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Effects of organic acid coagulants on the physical properties of and chemical interactions in tofu

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ABSTRACT

To improve tofu quality, the effects of using 0.12–0.18 g/100 mL citric acid, l-(-)-malic acid, or tartaric acid as coagulation agents were investigated. The results showed that storage modulus, hardness, water-holding capacity, non-freezable water content, and in-gel hydrophobic interactions were optimal when tofu was prepared with 0.14 g/100 mL organic acids, but deteriorated when more than 0.16 g/100 mL was used. Slower acidification during gelling in the presence of 0.14 g/100 mL organic acid promoted protein–protein hydrophobic interactions, resulting in a higher elastic modulus. Moreover, the tofu products showed higher water-holding capacity and non-freezable water content, as well as more compact gel microstructures. Notably, tofu prepared with citric or l-(-)-malic acid was of better quality than tofu prepared with tartaric acid. Collectively, the results demonstrate that soft or firm tofu with desirable physicochemical properties can be prepared with organic acids if acidification is adequately controlled during gelation.

1. Introduction

Tofu has historically been popular in Asia as an excellent source of protein and essential amino acids, and has been growing in popularity worldwide (Cai, Chang, Shih, Hou, & Ji, 1997; Zhu, Wu, Saito, Tatsumi, & Yin, 2016). Accordingly, tofu has been extensively studied for many years as a form of soybean protein matrix. Tofu is produced by soaking, milling, filtering, cooking, coagulating, and pressing soybeans, with coagulation being the most important step (Rui et al., 2016; Zhang, Li, Feng, & Dong, 2013). During coagulation, soy proteins aggregate via protein–protein and protein–water crosslinking into gels with a random or a regular honeycomb structure (Zhang et al., 2013). To produce firm, silken, and soft tofu, coagulation is induced using salt, enzymes, and acid, respectively.

Calcium sulfate and magnesium chloride are widely used as salt coagulants, although residual undissolved calcium sulfate in tofu or rapid release of magnesium chloride typically results in a coarse texture, an indicator of poor quality (Meng et al., 2015; Ting, Kuo, Lien, Li, & Sheng, 2009). Microbial transglutaminase is typically used to enzymatically crosslink soy proteins into tofu with low gel hardness, although this process is time-consuming (Chang, Shiau, Chen, & Lin, 2011; Tang, Li, Wang, & Yang, 2007). Finally, glucono-δ-lactone (GDL) has been widely studied as an acidifying agent to produce tofu with a homogeneous network (Bi, Li, Wang, & Adhikari, 2013; Chang, Li, Wang, Bi, & Adhikari, 2014; Schuldt, Raak, Jaros, & Rohm, 2014). Of note, proteins gel at pH 5.6 to 5.8 depending on the soy variety used, regardless of the GDL concentration (Malaki Nik, Alexander, Poysa, Woodrow, & Corredig, 2011).

Acid-induced gelation is driven by interactions that are formed when hydrophobic amino acids in soy proteins are exposed following the formation of hydronium ions that neutralize repulsive charges and reduce steric repulsion (Kohyama, Sano, & Doi, 1995; Grygorczyk & Corredig, 2013). These interactions are predominantly noncovalent and include salt bridges, hydrogen bonds, and hydrophobic and Van der Waals interactions (Kohyama et al., 1995; Lee & Kuo, 2011). However, little attention has been paid to organic acids, including citric acid, l-(-)-malic acid, and tartaric acid, as mild, nutritionally harmless, and water-soluble coagulation agents. These organic acids were initially identified in fruits and

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vegetables and are currently extensively used in the food industry (Huang, Xu, Zhang, Xue, & Chen, 2007; De'Nobili et al., 2016). Organic acids induce significant gelation at concentrations suitable for relatively slow acidification, a desirable property, as accelerated acidification typically results in weaker gels (Jacob, Nöbel, Jaros, & Rohm, 2011).

The objective of this study was to investigate the effects of organic acid (citric acid, l-(-)-malic acid, and tartaric acid) treatments on the soymilk gelation process and tofu quality. The relative contribution of various chemical interaction types, including ionic bonds, hydrogen bonds, and hydrophobic interactions, to tofu properties was evaluated. In addition, the feasibility of organic acid in the production of tofu with desirable physicochemical properties was assessed. Texture, water-holding capacity, and water distribution were assessed to measure gel strength, rigidity, and water state. pH, rheological properties, and in-gel chemical interactions were analyzed to investigate gel nucleation and formation. The gel microstructure was evaluated to investigate its relationship with gel macro-properties to allow quality control of organic acid-induced tofu gel.

2. Materials and methods

2.1. Materials

Zhonghuang 13 soybeans, determined to contain 45.80% total protein, 18.66% crude fat, 8.80% moisture, and 4.65% ash by AOAC methods were purchased from Xiangfeng Seed Station (Shandong, China), and stored at room temperature under 8–9% humidity. Food-grade citric acid, l-(-)-malic acid, tartaric acid, and GDL were purchased from Luyu Foods Industry Co. (Shanghai, China), while food-grade anti-foaming agent was obtained from Yingli Foods Industry Co. (Shanghai, China). All other chemicals were analytical grade.

