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Review

An overview on the role of lipids and fatty acids in barley grain and their products during beer brewing

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ABSTRACT

In recent decades, research in barley has led to improvements in several biochemical and chemical characteristics (e.g. protein, starch, β glucans) associated with malt composition and end product quality (e.g. beer). Although lipids and fatty acids (FA) represent between 1 to 3% of the grain weight (dw), they can play an important role in barley grain and malt derived materials. However, the role of lipids and FA in both barley and malt quality is still not well understood. The aim of this article is to provide an overview on the role of lipids and FA in the chemical and industrial properties of barley grain, malt and wort.

Contents

1. Introduction

In recent decades, research in barley has led to improvements in different biochemical and chemical properties (e.g. protein, starch, β glucans) associated with the end product quality (e.g. malt, beer). However, the potential of obtaining incremental gains in malt extract in particular, appeared to be limited by the physical structure of the endosperm and the composition of the starch (amylose and amylopectin), protein content as well as components of the cell wall (Cozzolino, Roumeliotis, & Eglinton, 2013, 2014a; Morrison, 1993, 1995; Seefeldt, Larsen, & Viereck, 2011; Tang & Copeland, 2007; Tester & Morrison, 1990, 1992; Welch, 1978). It has been suggested by some researchers that further attempts to enhance yield extract by reducing husk content could deteriorate barley quality or agronomic characteristics. However, the reduction of husk can determine an increase of fungal attack (e.g. split husks), an increase in embryo damage associated with environmental factors (e.g. rainfall and temperature) as well as with an increase

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of skinning damage during harvesting and grain handling (Agu, 2003; Agu, Devenny, Tillett, & Palmer, 2002; Agu & Palmer, 2001; Bewley, 1997; Briggs, Brookes, Stevens, & Boulton, 2004; Burger & LaBerge, 1985; Soares, De Francisco, Rayas-Duarte, & Soldi, 2007).

Although the lack of extractable and fermentable sugars in the wort can be associated with a poor malt modification, other factors such as the extent of starch hydrolysis during mashing, the physical properties of the starch (e.g. granule structure), and the amylose and amylopectin contents and their corresponding ratio can also contribute to its modification as suggested by different authors (Agu, Bringhurst, & Brosnan, 2008; Bathgate, Martinez-Frais, & Stark, 1978; Brennan, Harris, Smith, & Shewry, 1996; Brookes, Lovett, & MacWilliam, 1976; Chandra, Proudlove, & Baxter, 1999; Morrison, 1993, 1995; Morrison, Tester, Snape, Law, & Gidley, 1993; Seefeldt et al., 2011; Tang & Copeland, 2007; Tester & Morrison, 1990, 1992; Welch, 1978).

Barley starch represents between 60 and 75% (dw) of the mature grain weight; however, other components of the grain can influence the quality of the grain and consequently its malting properties (Cozzolino et al., 2013; Morrison, 1993, 1995; Morrison et al., 1993; Tang & Copeland, 2007; Tester & Morrison, 1990; Welch, 1978). In addition to starch and protein content, grain lipids (1–3% dw) can play an important role in regulating or modulating several chemical and physical properties of the grain and malt (Bravi, Marconi, Perretti, & Fantozzi, 2012; Bravi, Perretti, Buzzini, Della Sera, & Fantozzi, 2009; Seefeldt et al., 2011; Suh, Verhoeven, Denyer, & Jane, 2004; Wackerbauer & Meyna, 2002; Youssef, El-Fishawy, Ramadan, & El-Rahman, 2012). Approximately 45% of lipids are located in the starchy endosperm and in the embryo, having important structural and physiological functions (Bravi et al., 2009, 2012; Seefeldt et al., 2011; Youssef et al., 2012). In recent years, several studies have evaluated the effect of total lipids (TL) and the content of specific fatty acids (FA) in malt and their role in explaining different properties of the grain during the malting process (Anness & Reed, 1985; Bravi et al., 2009, 2012; Cozzolino, Roumeliotis, & Eglinton, 2015; Ighwela, Bin, Abdullah Md, & Abol-Munafi, 2011). In a similar way, the adverse effect of both lipids and FA on beer quality and its direct effect influencing flavour and foam stability, have been reported by several authors (Bravi et al., 2012; Cozzolino et al., 2015; Etokakpan, 2004; Garbe, Barbosa De Almeida, Nagel, Wackerbauer, & Tressl, 2006).

