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Effects of pulsed electric field treatment on (+)-catechin–acetaldehyde condensation

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ABSTRACT

Condensation of (+)-catechin contributes significantly to wine taste during its aging process. In order to simulate and explore a feasible method to enhance conversion of proanthocyanidins (PAs), the effect of pulsed electric field (PEF) treatment on the condensation efficiency between (+)-catechin and acetaldehyde in a wine model solution was investigated in this paper. The PEF intensity used ranged from 0 to 50 kV/cm. The content of (+)-catechin was monitored by HPLC–PAD. Results showed that the condensation reaction between (+)-catechin and acetaldehyde was enhanced by PEF treatment. The (+)-catechin decrease rate had an obvious increase with increasing PEF intensity. Furthermore, it increased with reaction temperature, as well as with decreasing pH values under PEF treatment (40 kV/cm). It was observed that the content of (+)-catechin after reaction for 31.12 ms under 40 kV/cm was approximately equivalent to that after reaction for 62.23 ms without PEF treatment. In addition, it was demonstrated that activation energy (E_a) of the condensation reaction was reduced remarkably by PEF treatment (from 41.59 kJ/mol to 28.98 kJ/mol under 40 kV/cm). Moreover, mass spectrometry analysis showed that both the reactions with and without PEF treatment fit the same pathway, indicating no change in reaction products. Future work will focus on the studies of changes of pH in the treatment chamber to verify the reaction mechanism.

Industrial Relevance: This study showed that pulsed electric field treatment (PEF) could be a novel and promising technology for the wine industry to accelerate the condensation between (+)-catechins, thus improving the quality of wine in a short time.

1. Introduction

Proanthocyanidins (PAs), which are polymers of subunits with C_4-C_6 or C_4-C_8 linkages, widely exist in seed, skin and stem tissues of grape and can be extracted during red wine making processes through maceration (Bordiga, Travaglia, Locatelli, Coïsson, & Arlorio, 2011; Sun et al., 1999). The subunits of PAs in wine mainly contain (+)-catechin, (−)-epicatechin, (−)-epicatechin-3-gallate, and (−)-epigallocatechin (Saucier, Mirabel, Daviaud, Longieras, & Glories, 2001; Souquet, Cheynier, Brossaud, & Moutounet, 1996), with (+)-catechin being the most common. All these polymers are responsible for essential organoleptic features of red wine, especially for bitterness, astringency, color, antioxidant activity, and colloidal stability (Arnold, Noble, & Singleton, 1980; Gawel, 1998; González-Manzano, Mateus, De Freitas, & Santos-Buelga, 2008; Rockenbach et al., 2011; Saucier, Bourgeois, Vitry, Roux, & Glories, 1997). Traditionally, wines need to be stored in cellular or oak barrels for a long time, from a few months to a few years, before entering the market. The taste of the wine becomes harmonious and dainty from harsh and coarse little by little. During the wine maturation period, highly reactive PAs undergo various types of reactions, which involve not only acid-catalyzed cleavage but also condensations (Drinkine, Glories, & Saucier, 2005; Es-Safi, Fulcrand, Cheynier, & Moutounet, 1999; Kennedy & Jones, 2001; Kimura, Ogawa, Akihiro, & Yokota, 2011; Nonier Bourden et al., 2008; Saucier, Little, & Glories, 1997; Saucier et al., 1997; Vidal, Cartalade, Souquet, Fulcrand, & Cheynier, 2002). There are two kinds of condensations between PAs, direct condensation and indirect condensation induced by aldehydes. The condensation reactions of subunits are as follows: (1) direct condensation between subunits; (2) direct condensation between subunits and anthocyanin (Remy, Fulcrand, Labarbe, Cheynier, & Moutounet, 2000; Santos-Buelga, Bravo-Haro, & Rivas-Gonzalo, 1995); (3) aldehyde induced condensation between subunits (Drinkine et al., 2005; Es-Safi et al., 1999; Nonier Bourden et al., 2008; Nonier, Vivas, Gaulejac, Pianet, & Fouquet, 2007); and (4) aldehyde induced condensation between subunits and anthocyanins (Es-Safi, Cheynier, & Moutounet, 2002; Nave, Teixeira, Mateus, & Freitas, 2010; Sun, Barradas, Leandro, Santos, & Spranger, 2008). These reactions result in the changes of taste and color of red wine. In indirect condensation, one of the most important electrophiles is acetaldehyde, which normally exists in wine to some extent (Saucier et al., 1997). Acetaldehyde in wine may be produced in two ways: oxidation of ethanol and production by yeast (Liu & Pilone, 2001).

