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Modeling and comparison of extraction kinetics of 8 catechins, gallic acid and caffeine from representative white teas

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ABSTRACT

In this work extraction kinetics of typical ingredients in representative white teas was investigated. Aqueous extraction of 4 epicatechins (EGC, EC, EGCG, ECG), 4 *trans*-catechins (GC, C, GCG, CG), gallic acid (GA) and caffeine at 65 °C, 75 °C, 85 °C, 95 °C respectively from Fuding Silver Needle (FSN), Fuding White Peony (FWP), Zhenghe Silver Needle (ZSN) and Zhenghe White Peony (ZWP) was examined. The total catechins, gallic acid, caffeine, EGCG, epicatechins, *trans*-catechins were compared in terms of rate, peak value, peak time and the extraction kinetics at different temperatures. It is exhibited that the contents of 8 catechins in ZWP, ZSN and FSN follow the order of EGCG > ECG > GC > EGC > GCG > CG > EC > C, and that in FWP is EGCG > ECG > EGC > GC > EC > GCG > CG > C. Structural transformation from epicatechins to *trans*-catechins and dissociation of gallic acid were observed during extraction by data analysis. Extraction kinetics over 240 min period were successfully modeled using Peleg's model with low MSR (0–2.232) and high R2 adj (0.903–0.999). Optimal extraction conditions (FSN(43.3 min, 95 °C); FWP(43.3 min, 95 °C); ZSN(53.8 min, 95 °C); ZWP(41.5 min, 95 °C)) were suggested by Peleg's model. As a result, this study will facilitate quality control of white tea during processing.

1. Introduction

Tea has received persistent attention for its health benefits. White, green, oolong and black teas are the most commonly types, categorized by variations in picking, processing and associated degree of oxidation of polyphenols in fresh tea leaves (Damiani, Bacchetti, Padella, Tiano, & Carloni, 2014; Horanni & Engelhardt, 2013; Rusak, Komes, Likić, Horžić, & Kovač, 2008; Sharangi, 2009). However, even though white tea actually contains higher antioxidant activity, there is comparatively less research on this valuable type of tea native to the south of China and mainly in Fujian Province (Deng, Wang, & Ding, 2013; Martins et al., 2014; Sharangi, 2009). White tea is a lightly fermented tea with only two simple processing called withering and drying (Ning et al., 2016). Because of minimal processing (Sadowska-Rociek, Surma, & Cieslik, 2014), white tea contains more nutrients than its black or green cousins, rendering it the ultimate health tea (Wang, Zhang, Chen, Shi, & Xiao, 2014).

White tea can be separated into four varieties: Silver Needle (or Baihao Yinzhen), White Peony (or Bai Mudan), Tribute Eyebrow (or Gong Mei) and Longevity Eyebrow (Shou Mei). Among them, Silver Needle and White Peony are the most popular ones. Silver Needle is made from single buds plucked from “big white tea” species, and White Peony tea is prepared by one bud with two/three leaves of “big white tea” or narcissus white species (Cai, 2007; Damiani et al., 2014; Hilal & Engelhardt, 2007). There are two representatively growing areas for white tea, Fuding County and Zhenghe County both in Fujian province of China. Due to the differences in geographical environment, Fuding white tea buds are fatter while Zhenghe white tea is slender.

The primary bioactive components in white tea are 8 kinds of catechins, including 4 kinds of epicatechins namely (−)-epigallocatechin (EGC), (−)-epicatechin (EC), (−)-epigallocatechin gallate (EGCG), (−)-epicatechin gallate (ECG) and 4 kinds of *trans*-catechins namely (+)-gallocatechin (GC), (+)-catechin (C), (−)-gallocatechin gallate (GCG), and (−)-Catechin gallate (CG), along with gallic acid (GA) and caffeine (Wang, Chen, & Zheng, 2011). Researchers have found that the levels of some catechins and gallic acid in white are higher than in those green teas (Unachukwu, Ahmed, Kavalier, Lyles, & Kennelly, 2010). There is a large amount of data about the bioactive compounds constituents

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of green and black tea, however, little is known about white tea in this respect. Accordingly, in this study, four typical white teas in China were analyzed from the point of extraction kinetics of 10 bioactive compounds. The overall content of 8 catechins, GA and caffeine were determined by UHPLC.

The main objectives of this study were (1) to evaluate the impact of different extraction temperature for these typical white teas; (2) to compare extraction kinetics of total catechins, caffeine and GA between four tea types; (3) to compare contents and extraction kinetics of EGCG and total epicatechins between four tea types; (4) to compare contents and extraction kinetics of *trans*-catechins between four tea types; (5) to construct an extraction model to describe the extraction process and optimize the extraction time.

2. Material and methods

2.1. Material

Fuding Silver Needle and Fuding White Peony both were purchased from Pinpinxiang Tea Co. Ltd. (Fujian, China). Zhenghe Silver Needle and Zhenghe White Peony both were obtained from Ruiming Tea Co. Ltd. (Fujian, China). Reference substance (caffeine, GA and 8 catechins including GC, EGC, C, EC, EGCG, GCG, ECG, CG) were obtained from Sigma. Methanol and acetonitrile (HPLC grade) for HPLC analysis were purchased from Siyou Chemicals Co. Ltd. (Tianjin, China). Ultrapure water was used throughout and obtained from a Milli-Q system by Millipore (Milford, MA, USA).

