with a range of molecules in food based cereals (Blazek, Gilbert, & Copeland, 2011; Morrison, 1995; Tang, Ando, Watanabe, Takeda, & Mitsunaga, 2001; Tang & Copeland, 2007; Tester & Morrison, 1990; Tester et al., 1995, 1991; Vasanthan & Bhatty, 1996).

Cultivated barley (*Hordeum vulgare*) is among the world's earliest domesticated crop species and today represents the fourth most abundant cereal in both area and tonnage harvested (Mayer, 2012). Approximately three-quarters of the barley global production is used for animal feed, while 20% is malted for use in alcoholic and non-alcoholic beverages, and 5% as an ingredient in a range of food products (Blake, Blake, Bowman, & Abdel-Haleem, 2011; Mayer, 2012). Barley is widely adapted to diverse environmental conditions and is more stress tolerant than wheat (Blake et al., 2011; Mayer, 2012). As a result, barley remains a major food source in poorer countries, maintaining harvestable yields in harsh and marginal environments, whereas in more developed societies, it has recently been classified as a true functional food (Blake et al., 2011; Mayer, 2012).

Several chemical and physical factors might influence the changes in beer aroma, taste and foam during processing and storage (Bravi, Marconi, Perretti, & Fantozzi, 2012; Bravi, Perretti, Buzzini, Della Sera, & Fantozzi, 2009). Recently, it has been suggested that lipids can adversely affect beer quality by influencing flavour and foam stability, where the level and the quality of the lipids in beer depend on their content and composition in the raw materials (barley and malt) and on the brewing process (Bravi et al., 2009, 2012).

Traditionally, the Rapid Visco Analyser (RVA) has been used in cereals and foods to provide information about pasting characteristics of starch of a particular sample under analysis (e.g. pasting temperature, final viscosity, among other pasting properties) (Zhou & Mendham, 2005; Cozzolino, Allder, Roumeliotis, & Eglinton, 2012). In addition, the combination of RVA with statistical methods can enhance the information generated allowing the comparison of patterns between samples in the data set, relating such measurements with different treatments or experimental conditions, genotypes, or localities while facilitating faster throughput of analysis.

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Although starch-lipid complexes have been analysed by various methods, relatively few studies have been concerned with the influence or the concentration of lipids on starch pasting properties in cereal grains (Tang & Copeland, 2007) and in particular on the basic data concerning barley varieties for malting and beer production (Tester & Morrison, 1990; Tester et al., 1991, 1994, 1995; Morrison, 1995). Therefore, considering that starch gelatinization and hydrolysis are key factors for efficient mashing and brewing (beer production), understanding starch functional properties such as gelatinization, pasting and retrogradation, and the interactions between amylose and lipids, is of vital importance for the effective use of barley for industrial applications (e.g. beer and whisky production), as well as for the use of these parameters for screening and selection of new and improved varieties.

Therefore, the aim of this study was to evaluate the use of the Rapid Visco Analyser (RVA) as a tool to examine differences and changes in starch functionality related with free fatty acids (FFAs) and amylose content in barley flour samples sourced from different genotypes grown in Australia.

2. Materials and methods

2.1. Samples

Whole grain barley samples (*H. vulgare* L) were sourced from The University of Adelaide, Barley Breeding Program. These included 17 commercial barley varieties namely Alexis, Flagship, Halcyon, Haruna Nijo, Commander, Navigator, VT Admiral, Sloop, Baudin, Schooner, Gairdner, AC Metcalfe, Clipper, Dhow, Franklin, Fleet, and Galleon. The same varieties were grown at two locations in South Australia [Roseworthy (n = 17) and Charlick (n = 17)] in the 2009/2010 season. Details about the commercial varieties used can be found on the Barley Australia website (http://www.barleyaustralia.com.au).

2.2. RVA analysis

Samples were milled using a UDY Cyclone Mill (Fort Collins, CO, USA) through a 0.8 mm screen. Ground barley samples (4.0 g of flour corrected using the moisture content of the sample, ±0.01 g) were slurred with distilled water (25.0 g as a function of the amount of adjusted sample, ±0.1 g) in an aluminium canister. The mixture was agitated by raising and lowering the plastic paddle through the aluminium canister before inserting the can into the instrument. The pasting properties of the slurries were determined with a RVA-TecMaster (Tecmaster, Perten Instruments, NSW, Australia). The test profile had a starting temperature of 50 °C, which was held for 1 min, raised to 90 °C in 4 min, held for 10 min, cooled to 50 °C in 1 min, and held for 1 min, with a stirring speed of 160 rpm for the remainder of the test period. Properties calculated by the software TCW3 (Tecmaster, Perten Instruments, NSW, Australia) included pasting viscosity (PV), trough (TH), breakdown (BRK), final viscosity (FV), setback (STB), time to peak (TTP) and pasting temperature (PT) (Batey, 2007). In addition, the RVA profiles were interpreted using the second derivative as previously reported elsewhere (Cozzolino et al., 2012).

