Food Chemistry 196 (2016) 347–354

Contents lists available at ScienceDirect

Food Chemistry

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

Differential behaviors of tea catechins under thermal processing: Formation of non-enzymatic oligomers

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ARTICLE INFO

Article history:
Received 14 May 2015
Received in revised form 11 September 2015
Accepted 14 September 2015
Available online 16 September 2015

Keywords:
Catechins
Steric configuration
Thermostability
Dimer
Low O_2

ABSTRACT

Tea catechins as a member of flavan-3-ols subclass with the same skeleton may behave differentially. This study investigated the chemical conversions of 8 catechins under heat treatment with the involvement of epimerization, hydrolysis and oxidation/condensation reactions. Three reactions were enhanced as temperature increased from 30 °C to 90 °C. The epimerization of non-gallated catechins was favored by epi-configuration but hindered by pyrogallol moiety, and the hydrolysis reaction of gallated catechins was facilitated by pyrogallol moiety. Epicatechin and epigallocatechin had the lowest thermostabilities due to epimerization and oxidation/condensation reactions respectively. Sufficient O_2 was not a precondition for the occurrence of chemical conversions of catechins under heat treatment. Non-enzymatic oligomerization occurred to epi type catechins and catechin under heat treatment, and dehydrodicatechins A were mainly responsible for the browning of epicatechin and catechin solutions. The evidence of generation of catechin oligomers provides a novel way to explain sensory change of tea and relevant products during thermal processing.

1. Introduction

Tea catechins are a group of natural polyphenols in tea leaf that have been associated with many health benefits and functionalities, such as antioxidative, anti-tumor and anti-inflammatory effects (Braicu, Ladomery, Chedea, Irimie, & Berindan-Neagoe, 2013; Gupta, Saha, & Giri, 2002; Higdon & Frei, 2003). It mainly comprises (−)-epigallocatechin gallate (EGCg), (−)-epigallocatechin (EGC), (−)-epicatechin gallate (ECg), (−)-epicatechin (EC), and their geometric isomers (−)-gallocatechin gallate (GCg), (−)-gallocatechin (GC), (−)-catechin gallate (Cg), and (−)-catechin (C) (Fig. 1), among which EGCg is regarded as the most important catechin due to high content in tea leaf and excellent bioactivity (Johnson & Loo, 2000). As a member of flavan-3-ols subclass, catechins contain two aromatic rings (the A- and B-rings), as well as a dihydropyran heterocycle (the C-ring) with a hydroxyl group or a gallate moiety at C-3 position (Fig. 1). In addition to epi and non-epi catechins (*cis* and *trans* isomers), catechins are classified into pyrogallol type (EGC, GC, EGCg, GCg) and non-pyrogallol catechins (EC, C, ECg, Cg) according to the presence of an additional —OH at B-5′ position, and are also well-known as gallated catechins (EGCg, GCg, ECg, Cg) and non-gallated catechins (EC, C, EGC, GC) according to the substitution of gallate moiety at C-3 position (Braicu et al., 2013).

Many investigations have been carried out on the structure–activity relationship of catechins (Braicu et al., 2013; Guo et al., 1999; Higdon & Frei, 2003; Mukai, Nagai, & Ohara, 2005; Nanjo et al., 1996; Xu, Yeung, Chang, Huang, & Chen, 2004). The scavenging abilities of EGCg and GCg were reported being higher than those of non-gallated catechins EGC, GC, EC and C due to the presence of a gallate moiety at C-3 position (Guo et al., 1999). Pyrogallol group with three —OH showed higher activity than catechol group with two —OH on quenching singlet oxygen, in addition to the remarkable contribution of gallate moiety (Mukai, Nagai, et al., 2005). Geometric isomerism was thought to exert no significant influence on the antioxidant activities of gallated catechins (Xu et al., 2004). Differential interactions of individual catechins with other substances, e.g. milk protein, enzyme, lipid bilayers and caffeine, have also been reported (Colon & Nerin, 2014; Kajiya, Kumazawa, & Nakayama, 2001; Miao et al., 2014; Wang, Song, Guo, & Tian, 2003; Ye, Fan, Xu, & Liang, 2013). Hence, molecular structure and steric configuration of catechins are closely related with their bioactivities and intermolecular interactions and possibly resulted in differential behaviors of individual catechins.

