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Development of an all rice malt beer: A gluten free alternative

Heidi Mayer [a], Dayana Ceccaroni [a], Ombretta Marconi [a], Valeria Sileoni [b, *], Giuseppe Perretti [a], Paolo Fantozzi [b]

[a] Italian Brewing Research Center, University of Perugia, Via S. Costanzo n.c.n., 06126 Perugia, Italy
[b] Department of Agricultural, Food and Environmental Sciences, University of Perugia, Via S. Costanzo n.c.n., 06126 Perugia, Italy

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ABSTRACT

In the current study three all-rice malt beers were produced in a traditional way from different rice malts each with sufficient endogenous enzyme activity for degradation of the rice components. The use of a simple infusion mashing program with acidification was mandatory as well as for improving hydrolytic enzymes activity as for protein degradation. Following this procedure, a complete saccharification was achieved 1 h after reaching 74 °C as ascertained with the iodine test. Lautering proceeded without difficulty, probably due to the low viscosity of the worts and to the rice husk which was ideal for filtration. Despite their low total nitrogen and FAN (Free-Amino Nitrogen) contents and suboptimal wort sugar compositions, the fermentation for all the samples proceeded regularly. The most important aroma-active substances were determined and compared to a barley malt bottom-fermented beer. Identification of the sensory profiles of the beers was also performed using a trained taste panel.

1. Introduction

Beer is a very popular beverage around the world. Generally the basic ingredient is barley or wheat malt. This can be problematic for individuals who suffer from celiac disease, an intolerance to the gluten proteins found in barley and wheat, and who should follow a gluten-free diet which would also exclude beer (Hager, Taylor, Waters, & Arendt, 2014). This is one reason for which it may be useful to replace the conventional barley or wheat ingredients in beer production with rice, a gluten-free and readily available cereal. Another reason is the possibility to produce beer with alternative raw materials in those countries where barley is not cultivated.

Rice beer production is not without challenges. Meanwhile the malting of barley and wheat produces malts that are suitable for brewing, the malting of rice has not yet yielded an appropriate malt despite several attempts made in recent years (Agu et al., 2012; Ceppi & Brenna, 2010a; Kongkaew, Usansa, & Wanapu, 2012; Zarnkow, Kessler, Burberg, Kreisz, & Back, 2005). The main problem with rice malt is that it fails to complete saccharification during mashing. This means the rice starch does not completely degrade into soluble sugars and low molecular weight starch degradation products in the wort, which is a necessary condition for beer production. As a result, the yield and the rate of lautering decrease and an undesirable haze forms during fermentation and the beer flavor suffers (Narziß & Back, 2012a). One of the reasons for the incomplete saccharification seems the high gelatinization temperature of the rice starch and an insufficiency of starch-degrading enzymes in the rice malt. But also a sufficient protein degradation, especially of the structural protein of the endosperm cell wall, is indispensable for the saccharification of the starch and has to occur prior to or simultaneously with starch modification (Narziß & Back, 2012a). This is more difficult in rice malt than in barley malt probably due to the different protein composition of rice that can be noted also in the absence of gluten. Even in the case of the alternative way to produce beer, by supplementing the unmalted raw material with commercial exogenous enzymes, it is not possible until today to produce a beer-like 100% rice beverage even though this technique is successfully applied to unmalted barley (Steiner, Auer, Becker, & Gastl, 2012), because the rice protein could not be degraded by synthetic enzymes and therefore the protein cannot solubilize in the wort (Narziß & Back, 2012a; Steiner et al., 2012; Zarnkow & Back, 2005). In this case the problem is the low nitrogen content in the wort which is crucial for several reasons. The high molecular weight proteins are important for foam quantity and stability while the low molecular weight nitrogen products e.g. amino acids, measured as FAN, are necessary for yeast nutrition and so for a complete fermentation. Moreover, the formation of

* Corresponding author.
E-mail address: vale.sileoni@tiscali.it (V. Sileoni).

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color and aroma substances by Maillard reactions, which are important for beer quality and flavor, is reduced.

On the other hand the malting process increases proteolytic activity even if the overall low protein content of rice malt and its weak modification during malting and mashing yields less soluble nitrogen in the wort than in barley malt (Ceppi & Brenna, 2010a; Narziβ & Back, 2012a). So the rice beer production is problematic both in the traditional way by using the malted cereal and in a more modern way by adding exogenous enzymes to the unmalted raw material.

The present work will show how to produce a 100% rice malt beer following a traditional method. The prerequisites are a well-modified and saccharifying rice malt and optimized mashing conditions as reported in a recent study (Mayer, Marconi, Regnicoli, Perretti, & Fantozzi, 2014), where three rice malts capable of completely saccharifying through the work of endogenous enzymes were produced for the first time in a laboratory test. Two of the malts were of the same variety, but differed in origin and had different protein contents. To obtain complete saccharification, it was necessary to adapt the pH and temperature settings of the laboratory mashing programs, because rice malt has a different composition of the endosperm cell walls (Shibuya, Nakane, Yasui, Tanaka, & Iwasaki, 1985; Shibuya & Iwasaki, 1978; Shibuya & Misaki, 1978) and a different content and behavior of the amylolytic enzymes than barley malt (Ceppi & Brenna, 2010b; Dziedzoave, Graffham, Westby, & Komlaga, 2010; Iwata, Suzuki, & Aramaki, 2003; Iwata, Suzuki, Takahashi, & Aramaki, 2002; Iwaki & Fuwa, 1981; Nakai et al., 2007; Yamasaki, Nakashima, & Konno, 2008).