2.3. Lipid extraction and fatty acid determination

The content of free fatty acids (FFAs) in the flour samples was measured using gas chromatography (GC). The analysis was done by extracting the total FFA content from the sample (0.25 g) using 5 ml of a 9:1 chloroform:methanol solution (Christie, 1989). The extracted lipids (approx 10 mg) were spiked with 400 μg heptadecanoic acid (Nuchek Prep Inc., Elysian, MN, USA) and methylated by heating at 70 °C for 3 h in a solution of 1% H_2SO_4 in methanol. Separation and detection of the FFA were performed by a Hewlett-Packard 6890 GC which was fitted with a flame ionization detector. Percentage of FFA was identified based on the retention time of a standard mixture ("GLC 463") obtained from Nuchek Prep Inc. Chemstation software was used to record and process the data. Results were expressed as mg per g of sample.

2.4. Amylose and amylopectin determinations

The amylose content of barley flour samples was measured using the Concanavalin (Con A) method involving the precipitation of amylopectin-Con A complex, according to the procedure described by the manufacturer for the Megazyme amylose/amylopectin assay kit (Megazyme International Ltd., Wicklow, Ireland) (Yun & Matheson, 1990). Before analysis, lipids from the flour were removed by precipitating the starch with ethanol (95% v/v). The concentration of amylose in the starch was estimated as the ratio of the glucose oxidase plus peroxidise reagent (GOPOD) absorbance at 510 nm of the supernatant of the Con A precipitated sample. Results were expressed as percent (%, w/w).

2.5. Data analysis

Principal component analysis (PCA) and partial least squares regression (PLS2) were performed using The Unscrambler (version X, CAMO, Norway). The data was mean centred and weighted (auto scaled) by the standard deviation (1/STD) prior to the PCA and PLS2 analysis in order to take into account that the variables were measured in different units (Naes, Isaksson, Fearn, & Davies, 2002). Full cross validation (leave one out) was used as a validation method during PCA and PLS2 analysis (Naes et al., 2002). The optimum numbers of terms in both PCA and PLS2 models were indicated by the lowest number of factors that gave the minimum value of the prediction residual error sum of squares (PRESS) in cross validation, in order to avoid over fitting of the models.

Bivariate correlations were carried out using Pearson correlation ($p < 0.05$). The mean differences between samples were analysed using ANOVA (JMP, version 4, JMP a business unit of SAS, Copyright© 1989–2001, SAS Institute Inc., USA).

3. Results and discussion

3.1. RVA and fatty acid analysis

Table 1 shows the mean and standard deviation for the pasting properties (RVA), FFA, amylose and amylopectin contents in the barley flour samples sourced from the two localities. A wide range in composition was obtained in the set of barley flour samples analysed due to the different genotypes and environments included.

The difference between the final and holding viscosities is referred to STB (Batey, 2007). These phases of the RVA profile correspond to the starch granules initially absorbing water and swelling, followed by a disruption of the granule structure under the shear force and leaching of the starch molecules (Tang & Copeland, 2007; Batey, 2007). A large variation in the STB values was observed in the barley samples sourced from two the localities as indicated by the large coefficient of variation (CV) obtained (RAC = 20% and CHA = 32%) (see Table 1). The large CV could be related to differences in environmental conditions associated to the localities as a consequence of differences in soil type, temperature and rainfall. The magnitude and time to STB also reflect the nature of the aggregates formed as the starch retrogrades, with the amylose molecules predominantly interacting closely to form junction zones between the chains (Tang & Copeland, 2007). It was reported that during the RVA analysis, amylose might have formed complexes with lipids, producing gels with increasing spacing between junction zones, giving aggregates that are less compact and yielding high viscosities (Tang & Copeland, 2007). In this study, this characteristic behaviour was also observed in some of the varieties analysed.