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Analysis of volatile compounds from a malting process using headspace solid-phase micro-extraction and GC–MS

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ABSTRACT

The aroma of malt is one of the most crucial factors that influence the flavor of beer. To better understand the behavior of aroma during malting process, we identified the volatile compounds from barley, green malt and malt by using headspace solid phase microextraction (SPME) and gas-chromatography/mass spectrometry. A total of 47 volatiles, comprising aldehydes, ketones, alcohols, acids, and furans, were identified during the complete malting process. In particular, the dynamics of 2-methyl-propanal 3-methylbutanal, 2-methylbutanal, hexanal, 2-hexenal and 2-nonenal, commonly considered as key odorants in barley and malt, was highlighted during the process. Among these compounds, the amounts of 2-methyl-propanal, 3-methylbutanal, 2-methylbutanal, and 2-nonenal increased during the roasting stage, and the ones of hexanal, 2-hexenal conversely decreased in the same stage. As to compounds of ketones, alcohols, organic acids and furans, there is no forming regularity for them, which they formed at different stages of the whole malting process. Meanwhile benzaldehyde, benzeneacetaldehyde, 1-hexanol and ethyl acetate were considered as possible key odorants during the whole malting process. Base on the results above suitable manipulation of the malting conditions could be supplied in an industrial scale.

1. Introduction

Beer is a popular alcoholic malt beverage resulting from a fermentation of the aqueous extract of malted barley with hops. Therefore, the volatile flavor compounds in barley were playing an important role in the aroma composition of the beer (De Schutter et al., 2008; Fritsch & Schieberle, 2005; Pinho, Ferreira, & Santos, 2006; Vanderhaegen et al., 2003).

A number of studies have analyzed the aroma components of the different types of barley and malt (Beal & Mottram, 1994; Fickert & Schieberle, 1998; Cramer, Mattinson, Fellman, & Baik, 2005). Twenty-six volatiles were identified by Cramer and co-works, comprising aldehydes, ketones, alcohols and a furan, in barley. They considered 1-octen-3-ol, 3-methylbutanal, 2-methylbutanal, hexanal, 2-hexenal, 2-heptenal, 2-nonenal and decanal were key odorants, and hexanal and 1-pentanol were major volatile compounds in barley cultivars. Malt is a product of malting, which usually involves the controlled germination, subsequent kilning and roasting process. During malting process there are some variations in the quality and quantity of volatile flavor compounds, which makes the final flavor of malt changes. Beal and Mottram (1994) have determined and identified 35 volatile compounds including similar ones in barley malt.

Because of the volatile flavor compounds from the malt that impart aroma and color to the beer, and consumers were critical about the beer flavor more and more in recent years, so advances in malting technology have improved these properties, but less attention has been paid to the development of flavor in brewing malt (Beal & Mottram, 1994). Uncovering the forming mechanism of volatile compounds in brewing malts through the analysis and identification of the volatile compounds during the whole malting process will facilitate the malting technology to improve these properties. This is the fundamental solution to the particular technical bottleneck about gaps among the different types of barleys in the malting industry.

The classical approach to flavor analysis involves isolation of the aroma volatiles from the matrix, followed by preconcentration, separation, and identification (Marsili, 1997; Zhou, Robards, Glennie-Holmes, & Helliwell, 1999), such as simple solvent extraction and supercritical fluid extraction (Ropkins & Taylor, 1996). Solid-phase microextraction (SPME), a technique for extraction and concentration or enrichment of volatile compounds from different sample matrices, has recently been developed (Pawliszyn, 1997). The combination of SPME with gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS) has proven to be a sensitive and precise method for the analysis of different classes of volatile compounds (Kaseleht, Leitner, & Paalme, 2011).

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Most applications of SPME are based on equilibrium extraction, but non-equilibrium extraction has proven to be feasible for the analysis of volatiles (Ai, 1997). Since Yang and Peppard (1994) and Steffen and Pawliszyn (1996) introduced SPME to the food industry, this technique has been widely used in the analysis of a range of volatile compounds in recent years (Roberts, Pollien, & Milo, 2000).

Here, with the aims to regulate the flavor of malt, the authors focus on the dynamics of the volatile compounds during the whole malting process in an industrial scale. Briefly, all the samples in the paper were collected from the malting workshop of the China Oil & Foodstuffs Corporation (COFCO) Malt (Dalian) Co. Ltd, which uses a tower malting system. By identifying the volatile compounds and summarizing variations of the key aromatic compounds during the malting process, the movement rule of those compounds in malting process should be clarified. Accordingly manipulation of the malting conditions might allow optimization of the character of malt, yielding a more flavorful product for the beer brewing industry.

2. Materials and methods

2.1. Materials

The barley cultivars used in this study, Metcalfe, was given by COFCO Malt (Dalian) Co. Ltd. It was harvested in Canada at 2010. The roasted malt used in the study was stored in a granary at least 20 days.