In addition to concentration, PA composition such as DP (degree of polymerization) affects colloidal stability, astringency, and color of

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wine. The condensation of PAs leads to an increasing DP. The lightening of astringency taste during wine aging is also usually due to the polymerization of PAs. When the mDP value of PAs reaches decamer level, the astringency taste of the wine will be apparently lighter because larger PAs are thought to be insoluble and thus non-astringent (Vidal et al., 2003). Some studies have been carried out on the influence of the mDP on the copigmentation between anthocyanins and PAs and it was shown that catechin was the poorest anthocyanin co-pigment compared to oligomers (González-Manzano et al., 2008).

Pulsed electric field (PEF) processing (Abenoza et al., 2013; De Vito, Ferrari, Lebovka, Shynkaryk, & Vorobiev, 2008; Lin, Zeng, Yu, & Sun, 2012; Marsellés-Fontanet, Puig-Pujol, Olmos, Mínguez-Sanz, & Martín-Belloso, 2013; Martin-Belloso, & Sobrino-Lopez, 2011; Ortega-Rivas, 2011; Wang et al., 2011; Xiang, Ngadi, Ochoa-Martinez, & Simpson, 2011; Yu, Ngadi, & Raghavan, 2012), is an emerging non-thermal food treatment method, which has the potential to be an alternative to conventional processing methods (Jaeger, Balasa, & Knorr, 2009). Compared with traditional thermal processing such as drying that is widely used in the agri-food industry (Sun, & Woods, 1993, 1994a, 1994b, 1994c, 1997; Sun, & Byrne, 1998; Sun, 1999; Delgado, & Sun, 2002; Cui, Xu, & Sun, 2004), PEF technology offers minimal damage to food structure, better preservation of flavor and nutrients, an ability to sterilize microorganisms and inactivate enzymes at low temperatures with a low energy cost (Marsellés-Fontanet, Puig, Olmos, Mínguez-Sanz, & Martín-Belloso, 2009; Riener, Noci, Cronin, Morgan, & Lyng, 2008; Zhao et al., 2008). It was reported that pretreatment of the grape skin with PEF before the maceration step resulted in an increase in the total polyphenolic index of red wine due to the increase of permeability of cells (López et al., 2008a, 2008b; Puértolas, López, Condón, Álvarez, & Raso, 2010). In addition, the concentration of subunits and PAs in red wine after being treated by PEF exhibited the same trend as naturally aged samples (Chen, Zhang, Wang, & Mo, 2009). In our previous work, young wine treated with an electric field of 600 V/cm for 3 min showed a much better sensory quality than untreated wine and it was proved that the aging process was accelerated by the application of an AC electric field (Zeng, Yu, Zhang, & Chen, 2008). Furthermore, applications of PEF to reduce the activation energy (E_a) of esterification between ethanol and acetic acid from 76.64 kJ/mol (without PEF) to 59.10 kJ/mol (PEF-treated) were reported by Lin, Zeng, Yu, and Sun (2011).

In spite of the above studies, little focused on the effects of PEF on indirect condensation. In this study, the reaction between (+)-catechin and acetaldehyde with or without pulsed electric field treatment was investigated. A model wine solution with ethanol was used to simulate wine and simplify the red wine system. One of the major subunits of PAs, i.e., (+)-catechin, was used in this research. The aim of the present work was to investigate the effect of different pulsed electric field intensities on the reaction rate and to further explore the possible mechanism of condensation reactions affected by a pulsed electric field. In addition, a kinetic model of the reaction was proposed and the activation energies were calculated and compared.