Lipids in cereals can be grouped into three main categories or classes according to their location in the grain or flour as well as the method of extraction used during analysis (Bahrami et al., 2014; Liu, 2011; Price & Parsons, 1975, 1979; Youssef et al., 2012). These groups are defined as non-starch lipids, starch lipids and starch surface lipids (Bravi et al., 2009, 2012; Seefeldt et al., 2011; Youssef et al., 2012). The cells of the aleurone not only contain proteins but also lipids and minerals that are important to provide the embryo with the necessary nutrients during seed germination (Miransari & Smith, 2014; Simon, 1974; Zheng & Wang, 2010, 2011; Zheng, Wang, & Gu, 2014). Both TL and FA content of malt have now been considered in some countries as part of the malting and brewing specifications (Bravi et al., 2012; Thomas, Scholz, Peter, & Heinz, 2011). The amount, nature, and quality of the lipid fractions in the grain can also exert considerable influence on the susceptibility to oxidative changes during storage and processing of the grain as well as the malt (Etokakpan, 2004; Garbe et al., 2006; Kobayashi, Kaneda, Kano, & Koshino, 1993; Kobayashi et al., 2000). Lipids in wort are also important, mainly because of their role in yeast metabolism as well as in determining beer quality, in which long-chain FA are precursors of compounds that contribute to the flavour profile of beer (Bravi et al., 2012; Etokakpan, 2004; Garbe et al., 2006). In fermenting wort, both lipids and long-chain unsaturated FA are essential in yeast activation as well as for cell growth under anaerobic conditions, affecting the fermentation process and leading to a more intensive and faster fermentation (Bravi et al., 2009; Kuhbeck, Back, & Krottenthaler, 2006; MacWilliam, 1968). In particular, unsaturated FA (e.g. linoleic and linolenic acids) have received greater attention because of their oxidative degradation leading to the formation of a characteristic aging flavour (Ang & Bamforth, 2014; Bravi et al., 2012; Kuhbeck et al., 2006; Leisegang & Stahl, 2005; Siebert, 2014; Van Nierop, Evans, Axcell, Cantrell, & Rautenbach, 2004).

The aim of this article is to provide an overview on the role of lipids and FA in the chemical and industrial properties of barley grain, malt and wort on the production of beer.

2. Lipid transfer protein (LPT)

During beer production, brewers worldwide strive to obtain product consistency in terms of flavour, colour and foam as reported and reviewed by various authors (Ang & Bamforth, 2014; Kader, 1996; Murakami-Yamaguchi et al., 2012; Nieuwoudt, Lombard, & Rautenbach, 2014; Siebert, 2014). In recent years, studies on proteins that contribute to the formation of beer foam are the well-known lipid transfer proteins (LTPs), in particular LTP1 and its lipid-bound isoform namely LTP1b (Nieuwoudt et al., 2014; Perrocheau, Bakan, Boivin, & Marion, 2006). These LTPs have been reported to be associated with the transport of lipids in vivo, preventing lipids from destabilising the beer foam (Nieuwoudt et al., 2014). Both LTP1 and LTP1b were successfully purified where circular dichroism of LTP1 and LTP1b confirmed that both proteins are highly tolerant to high temperatures (>90 °C), are pH stable, particularly at a neutral to a more basic pH (Nieuwoudt et al., 2014). Only LTP1 exhibited anti-yeast and thermostable activity, while LTP1b was inactive, indicating that the fatty acid moiety compromised the antimicrobial activity of LTP1. According to Nieuwoudt et al. (2014) the lack of anti-yeast activity and the positive foam properties of LTP1b can benefit beer fermentation and quality (Iimure & Sato, 2013; Iimure et al., 2012; Nieuwoudt et al., 2014). Iimure and collaborators have also evaluated crude extracts of barley albumin, reporting that these extracts can behave like beer in model system (Iimure & Sato, 2013; Iimure et al., 2012). The results reported by these authors suggested a greater involvement of LTP1 alike proteins in the formation of beer foam (Iimure & Sato, 2013; Iimure et al., 2012; Siebert, 2014). Several authors also reported the effect of LTP on different wort and beer properties such as the quantity, quality and stability of the beer foam (Gorjanovic, 2007; Gorjanovic et al., 2004; Iimure & Sato, 2013; Murakami-Yamaguchi, Hirose, Honjoh, & Narita, 2009; Perrocheau et al., 2006; Runavot et al., 2011; Siebert, 2014).

3. Interactions between lipids and starch (amylose and amylopectin)

Several reports highlighted both the main influences and interactions between total amylose content and free amylose with lipids (e.g. lipid complexed amylose), as well as the chain length distribution of amylopectin on different properties of the starch (e.g. swelling behaviour and pasting properties) in several starchy foods including barley (Wang & Copeland, 2015). These authors reported a direct relationship on the pasting properties of starch such as a decrease in peak (PV), breakdown (BKD) and final viscosity (FV) with an increase in the total amylose content, as well as an effect of the interactions between amylose in the presence of lipids (Blazek, Gilbert, & Copeland, 2011; Cozzolino, Allder, Roumeliotis, & Eglinton, 2012; Cozzolino et al., 2013, 2014a; Lauro, Poutanen, & Forssell, 2000; Pycia, Galkowska, Juszczak, Fortuna, & Witczak, 2015; Wang & Copeland, 2015; Zhou & Mendham, 2005). It has been reported that in starches isolated from 12 waxy and 6 non-waxy genotypes of barley grown in adjacent field plots the structure of the amylopectin in all of the starches appeared to be very similar (Tester & Morrison, 1992). However the waxy starches contained more amylose (<7.4%) and lipids (120–630 mg 100 g^{-1}), giving an amylose–lipid relationship ($r = 0.99$) different from that in the non-waxy starches (Tester & Morrison, 1992). In the same study, these authors reported that the B granules in the waxy starches had about half of the amylose and lipids found in the A granules (Tester & Morrison, 1992). The FA composition of the lipids in the waxy starches was much more