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The role of total lipids and fatty acids profile on the water uptake of barley grain during steeping

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ABSTRACT

Steeping is the first operation of malting and its overall purpose is to increase the water content of the grain, as well as to activate the enzymatic pool in the endosperm. The aim of this study was to evaluate the effects of total lipids content and individual fatty acids on water uptake, by commercial barley varieties. The results from this study showed that unsaturated fatty acids, such as oleic acid (18:1-n9), have a role in controlling water uptake by the barley endosperm during steeping. When partial least squares (PLS) regression was used to relate total lipids, individual fatty acids and water uptake, oleic (18:1-n9) acid had a positive effect, while long chain unsaturated fatty acids such as arachidic (20:0) and lignoceric (24:0) acids had a negative effect on explaining 72% of the total variability in water uptake. Water uptake by the endosperm is just a component of the system that is responsible for the overall malt quality properties and chemical characteristics of a given material. In this context, both total lipids and individual fatty acids have a role on determining malt quality in barley.

1. Introduction

Although a comparatively small proportion of the barley crop is used for malting, in recent years the major proportion of plant breeding efforts have been directed towards the production of high-quality malting varieties (Bravi, Marconi, Perretti, & Fantozzi, 2012; Bravi, Perretti, Buzzini, Della Sera, & Fantozzi, 2009; Seefeldt, Larsen, & Viereck, 2011). Lipids in cereals can be grouped into three categories according to their location in the flour, as well as to their extraction methods (Youssef, El-Fishawy, Ramadan, & El-Rahman, 2012). These groups are namely non-starch lipids, starch lipids and starch surface lipids, respectively (Bravi et al., 2009; Seefeldt et al., 2011; Youssef et al., 2012). Overall, total lipids account between 2% and 4% of barley chemical composition and about 45% of these are located in the starchy endosperm (Bravi et al., 2009, 2012; Seefeldt et al., 2011; Youssef et al., 2012).

To assist in efficient endosperm modification and development of high-quality malt, breeders and maltsters must understand how kernel hydration is affected or regulated (Brookes, Lovett, & MacWilliam, 1976; Gruwel, Chatson, Yin, & Abrams, 2000; Seefeldt et al., 2011). Therefore, the uptake of water by seeds is the essential and initial step towards germination (Gruwel et al., 2000). For malting barley, this stage represents the first stage of the malting process, often referred as steeping (Gruwel et al., 2000; Mayolle, Lullien-Pellerin, Corbineau, Boivin, & Guillard, 2012). The main purpose of steeping is to increase the water content of the grain up to 43–46%, however, such a simple step encompasses several and different metabolic processes that affect germination and the final malt quality (Gruwel et al., 2000; Molina-Cano, Ramo, Ellis, Swanston, & Bain, 1995). The initial hours of barley steeping are also critical in trigging and controlling different processes, such as enzymatic activity, hormonal development and release that will determine the final quality of the malt (Bewley, 1997; Gruwel et al., 2000; Sarkar, Yang, Wu, Tang, & Ding, 2009; Seefeldt et al., 2011). In this context, steeping plays a crucial role in the determination of the final malt quality and, accordingly, detailed knowledge of water uptake in barley kernels is important in order to optimise the malting process or to select new varieties (Cozzolino, Roumeliotis, & Eglinton, 2013a; Mayolle et al., 2012).

Many reports can be found on the relationships between protein, starch, kernel morphology, cell wall characteristics and composition, genetics, as well as environmental factors (e.g. temperature) that influence the amount and rate of water uptake by the barley kernel during initial hours of steeping (Agu, 2003; Agu & Palmer, 2001; Brookes et al., 1976; Gruwel et al., 2000; McEntyre, Ruan, & Fulcher, 1998; Molina-Cano et al., 1995). However, despite the fact that lipids have important effects on functional and storage properties of cereal, as well on processing and industrial uses, there has been very little scientific interest in characterising the lipid fraction of the barley grain and its effect on water uptake (Bravi et al., 2012; Srichuwong & Jane, 2007; Youssef et al., 2012). Therefore, considering that water uptake by the barley grain is of importance in order to activate enzymes that are

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associated to malt quality, it will be of importance to understand the effect of total lipids and the role of fatty acids on water uptake (Srichuwong & Jane, 2007; Youssef et al., 2012).

The aim of this study was to evaluate the effect or role of total lipids content and individual fatty acids on water uptake by different commercial barley varieties.

2. Materials and methods

2.1. Samples

Whole barley samples (*Hordeum vulgare* L.) were sourced from commercial malting varieties namely Commander ($n = 4$), Schooner ($n = 4$), Gairdner ($n = 4$), Admiral ($n = 4$) and Navigator ($n = 4$). Samples were harvested in 2010 and 2012, at two localities in South Australia (Roseworthy and Charlick). Details about these malting varieties (e.g. grain and malting characteristics) can be found on the Barley Australia website (http://www.barleyaustralia.com.au).

