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Volatile organic compounds of a Swiss cheese slurry system with and without added reduced glutathione, compared with commercial Swiss cheese

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A B S T R A C T

The volatile organic compound (VOC) profile of a Swiss cheese curd slurry system, with and without addition of reduced glutathione (GSH), was investigated on a daily basis for six days of incubation at 30 °C. The VOC profiles of commercial Swiss cheese samples from different stages during manufacture (after press, end of pre-cool, end of warm room and at cut) were also measured. Using the volatiles produced, the time scale of the slurry was matched to that of conventional ripening to determine which day of accelerated ripening corresponded to each stage of commercial ripening. The profiles of most of the VOCs in the slurry system with GSH more closely matched the profiles at the different stages of Swiss cheese ripening than the slurry system without GSH. Moreover, the headspace concentrations of volatiles that are considered to produce off-flavors were significantly decreased in the Swiss cheese slurry system with GSH.

1. Introduction

The flavor, aroma, and textural qualities of a particular cheese variety develop during the ripening stage of manufacture. It is during cheese ripening when factors such as curd composition interact with microflora to create the distinguishing characteristics of each variety of cheese. For the vast majority of rennet-coagulated cheeses, ripening varies from only a few weeks to two or more years. In Swiss-type cheeses, most volatile flavor compounds develop between 3 and 12 months of ripening (McSweeney, 2004; Noël, Boyaval, Thierry, Gagnaire, & Grappin, 1999).

Laboratory investigations of the factors and agents involved in ripening and flavor development are difficult due to the long ripening periods essential for full cheese flavor development. Several cheese slurry model systems have been established for accelerated ripening and cheese flavor development studies (Dias & Weimer, 1999; Madkor, El Soda, & Tong, 1999; Wijesundera, Drury, Muthukumarappan, Gunasekaran, & Everett, 2000). Addition of reduced glutathione (GSH) creates more rapid characteristic flavor development and much more reproducible fermentation than the control slurry system without glutathione (Harper & Kristoffersen, 1970; Singh & Kristoffersen, 1971). However, no attempts have been made to match the time scale for accelerated ripening to commercial ripening.

In addition, the effect of GSH on specific key volatiles in Swiss cheese has not been measured. The volatile components of cheese aroma consists of a well-proportioned ratio of a complex group of compounds from alcohols, aldehydes, amino acids, carbonyl compounds, esters, fatty acids, furans, ketones, lactones, nitrogen compounds, phenolic compounds, pyrazines, sulfur compounds and some inorganic compounds. These compounds are produced via specific fermentation systems and through the underlying biochemical control of interrelated pathways (Castada, Wick, Harper, & Barringer, 2015; Marilley & Casey, 2003; Schormüller, 1968). Volatile compounds with a flavor impact at low threshold values are of particular importance in flavor of cheese. The analysis of the flavor fingerprint of cheese and the specific compounds with flavor impact is important in maintaining and monitoring the flavor and perception quality of cheese. The key volatiles in Swiss cheese include 2–3, butanedione, 2-methylpropanal, 3-methylbutanoic acid, 3-methylindole, acetic acid, butanoic acid, ethyl butanoate, dimethyl disulfide, dimethyl sulfide, dimethyl trisulfide, ethyl

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hexanoate, furaneol, methional, methanol, methanethiol, propanoic acid, and tetramethylpyrazine (Smit, Smit, & Engels, 2005; Taylor, Wick, Castada, Kent, & Harper, 2013).

Although the exact mechanism of GSH in a slurry is not fully known, previous authors have theorized that it plays multiple roles in the accelerated flavor development of slurry systems, which more closely matches what occurs with normal cheese ripening (Harper & Kristoffersen, 1970). When GSH is added to the system, it is immediately oxidized and rapid dissociation of casein peptides occurs, making them more available for proteolytic attack and thus increasing the rate of proteolysis in the curd slurry system. GSH also slightly increases total esterase activity and slows the decline in esterase activity that occurs during the later stages of incubation, helping flavor intensity (Harper & Kristoffersen, 1970; Harper, Mikolajcik, & Chen, 1969). Finally, GSH changes the reduction–oxidation cycle and activity of diacetyl and acetaldehyde.

One goal of this study was to determine the effect of adding reduced glutathione on specific volatile organic compounds in a Swiss cheese curd slurry system for accelerated ripening studies. The other goal was to use the volatile organic compound (VOC) profile to match the time scale of the curd slurry system with the VOC profile of Swiss cheese samples obtained at different stages of ripening.

2. Materials and methods

2.1. Swiss cheese curd system

Fresh Swiss cheese curds were obtained just before pressing from an Ohio-based Swiss cheese manufacturing plant. The pH of the curds was 6.41 ± 0.02 with percent moisture of 51.5 ± 0.4% and percent fat of 19.9 ± 0.3%. Three batches of Swiss cheese curds with different manufacturing dates were shipped to the laboratory and immediately processed upon receipt. Lactic acid, potassium hydroxide and reduced glutathione (GSH) were all certified A.C.S reagent grades and were purchased from Fisher Scientific (Waltham, MA, USA).