2.2. Preparation of soymilk

Soymilk was prepared according to Kamizake, Silva, and Prudencio (2016), with some modification. Soybeans were rinsed, soaked in distilled water for 18 h at 4 °C at a ratio of 1:3 g/g, and ground for 3 min with distilled water at a ratio of 1:7 g/g in a JS30-230 mill (SUPOUR, Zhejiang, China). The raw milk was mixed with 0.3 g anti-foaming agent, boiled for 5 min with constant stirring on an electromagnetic oven (MAZUBA Co. Ltd., Jiangsu, China), filtered through a 100-mesh screen, and quickly cooled to room temperature in an ice bath. Finally, the milk was diluted to obtain standard soymilk with 8° brix and pH 6.6 ± 0.1, and stored for 12 h at 4 °C prior to analysis.

2.3. Preparation of tofu

Soymilk (100 mL) was poured into a 200-mL beaker, heated to 80 °C in a water bath, and coagulated for 30 min at 80 °C, using 0.30 g/100 mL GDL or 0.12, 0.14, 0.16, or 0.18 g/100 mL citric acid, l-(-)-malic acid, or tartaric acid as a coagulation agent. Tofu curds were immediately transferred to a 7 × 7 × 7-cm mold lined with cheese cloth and pressed at 8 g/cm^2 for 30 min using an in-house press to remove whey. Products were then stored at 4 °C for 12 h prior to analysis. pH was measured every 5 min using a handheld pH meter in parallel samples processed and kept in identical conditions.

2.4. Texture analysis

Tofu samples were cut into 1 × 1 × 1-cm cubes using a razor and analyzed on a TA-XT texture analyzer (Stable Micro System Co. Ltd., Godalming, UK) according to Zhang et al. (2013). The samples were compressed twice to 50% deformation using a P/36R probe, with trigger force 5 g, pretest speed 5.0 mm/s, test speed 1.0 mm/s, and post-test speed 10.0 mm/s. Hardness, springiness, cohesiveness, and gumminess were determined (Zhang et al., 2013).

2.5. Determination of water-holding capacity

Approximately 3 g of each tofu sample was used to measure water-holding capacity according to Hu et al. (2013), with some modification. Samples were cut into 5 × 5 × 5-mm cubes, weighed (W_t), and centrifuged at 5632 ×g for 20 min at 4 °C in a CR21 centrifuge (Hitachi, Japan). Supernatants were discarded and residual liquids were carefully removed with dry filter paper. The removed water was weighed (W_r), and water-holding capacity was calculated according to equation (1):

$$WHC = (W_t - W_r)\,/W_t \times 100\,\% \quad (1)$$

2.6. Differential scanning calorimetry

Freezable water content was measured by differential scanning calorimetry on a DSC-Q200 system (TA Instruments, USA) according to Chen, Wei, and Zhang (2010), with some modification. A small sample (5–10 mg) was heated from −60 °C to 50 °C at 5 °C/min under a 50-mL/min flow of nitrogen gas. Freezable water (W_f) was calculated according to Yoshida, Hatakeyama, and Hatakeyama (1993) as the ratio of the melting enthalpy per gram of wet sample at 0 °C to that of pure water. Non-freezable water (W_{nf}) was determined using equation (2):

$$W_{nf} = W_t - W_f \quad (2)$$

where W_t is the total water content as measured by the oven-heating method (Yoshida et al., 1993).

2.7. Dynamic rheological properties

Rheological behavior was analyzed according to Chang et al. (2014), with some modification, using a DHR-3 rheometer (TA Instruments, Leatherhead, UK) equipped with parallel 40-mm-thick plates at 1-mm distance and thermo-controlled by a circulation system. Samples were analyzed with strain amplitude sweeps to determine the linear viscoelastic region, and storage (G') moduli were recorded at a constant frequency of 1 Hz and a strain amplitude of 0.5%.

Soymilk (10 mL) was prepared at room temperature and mixed with 0.12–0.18 g/100 mL organic acid or 0.30 g/100 mL GDL. A 2-mL sample of the mixture was immediately injected between the plates and equilibrated for 2 min. Gelation was monitored for 30 min using a small-amplitude oscillatory time sweep at 80 °C. Once completely gelled, the sample was cooled from 80 °C to 25 °C at 5 °C/min. Data were collected in triplicate, and a solvent trap was used to cover sample edges and minimize evaporation during measurements.

2.8. Chemical interactions

The contributions of various chemical interactions to gelation and gel structure were assessed using modified procedures described by Wang et al. (2017), in which powder samples are dissolved in reagents that break formation of ionic bonds, hydrogen