2.2. Preparation of malt

The malted barley was from a normal production run of crystal malt manufactured by COFCO Malt (Dalian) Co. Ltd using a tower malting system. The grain was loaded into tall tanks and subjected to a cycle involving one 6 h and two 8 h soaks, after which the grain was transferred to a germinating box for a further 4 days at 16 °C. The green malt was then transferred to the baking box, where the grain was dried. Then roasting was continued in a dry current of air until the malt had attained the characteristic color of crystal malt. Samples of malt were collected after 24, 48, 72, 96, 120 and 144 h during malting, then they were freeze-dried to a moisture content of approximately 5% and stored in sealed polythene containers at −20 °C. In final, a total of 8 samples had been analyzed including barley (0 h) and roasted malt.

2.3. Solid-phase micro-extraction sampling

To identify and quantify the volatile compounds in barley or malts, the headspace (HS) SPME technique was employed. For this study, the temperature was maintained at 18 ± 1 °C to avoid formation of flavor compound artifacts. The barley slurry was prepared by blending freshly ground flour (3.0 g), 20% sodium chloride solution (2 mL), in a 20 mL flask with a cap and Teflon-faced silicone rubber septa (Supelco, Co., Bellefonte, PA). The flask containing sodium chloride, flour and water was placed on a magnetic stirring plate (model PC-220, Corning, NY) and stirred at 1100 rpm for 20 min. A SPME fiber (DVB/CAR/PDMS) was then exposed to the headspace of the barley slurry for 1 h in a water bath at 18 ± 1 °C (Zeng, Zhang, Chen, Zhang, & Matsunaga, 2007).

2.4. GC–MS analysis and odor description

Gas chromatography–mass spectrometry (GC–MS) analyses were conducted using a GC mass spectrometer (Agilent 6890-5975c mass selective detector). The desorption time was 5 min in the injection port at 250 °C and using a column, HP-5 ms (30 m × 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific). Thus the temperature was programmed to be held at 40 °C for 5 min, then increased to 50 °C at a rate of 2 °C/min, then finally increased to 250 °C at a rate of 5 °C/min. The carrier gas was helium, which was delivered at a linear velocity of 2 mL/min. The mass selective detector was operated in the electron impact ionization mode at 70 eV, in the scan range m/z 40–400. The interface temperature was 230 °C. The retention time of each volatile was converted to the Kovats retention index using n-alkanes (Supelco) as references. The volatile compounds were tentatively identified by matching the mass spectra with the spectra of reference compounds in both the Wiley mass spectra library (6th edition) and the NIST/EPA/NIH mass spectra library (version 1.5a), and verified on the basis of mass spectra obtained from the literature and comparison of Kovats retention indices with those reported in the literature. The results from volatile analyses are provided in peak area counts of the compounds identified. All experiments were performed in triplicate, and the odor description of all the compounds in the paper were reported at www.flavornet.org and by Giri, Osako, and Ohshima, (2011).

2.5. Statistical analysis

The results for the volatile compounds were reported as mean values ± standard deviation. Statistical analysis was performed using SPSS 18.0 for Windows. Data were analyzed by analysis of variance (ANOVA), and a statistically significant difference was identified at the 95% confidence level. Post-hoc mean comparisons were made on the basis of the P values ($\alpha = 0.05$) by using Duncan's multiple range test.

3. Results and discussion

3.1. Comparison of volatile flavor compounds of the barley and malt

The barley cultivar Metcalfe, harvested in Canada, popularity in the malt manufacturing industry was used to the detection and comparison of the volatile flavor compounds from barley and malt by GC–MS combined with SPME extraction method.

Cramer et al. (2005) have identified a total number of 26 volatile compounds from different barley cultivars by using the SPME combined with GC/MS method. This suggests the DVB/CAR/PDMS fiber to be more appropriate for flavor volatile analysis by the manufacturer because of their intermediary polarity. It was also proven to be the most efficient in trapping a range of volatile compounds with different polarities (Ceva-Antunes, Bizzo, Silva, Carvalho, & Antunes, 2006) and the most useful in covering the wide range of physical–chemical properties of flavor volatiles (Mondello et al., 2005). As shown in Fig. 1A and C, there were a significant variation in the numbers and amounts (peak area) of the volatile compounds from barley and malt. Here, the authors also determined volatile compounds from the freeze-dried green malt by SPME extraction combined with GC–MS method (Fig. 1B), indicating that this method could not only be used to identify the real composition of volatile compounds from barley and malt but also in the green malt to clarification the dynamic of volatile compounds during the malting process.

In the malting process, there were various enzymes in barley grains to modify the grain's starches or proteins into mono-, disaccharides, or amino-acids, respectively. Besides, there were also big changes in the composition of the volatile compounds. As shown in Table 1, a total number of 28 volatile compounds were identified and confirmed that the aldehydes, alcohols and ketones were the predominant constituents of volatile compounds in barley. Simultaneously, a total number of 32 volatile compounds were identified in malt, and the amounts of most of those compounds were increased after the controlled germination, subsequent kilning and roasting process. Although the mix of volatile compounds was generally the same from them there were still some differences between them. Briefly, 2-hexenal, (E,Z)-6-nonadienal, 3-methyl-1-butanol, (Z)-2-nonen-1-ol, 2,3-butanedione, 6-methyl-5-