Food Chemistry 269 (2018) 347–354

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Investigation on the formations of volatile compounds, fatty acids, and γ-lactones in white and brown rice during fermentation

Sang Mi Lee[a,1], Hyeon Ji Lim[a,1], Ji Won Chang[b], Byung-Serk Hurh[b], Young-Suk Kim[a,*]

[a] Department of Food Science and Engineering, Ewha Womans University, Seoul 120-750, South Korea
[b] Sempio Foods Company R&D Center, Cheongju 363-954, South Korea

ARTICLE INFO

Keywords:
Brown rice
White rice
Fermentation
Volatiles
γ-Lactones
Fatty acids

ABSTRACT

Volatile compounds, including γ-lactones, in brown and white rice fermented by *Lactobacillus paracasei*, were compared using gas chromatography-mass spectrometry (GC–MS) with stir-bar sorptive extraction (SBSE). The contents of most esters, alcohols, lactones and some aldehydes were higher in brown rice samples containing higher amount of free fatty acids after fermentation. In particular, the contents of γ-lactones increased more in fermented brown rice containing high amounts of fatty acids than in fermented white rice, suggesting that γ-decalactone and γ-nonalactone were formed from oleic acid and linoleic acid during rice fermentation. In addition, the contents of γ-decalactone in fermented brown rice samples with added 4-hydroxydecanoic acid and ricinoleic acid were determined. The content of γ-decalactone in fermented brown rice samples with added 4-hydroxydecanoic acid was considerably higher than that in the control after fermentation, indicating that 4-hydroxydecanoic acid could be an effective intermediate for the formation of γ-decalactone in rice during fermentation.

1. Introduction

Rice has relatively high contents of various nutrients, including carbohydrates, proteins, lipids, vitamin B, and fiber, and is widely consumed as the staple food in many Asian countries (Liu, Cao, Bai, Wen, & Gu, 2009). Rice is typically consumed after de-hulling and milling (Rodríguez-Arzuaga, Cho, Billiris, Siebenmorgen, & Seo, 2016). Brown rice, which is obtained after de-hulling, contains bran layers (6–7% of total weight), embryo (2–3%), and endosperm (about 90%), while white rice is produced after removing the bran from brown rice (Schütt, & Schieberle, 2017; Liu et al., 2009). Accordingly, brown rice contains more nutrient components, such as lipids, proteins, dietary fiber, fatty acids, vitamins, minerals, phytic acid, and GABA (γ-aminobutyric acid) than white rice (Lamberts et al., 2007; Liu et al., 2009). These differences between white and brown rice can also affect their organoleptic properties (Lamberts et al., 2007). The specific aroma and flavor characteristics, such as sulfury, starchy, and metallic, of cooked rice were perceived as significantly more intense in white rice than in brown rice (Billiris, Siebenmorgen, Meullenet, & Mauromoustakos, 2012).

Grains can undergo fermentation by microorganisms, such as lactic acid bacteria (LAB), bifidobacteria, fungi and yeast, to produce fermented foods. Several studies have investigated the formation of volatile compounds in grain substrates and grain-based products by microorganisms (Annan, Poll, Sefa-Dedeh, Plahar, & Jakobsen, 2003; Salmeron, Fuciños, Charalampopoulos, & Pandiella, 2009; Kedia, Vazauez, & Pandiella, 2008). Rice-based products fermented with microorganisms can generate diverse volatile compounds associated with alcoholic fermentation, including sweet, fruity, buttery, and other aroma notes (Chuenchomrat, Assavanig, & Lertsiri, 2008; Patáková-Jůzlová, Řezanka, & Viden, 1998). Chuenchomrat et al. (2008) studied the volatile components in Thai rice fermented by fungi (*Aspergillus* and *Rhizopus* spp.) and yeast (*Saccharomyces cerevisiae*), and found volatiles, such as acetoin, diacetyl, and ethyl lactate, which are related to buttery, sweet, and fruity aroma notes. Patáková-Jůzlová et al. (1998) demonstrated that some volatile compounds, such as ethanol, 2-methyl-l-propanol, 3-methyl-l-butanol, 2-methyl-l-butanol, 2,2′-oxydiethanol, 2-methylisoborneol, geosmin, hexadecane, heptadecane, and α-bergamotene, were the predominant compounds in red rice fermented by the fungus *Monascus purpureus*. Volatiles produced from maize dough fermented by *Lactobacillus fermentum*, *Saccharomyces cerevisiae*, and *Candida krusei* were compared, and the dough fermented with *L. fermentum* showed the highest content of acetic acid, whereas *S. cerevisiae* produced higher amounts of fusel alcohols (Annan et al., 2003). Also,