In the present study, the authors intended to verify if the good results of the laboratory mashing trials can be achieved also under brewhouse conditions and if the quality and quantity of the obtained protein degradation products is sufficient or can affect the course of fermentation or the organoleptic features of the final product. In fact the presence of a balanced amino acid and sugar composition of the wort is necessary for proper fermentation and the formation of fermentation by-products like esters, aldehydes and higher alcohols, which contribute to a beer's flavor and determine its sensory profile.

The main objective of this study was to use the three rice malts that have been previously developed to brew a beverage similar in aroma, taste and mouthfeel to beer. The all-rice malt beers were produced for the first time in a traditional way in a pilot brewery and the final rice beers were evaluated and compared to a barley malt beer. Finally the levels of major aroma-active components of bottom-fermented beers were determined and a sensory analysis was performed to assess the beer-like character of the rice beverages.

2. Materials and methods

2.1. Rice

Three samples of Italian rice were used in this study and all were harvested in 2011. The first sample was Centauro from Sardinia (8.51% protein dry matter), the second sample was Centauro from North Italy (7.62% protein d.m.) and the third sample was Balilla (7.44% protein d.m.). Each rice sample was malted in duplicate as paddy rice in an automatic micromalting system from Custom Laboratory Products (Keith, UK) as has been described in a previous article by the authors (Mayer et al., 2014).

2.2. Brewing

2.2.1. Wort production

The aforementioned malt samples (3 kg) were processed in a 20-L pilot scale brewery (Braumeister, Speidel, Ofterdingen, Germany) in duplicate. The malt was crushed in a two-roller mill (Engl-Maschinen GmbH, Schwebheim, Germany) with a 0.5 mm gap between the rollers. A 1:4 ratio of rice malt grist to brewing water (3 kg of malt to 12 L of water) was used and supplemented with $CaCl_2 \times 2H_2O$ to 85 mg/L of Ca. After mixing the malt grist with water the pH was quickly adjusted with lactic acid to 5.3. The same infusion mashing program was used for the three different rice malt samples.

The optimal pH and temperature conditions for rice malt enzymes have not been described in the literature to our knowledge with the exception of α-glucosidase (55 °C, pH 4.5 (Iwata et al., 2003)), pullulanase (60 °C, pH 5.5 (Iwata et al., 2002) or 55 °C, pH 6.0 (Yamasaki et al., 2008)). Therefore, all temperature rests were empirically developed. Mashing was conducted by increasing the temperature by 1 °C/min and by maintaining the following temperature rests: 30 min at 45 °C, 45 min at 65 °C, 60 min at 74 °C, 10 min at 78 °C. A temperature rest at 55 °C, optimal for α-glucosidase, was avoided because of the already high amount of glucose in the wort (Mayer et al., 2014). The saccharification test with iodine solution was performed every 10 min after the beginning of the temperature rest at 74 °C. All the samples completely saccharified 1 h after reaching 74 °C, before increasing the temperature to 78 °C.

After 10 min of mashing-out, the wort was transferred to the lauter tun for filtration. The lautering time for all samples was approximately 1 h. Sparging was conducted twice with 4 L and once with 2 L of water at 78 °C. The mash was boiled for 60 min. At the beginning of this phase, hop pellets (variety Perle, 7.7 α-acids) were added to achieve 15 International Bitter Units (IBU). The hopping in the final part of wort boiling was avoided in order to minimize the development of flavor compounds from the hop. After boiling and elimination of the hot trub, the wort was cooled to 13 °C. Aeration of the wort was then performed before yeast pitching.

2.2.2. Fermentation

Pitching of the yeast was carried out at 13 °C using 1 g yeast per L of wort. A dry, bottom-fermenting yeast that is commercially-available (Saflager S-23, Fermentis, Marcq-en-Barœul Cedex, France) was introduced after rehydration with sterile water to achieve 10^7 cells/mL in the wort. The use of a bottom-fermenting yeast allowed for better identification of the typical rice malt flavor. The fermentation temperature was maintained at 13 °C for 6 days. Then, after cooling down to 2 °C, the yeast was discharged from the bottom of the tank. The maturation lasted for 10 days. At the end of maturation, the beer was analyzed.

2.3. Chemical analyses

2.3.1. Wort analyses

The following analyses were performed on the worts in duplicate according to the official Analytica-EBC methods (European Brewery Convention, 2007): Extract of Wort (°P), EBC method 8.3; pH of Wort, EBC method 8.17; Color of Wort: Spectrophotometric Method (EBC-U), EBC method 8.5; Viscosity of Wort (mPa*s at 20 °C), EBC method 8.4; Fermentability, Attenuation Limit of Wort – Rapid Method (%), EBC method 8.6.2; Total Nitrogen in Wort: Kjeldahl method (mg/L), EBC method 8.9.1; Free Amino Nitrogen (FAN) in Wort by Spectrophotometry (mg/L), EBC method