2.2. Extraction experiments

The experiments were performed at different temperatures (65 °C,75 °C,85 °C,95 °C) in two repetitions. 5 g (measured precisely) of 4 kinds of tea were respectively extracted with 500 mL distilled water (65 °C,75 °C,85 °C,95 °C) in sealed glass beaker placed in the digital magnetic stirring bath (65 °C,75 °C,85 °C,95 °C) agitated at 200 rpm 2 mL 1.2% formic acid solution was added into distilled water in advance to protect catechins. An aliquot of extraction solution (0.5–1 mL) was sampled at 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240 min and immediately cooled in a freezer at −20 °C (Mo, Hu, & Mo, 2008). The extraction mixture was then filtered (0.22 μm) and diluted (1:4, v/v) with ultrapure water, followed by filtration (0.22 μm) and UHPLC analysis. The content of 10 materials was determined as an average of duplicates.

2.3. UHPLC analysis methods

UHPLC was performed using an Agilent system (1290 series, Agilent Technologies, USA) with a Zorbax Eclipse XDB-C18 column (2.1 × 150 mm, 3.5 μm pore size; Agilent Technologies) and a UV detector (Variable Wavelength Detector, Agilent Technologies). UHPLC analysis of 8 kinds of catechins, GA and caffeine was conducted with the Absorbance Detector at 278 nm. The mobile phase was constituted with water/formic acid, 99:1, v/v (solvent A) and acetonitrile/formic acid, 99:1, v/v (solvent B), with a flow rate of 0.4 mL/min. Basically, the elution was performed with a gradient beginning at 98% A to reach 95% at 5 min, 87.5% at 10 min, 85% at 15 min, 82.5% at 20 min, 15% at 25 min and post-time 5 min before next injection. The volume of sample injected was 2.5 μL. The mobile phase was pumped at 30 °C. Quantification of the compounds at 278 nm was performed using external standards. A series of each standard (0.01–0.1 mg/mL) were prepared for quantification (Cheigh, Yoo, Ko, Chang, & Chung, 2015; Chen, Zhao, & Yu, 2015; Dong, Gu, Xu, & Wang, 2014; Perva-Uzunalić et al., 2006; Tsuchiya et al., 1997).

2.4. Mathematical model

Peleg's model is a classic hyperbolic model to describe moisture sorption curves (Peleg, 1988). It is confirmed by previous study that the shape of the extraction curves was similar to that of sorption curves. The Peleg's equation has been widely used to describe the extraction curves of biologically active substances (Jokic et al., 2010; Karacabey, Bayindirli, Artik, & Mazza, 2013). Peleg's model was fitted to the experimental data from the extraction of total catechins, GA and caffeine, which is expressed as follows:

$$C(t) = \frac{C_{eq}t}{K_1 + t} \tag{1}$$

where C(t)is the content of targeted compound at time t (min), C_{eq} is the theoretical equilibrium content as $t \to \infty$, and K_1 is the parameter of the hyperbolic model (Dong et al., 2014; Kiew, Mashitah, & Ahmad, 2014).

2.5. Data analysis and model evaluation

The analysis of nonlinear regression was carried out using Origin Version 9.0 software. The adjusted correlation coefficient (R2 adj) and the mean square of residual (MSR) were calculated to evaluate the goodness of fit the non-linear regression model to the experimental data. The formulas are expressed as follows:

$$\mathrm{MSR} = \mathrm{RSS}/\mathrm{dof} = \sum_{i=1}^{n}\left(y_{calc} - y_{\exp}\right)^2 \Big/ n \tag{2}$$

$$\mathrm{R}^2_{\mathrm{adj}} = 1 - \frac{(n-1)*\sum_{i=1}^{n}\left(y_{\mathrm{calc}} - y_{\exp}\right)^2}{(n-1-m)*\sum_{i=1}^{n}\left(\overline{y}_{\exp} - y_{\exp}\right)^2} \tag{3}$$

where RSS is residual sum of squares and dof is degree of freedom. y_{calc} and $y_{\exp}$ are the predicted and experimental yields of desired compounds respectively. n is the number of experimental data. Here its value equals to dof. m is the number of independent variable.

3. Results and discussion

3.1. Comparison of total catechins, caffeine and GA from four types of white tea

To explore the profile of extraction kinetics for different types of white tea, the total amount of catechins (TAC, the sum of concentrations of all determined catechins) was firstly examined. Taking Fuding Silver Needle as an example (Fig. 1), the same maximum TAC of around 95.6 mg/g was observed along with the variation of temperature. However, it takes from 240 min down to 100 min to reach it as temperature increases. Presumably, the elevated temperature cuts down the viscosity of extraction solution and then increases the diffusion rate of 8 kinds of the catechins and GA, Caffeine (Cacace & Mazza, 2003; Cissé et al., 2012). As a result, diffusivity is closely related to the change of temperature. Elevated temperature would not only enhance diffusivity but also rupture cell walls, leading to improved extraction efficiency (Haldar, Majumdar, & Mishra, 2015; Pinelo, Arnous, & Meyer, 2006). As shown in Fig. 2A, the maximum TAC in Fuding Silver Needle is higher than in Fuding White Peony. And the catechins in Fuding Silver Needle diffuse more easily into water than Fuding White Peony at 65 °C–95 °C.

Fuding white tea is produced from very young *C. sinensis* leaves