* Corresponding author at: Ewha Womans University, Department of Food Science and Engineering, Seoul 120-750, South Korea.
E-mail address: yskim10@ewha.ac.kr (Y.-S. Kim).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.foodchem.2018.07.037
Received 20 February 2018; Received in revised form 24 June 2018; Accepted 4 July 2018
Available online 05 July 2018
0308-8146/

barley and malt fermented using *Lactobacilli* strains *L. reuteri, L. plantarum*, and *L. acidophilus* produced high contents of some major flavor compounds (acetaldehyde, ethanol, acetone, diacetyl, and ethyl acetate), which could affect the organoleptic qualities of fermented cereal-based products (Salmerón, Loeza-Serrano, Pérez-Vega, & Pandiella, 2015).

A particularly interesting finding is that among various volatile compounds of fermented rice, lactones can be produced from unsaturated fatty acids, such as oleic acid and linoleic acid, during fermentation (Romero-Guido et al., 2011). These lactones, which have buttery, coconut-like, and peach-like odor notes, can contribute significantly to the flavor characteristics of some fermented foods, such as dairy products, rice beer, and Chinese rice wine (Schütt, & Schieberle, 2017; Mo, Fan, & Xu, 2009; Lyu, Nam, Lee, & Lee, 2013). A significant amount of γ-nonalactone was formed in wheat rice wine, indicating it can be formed by a bacterial fermentation (Mo et al., 2009). In addition, various lactones, such as γ-hexalactone, γ-nonalactone and γ-decalactone, were detected in rice beer (Lyu et al., 2013). Some microorganisms such as *Ceratocystis moniliformis*, *Trichoderma viride*, *Sporobolomyces odorus*, and certain *Candida* species have been verified as lactone producers, but at low production yields (Endrizzi, Pagot, Clainche, Nicaud, & Belin, 1996; Vandamme, 2003). The addition of castor oil to the culture medium increased the formation of lactones by *Sporobolomyces odorus*. Castor oil contains high levels of ricinoleic acid, which can be a precursor of γ-decalactone (Romero-Guido et al., 2011). Moreover, lactic acid bacteria (LAB) can contribute to the formation of free fatty acids, which can be precursors of characteristic aroma compounds and lactones in some fermented products, such as ripened cheese, sourdough, butter, buttermilk, fermented vegetables, and yogurt (Leroy & De Vuyst, 2004). In particular, *Lactobacillus paracasei* has been found in various cheese products that have low acidity and oxygen levels, and it can produce high levels of lactic acid (Giraffa, Chanishvili, & Widyastuti, 2010).

However, no study has investigated the formation of volatiles and lactones during the fermentation of rice by LABs, including *L. paracasei*. Accordingly, the present study focused on the formation of volatile compounds and lactones in fermented rice, which can be used as a dairy replacement. Some volatile compounds, especially, lactones, 2,3-butanedione, and 3-hydroxy-2-butanone, which were produced in rice samples fermented by *L. paracasei*, can be commonly found in dairy products, including cheese, fermented milk and butter. They can improve the organoleptic qualities of rice-based probiotic functional foods, which have the potential for dairy replacement together with lactic acid.

The objective of this study was to compare differences in the profiles of volatiles, including lactones, in samples of white and brown rice fermented by *L. paracasei* according to the fermentation time, and to also determine the changes of γ-lactones and their precursors (oleic acid and linoleic acid) in fermented white and brown rice samples. In addition, the effect of different intermediates, such as ricinoleic acid and 4-hydroxydecanoic acid, on the formation of γ-decalactone in fermented rice during fermentation, was investigated.