2.2. Water uptake measurement

Barley samples (1.5 ± 0.01 g) were placed (in triplicate) in a sample holder (40 mm × 32 mm × 5 mm), and soaked at constant temperature at 22 °C (±1 °C) in a water bath filled with distilled water. Samples were taken at every hour from 1 h to 8 h. Before weighing of the samples, excessive water on the sample holder was removed by shaking and from the grain surface using filter paper. The water uptake was calculated by subtracting the initial weight of grains from the weight of the water absorbed by the grain as reported elsewhere (Cozzolino et al., 2013a; Mayolle et al., 2012).

2.3. Fatty acid and total lipid analysis

Fatty acids (FA) and total lipids content were measured using gas chromatography (GC). The analysis was done by extracting the total FA content from the sample (0.25 g) using 5 ml of a 9:1 chloroform: methanol solution (Christie, 1989; Cozzolino, Roumeliotis, & Eglinton, 2013b). The extracted lipids (approx. 10 mg) were spiked with 400 μg heptadecanoic acid as internal standard (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 FA was performed by a Hewlett–Packard 6890 GC which was fitted with a flame ionisation detector. Individual FA were identified based on the retention time of a standard mixture ("GLC 463", Nuchek Prep Inc.). Chemstation software was used to record and process the data. Results were expressed as mg per g of sample (Cozzolino et al., 2013b).

2.4. Data analysis

Relationships between fatty acids, total lipids and water uptake were evaluated using partial least squares (PLS) regression. The PLS regression was performed using The Unscrambler (version X, CAMO, Norway). The data (fatty acids, total lipids and water uptake) was mean centred and weighted (auto scaled) by the standard deviation (1/STD) prior to the PLS analysis in order to take into account that the measured variables were in different units (Naes, Isaksson, Fearn, & Davies, 2002). The PLS models were developed using full cross validation (leave one out) as the validation method (Naes et al., 2002). The optimum numbers of terms in PLS 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 also carried out using Pearson correlation ($p < 0.05$). 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

The mean, range, standard deviation and coefficient of variation of the water uptake values measured from 1 h up to at 8 h of steeping are shown in Table 1. Only the data for the 8 h for the commercial barley samples analysed is shown in Table 1. Differences in water uptake were observed between the commercial varieties analysed. Samples from the samples Commander variety showed the highest values in water uptake (mean = 53.3%), while samples from the Schooner variety showed the lowest values in water uptake (mean = 42.9%). Differences in water uptake between the different commercial varieties analysed might be associated with different endosperm structure, porosity, starch content as well other physical characteristics of the grain that influence the diffusion and rate of water into the grain, as suggested by other authors (Cozzolino et al., 2013a; Ferrari, Baronchelli, Stanca, & Gianinetti, 2010; Mayolle et al., 2012; Molina-Cano et al., 1995; Swanston, Newton, Hoad, & Spoor, 2006).

The total lipids content and fatty acid profiles for the commercial barley samples analysed are shown in Table 2. The highest lipid content was observed for samples sourced from the Schooner variety, while samples from Gairdner had the highest per cent of fat (3.5% db). Samples from the Commander variety showed the lowest content in unsaturated fatty acids such as oleic acid. Statistically significant high and positive correlations were observed between unsaturated fatty acids such as oleic acid ($r = 0.50$), linolenic acid ($r = 0.40$) and water uptake (8 h) between the commercial varieties analysed (Table 3).

In order to further evaluate the relationships between total lipids, individual fatty acids and water content in the set of samples analysed, PLS modelling was used. Fig. 1 showed the predicted versus actual water content values using the fatty acid profiles as independent variables. Water uptake between 1 and 3 h was poorly explained by the PLS models ($R^2 < 0.30$) (data not showed), while 72% ($R^2 = 0.72$) of the total variability in water uptake at 8 h was explained by the combination of total lipids and individual fatty acids measured. The loadings (Fig. 2) indicated that both myristic (14:0) and oleic acids (18:1-n9) have a positive influence in the model while unsaturated fatty acids such as stearic (18:0), and long unsaturated chain fatty acids such as arachidic (20:0) and lignoceric (24:0) acids have a negative effect on water uptake by the barley endosperm. These results showed that total lipids and individual fatty acids can play a role on regulating water uptake in barley.

It has been reported that during germination, extensive hydrolysis of triacyl-glycerols occurs (Bravi et al., 2012; Youssef et al.,

Table 1
Descriptive statistics for water uptake (8 h steeping) for different commercial barley varieties.

	Commander	Gairdner	Navigator	Schooner	Admiral
Mean (%)	53.3	44.2	47	42.9	47.8
SD	7.2	3.4	5.1	4.3	3.9
SEM	2.1	1.4	1.6	1.9	1.3
CV (%)	13.5	7.7	10.8	10	8.2
Range (%)	48.7–57.9	40.6–47	43–50.7	35.0–48.1	44.7–50.8

SD, standard deviation; SEM, standard error of the mean; CV, coefficient of variation.