2. Materials and methods

2.1. Materials

Ethanol, water, (+)-catechin and acetaldehyde were used to prepare a model wine solution. The water was deionized and purified by treatment with a reverse osmosis water purification apparatus (Guangzhou Jason Membrane Technology Co. Ltd, Guangzhou, China). Ethanol (purity > 99.9%) was obtained from Tianjin Fuyu Chemical Reagent Co., Ltd (Tianjin, China). Acetonitrile and acetic acid were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd (Tianjin, China). (+)-Catechin and acetaldehyde were purchased from Shanghai Aladdin Chemical Reagent Co., Ltd (Shanghai, China). All chemicals except ethanol were of HPLC grade purity.

2.2. Solvents and reagents

The model wine solution was prepared as described in literature, with some slight modifications (Saucier et al., 1997). A model wine solution was prepared with 12% (v/v) ethanol in water. The pH was adjusted to 3.0 with acetic acid. The concentration of (+)-catechin was 0.6 g/L. The molar ratio of (+)-catechin to acetaldehyde was 1:60. The reaction was performed in a continuous pulsed electric field system (SCUT PEF Team, China). The concentration of (+)-catechin was monitored by a high-performance liquid chromatography (HPLC) system (Waters Co., Milford, MA, USA) coupled with a photodiode array detector. Each reaction was replicated three times, and the average values and standard deviations were calculated.

2.3. PEF equipment

The PEF equipment used was a bench scale system, which was designed by the PEF Team (South China University of Technology, China). A microgear pump (Model 323E/D, Watson-Marlow Pumps Group, USA) was used to maintain a continuous flow of the samples. A rotameter (Model FM-01, Ningbo Jiutian Meter Co., Ningbo, China) was used to measure and control the flow rate. A digital oscilloscope (TDS220, Tektronix Inc., Beaverton, OR, USA) was applied to monitor various electrical signals including voltage, current, frequency, and waveform. The treatment chamber contained two paralleled stainless-steel electrodes and a set of PTFE shells. The distance between the two electrodes was 0.2 cm and the flow volume in the treatment chamber was about 0.02 mL. Monopolar square waves with a pulse frequency of 1.08 kHz, a pulse width of 20 μs and a flow rate 50 mL/min were used as the PEF treatment conditions in the current study. The electric field intensity was set at 0, 30, 40 and 50 kV/cm. When the PEF generator was operated, the untreated model wine solution was pumped through the treatment chamber and subjected to a high-intensity electric pulse treatment (Lin et al., 2011). The solution was then cooled by a coiled tube submerging in a water bath. The temperature of the water bath was set at 20, 25, 30, and 35 °C, the designated reaction temperatures. The model wine solution was continuously recycled in the system. The PEF treatment time (t), number of pulses (n) and the total PEF treatment time ($T = 7.779$ ms) in the reaction time of 1 h can be obtained from the following equations (Han, Zeng, Yu, Zhang, & Chen, 2009; Zhao et al., 2008):

$$n = Vf/u \tag{1}$$

$$t = n\tau \tag{2}$$

$$T = t \times N = {}^{3600Vf\tau}\Big/_{A}, \tag{3}$$

where $V$is the volume of the chamber (mL), f is the pulse frequency (pulse number per second, pps), u is the model wine solution flow rate (mL/min), τ is the pulse width (μs), and A (=200 mL) is the volume of the model wine solution.

Under the same experimental procedure and conditions, the model wine solution treated with 0 kV/cm was used as control for comparison. Samples were analyzed with HPLC immediately.

2.4. HPLC analysis

High-performance liquid chromatography (HPLC) analysis was performed with a chromatogram system (Waters Co., Milford, MA, USA) containing a chromatogram controller (Waters 600), a pump (Waters 600E), an injector (Rheodyne 7725i Manual Injector), a detector (Waters 2998 Photodiode Array Detector), and a column (5 μm Boston Green ODS 250 × 4.6 mm column) (Zhang et al., 2012).

In order to obtain the content of (+)-catechin, an elution condition was described as follows, the injection volume was set at 20 μL, and a