2. Materials and methods

2.1. Chemicals

Chloroform, diethyl ether, acetic acid, heneicosanoic acid, 6-amyl-α-pyrone, pyridine, *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) and methoxyamine hydrochloride were purchased from Sigma-Aldrich (St. Louis, MO). Methanol was obtained from J.T. Baker (Phillipsburg, NJ). 2-Propanol was purchased from Fisher Scientific (Pittsburgh, PA). Sodium 4-hydroxydecanoate (> 95%) was supplied from Enamine (South Brunswick, NJ). Authentic standard compounds for positive identification of non-volatiles and volatiles were purchased as follows: toluene was purchased from Samchun (Yeosu-si, Jeollanam-do, Korea); 1-pentanol was obtained from Junsei (Nihonbashi-honcho, Chuo-ku, Tokyo), while all of the other authentic standards were obtained from Sigma-Aldrich (St. Louis, MO).

2.2. Preparation of fermented rice samples

Brown rice (*Oryza sativa* L., cultivar: Chucheong) was purchased at a local market (Soeul, Korea). White rice was obtained by dehusking of brown rice up to 95% using a milling machine (Yamamoto, Higashine-shi, Japan). White rice (milled rice) and brown rice were ground using a hammer mill (AscoKorea, Daegu, South Korea) to 170 mesh. Then distilled water was added at the ratio of 2.3:7.7 (ground rice: water, *w/w*). After that, saccharification of the pretreated rice with commercial 0.05% (*w/w*) α-amylase (BAN480L; Novozymes) and 0.05% (*w/w*) glucoamylase (AMZ1100; Novozymes, Bagsvaerd, Denmark) was performed by shaking slowly at 100 rpm and 65 °C for 20 h. After enzyme deactivation (85 °C for 30 min), rice samples were inoculated with 1% (*w/w*) of *L. paracasei* (SMB 092, KCCM 115579) at a level of 10^7 CFU/mL. *L. paracasei* was selected in the preliminary test based on organoleptic qualities as well as acid tolerance (data not shown). The control sample (at 0 h) was obtained after enzyme deactivation. The inoculated samples were fermented at 30 °C, which is the optimal temperature for *L. paracasei* growth, for 1, 2, 3 and 4 days. All samples were kept at −70 °C until use. All experiments were conducted in triplicate.

2.3. Preparation of fermented rice samples spiked with intermediates of γ-decalactone

The ground brown rice samples were treated with enzymatic saccharification of the pretreated rice. After enzyme deactivation at 85 °C for 30 min, both rice samples were each added with intermediates of γ-decalactone, including ricinoleic acid and sodium 4-hydroxydecanoate, at a concentration of 5 mmol/L. Then, each sample was inoculated with 1% (*w/w*) *L. paracasei* (SMB 092, KCCM 115579) at a level of 10^7 CFU/mL. These samples were fermented at 30 °C for 4 days. After fermentation, all samples were kept at −70 °C. The samples were thawed in a refrigerator before analysis.

The samples for the quantitative analyses of γ-decalactone are as follows: rice sample inoculated with *L. paracasei* without addition of intermediate (Con-0D-L); brown rice sample fermented by *L. paracasei* for 4 days without any added intermediate (Con-4D-L); brown rice sample fermented by *L. paracasei* for 4 days with spiking with ricinoleic acid (RA-4D-L); brown rice sample fermented by *L. paracasei* for 4 days with spiking with sodium 4-hydroxydecanoate (HD-4D-L); brown rice sample fermented for 4 days with spiking with sodium 4-hydroxydecanoate, but without inoculation with *L. paracasei* (HD-4D).

2.4. Analysis of volatile compounds in fermented rice samples

2.4.1. Extraction of volatile compounds by stir-bar sorptive extraction (SBSE) method

Aliquots (8 mL) of fermented rice samples were transferred to 10-mL amber glass vials, and spiked with 8 μL of 6-amyl-α-pyrone (10 μg/L in methanol (*w/v*)) as an internal standard. For the equilibrium and adsorption of volatiles, the samples in the vials were placed on a Gerstel twister plate (Gerstel, Mülheim an der Ruhr, Germany) and a Twister® coated with polydimethylsiloxane (PDMS, 10 mm length, 0.5 mm film thickness; Gerstel, Mülheim an der Ruhr, Germany) was placed in the sample. Then samples were stirred at 900 rpm and 25 ± 3 °C for 60 min. After the extraction, the Twister was washed with HPLC-grade water (J.T. Baker., Phillipsburg, NJ) and dried with lint-free tissue paper. Then the Twister was moved into Twister desorption liner tubes (Gerstel), and the adsorbed volatile components were desorbed in a thermal desorption unit (TDU).