2.2. Swiss cheese samples from different stages of manufacture

The volatile organic profile data of Swiss cheese samples from different stages of manufacture were reported in a previous study (Castada & Harper, 2014). The cheese samples were obtained from the same factory from each of the four stages of manufacture namely: (i) after pressing, (ii) end of pre-cool, (iii) end of warm room and (iv) at cut (at the time of cutting and packaging). Two batches, from different days, were obtained for each stage of manufacture. In each batch, a sample was taken from each of five different vats, giving a total of 40 cheese samples. Homogeneous representative sub-sampling of Swiss cheese for the headspace (H/S) VOC analysis was ensured via coning and quartering of the shredded cheese sample. If not immediately utilized, shredded cheese samples were vacuum packed and stored at −40 ± 1 °C.

2.3. Swiss cheese curd slurry system

The Swiss cheese curd slurry system used in this study was modeled after the slurry process developed by Harper and Kristoffersen (1970) and Singh and Kristoffersen (1971). The slurry mixture was prepared by mixing 500 g of cheese curd with 250 mL 3% sterile brine solution to produce 1.0% ± 0.2 final salt concentration in the slurry. The pH of the resulting brined-curd mixture was adjusted to a final pH of 5.2 ± 0.1 by the gradual addition of 86% (w/w) lactic acid or 4 M KOH. To a portion of this brined-curd slurry, reduced glutathione (GSH) was added to produce 100 ppm GSH in the mixture. This resulting mixture served as the experimental slurry system and the mixture without GSH as the control. The slurry mixtures (150 g) were transferred to individual airtight/re-sealable and sterile 450 mL polypropylene containers (Lock & Lock Co. Ltd., Asan, Korea) and incubated in the dark at 30 °C for six-day sampling and analysis. Three replicates were prepared for each sample. The pH values of the mixtures were monitored using a Fisher Accumet® glass electrode pH meter (Fisher Scientific).

2.4. VOC analysis

Each of slurry cheese samples (5 g) were weighed into individual 500 mL Schott bottles capped with a septum-lined screw cap. All bottles were incubated in a 40 ± 1 °C water bath for 1 h to allow for headspace (H/S) equilibration prior to selected ion flow tube-mass spectrometry (SIFT-MS) scan. The H/S sampling was done by inserting 3.5 cm of the SIFT-MS passivated sampling needle (3.8 cm) through the septa. A second, open, needle (15 cm) was inserted through the septa to allow for pressure stabilization during sampling. An empty bottle was scanned between samples to act as blank and zero the instrument before running the next sample.

2.5. Instrumental analysis

A Voice 200™ SIFT-MS (Syft Technologies, Christchurch, New Zealand) was used to detect and quantify the VOCs in the H/S of aqueous samples at ppb level. The V200 was operated using the more sensitive selected ion mode (SIM) to quantify specific compounds of interest. SIM scans limit the number of masses to be counted per scan thus allowing longer detection time per mass and delivers higher precision of quantification. A method containing 29 compounds considered to be of high impact in Swiss cheese (Taylor et al., 2013) was developed using the SIM scan mode and method development software (LabSyft) of the V200™. The scan duration was 2 min 10 s. Standards were run at the start of each day and calibrated with ethylbenzene, tetrafluorobenzene, toluene, hexafluorobenzene, ethylene, octafluorotoluene, benzene and isobutene.

2.6. Statistical methods and post-data analysis

Data fitting and least square means (LSM) analyses of the H/S VOC concentrations, percent moisture, fat, and solids were carried out using the PROC MIXED of SAS. A randomized complete blocked design experimental model was used that included the fixed effects of the type of mixture (2 degrees of freedom, DF) and the random effects of replicate, replicate-x-type of mixture and residual errors. The H/S concentrations were used for SAS modeling using PROC MIXED procedure to produce the LSM of a particular volatile organic compound with 95% confidence interval. Graphical representation of data was done using GraphPad Prism 6 software (GraphPad Software, Inc., La Jolla, CA, USA).

3. Results and discussion

The volatile organic compound (VOC) profiles of the curd slurry system, with and without the addition of reduced glutathione (GSH), were used to determine which day of the accelerated slurry system corresponded to which stage of ripening in commercial Swiss cheese. The after pressing (AP) period occurs during the first 24 h of Swiss cheese making; the end of pre-cool (EPC) is a 10–15 days of storing the cheese for pre-cooling and pre-ripening in a 10 °C cold room; the end of warm room (EWR) is after 30 days of storing the cheese in a 23 °C warm room for curing and eye