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http://dx.doi.org/10.1016/j.foodchem.2015.09.056
0308-8146/

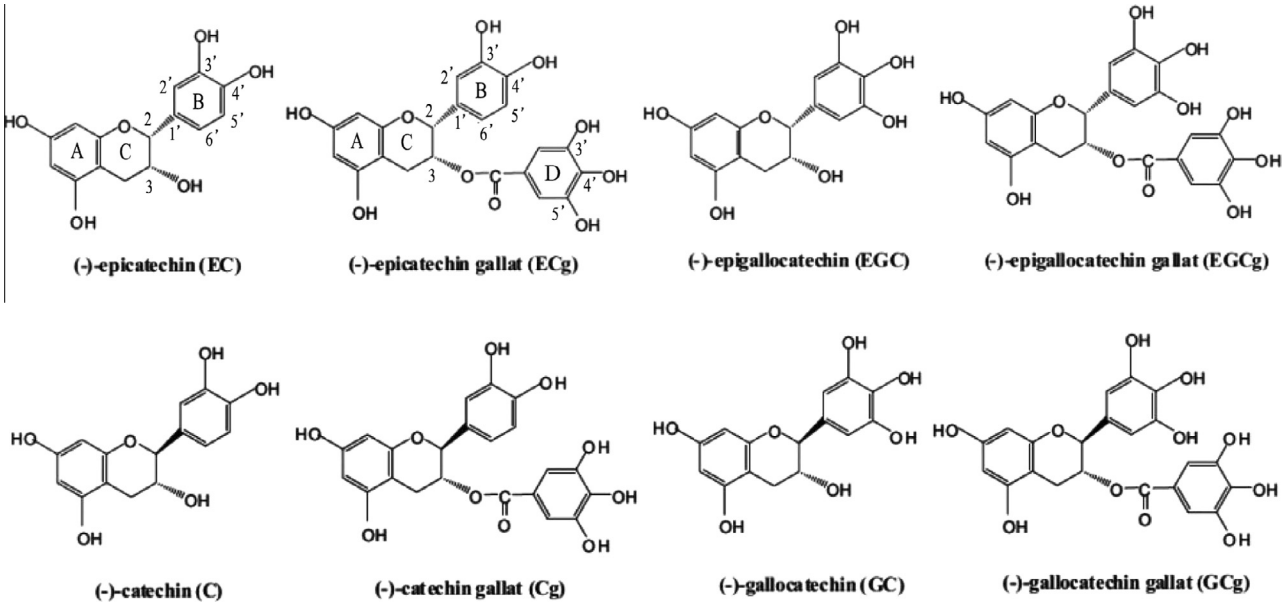

Fig. 1. Molecular structures of major tea catechins.

Thermal processing is a conventional procedure in productions of dry tea leaves, tea drinks, tea extracts and foods with tea or tea powder as ingredients (Ananingsih, Sharma, & Zhou, 2013; Bazinet, Araya-Farias, Doyen, Trudel, & Têtu, 2010; Sharma & Zhou, 2011; Wang & Zhou, 2004). Chemical changes of catechins under heat treatment are often associated with negative quality changes of dry tea, tea drink and derivative food products, such as off-color, off-flavor and nutrition loss (Lee & Chambers, 2009; Lin et al., 2010; Wang, Kim, & Lee, 2000). Epimerization is regarded as one of the most important reactions occurring to catechins under thermal processing (Ananingsih et al., 2013), while other reactions, e. g. hydrolysis, oxidation and polymerization, may also be crucial considering the generation of new products other than catechins (Li, Taylor, Ferruzzi, & Mauer, 2013). However, abundant studies mainly focused on the apparent degradation and kinetic parameters of catechins in various food systems under heat treatment (Chen, Zhu, Tsang, & Huang, 2001; Li, Taylor, Ferruzzi, & Mauer, 2012; Li, Taylor, & Mauer, 2011; Sharma & Zhou, 2011; Wang & Zhou, 2004), and the participations of different reactions and relevant thermal products of catechins have not been well documented. These are possibly due to the difficulties in isolation and determination of thermal products of catechins at trace levels in multi-component systems as well as the involvement of other reactions such as Maillard reactions. Hence, understanding heat-induced differential behaviors of individual catechins is important to predict chemical conversions of catechins in various food systems, and is also helpful to interpret sensory changes of tea, tea drinks and derivative foods due to thermal processing. In the present study, the thermal stabilities of individual catechins in aqueous solutions were studied with the involvements of epimerization, hydrolysis and oxidation/condensation reactions. The effects of temperature, time and O_2 level on the chemical conversions of catechins were investigated, and the impacts of substituent group and steric configuration (geometric configuration) of catechin molecules were discussed. The thermal products of individual catechins were analyzed by ultra performance liquid chromatography–diode array detection–tandem mass spectrometry (UPLC–DAD–MS), and non-enzymatic oligomers of epicatechins (EC, EGC, EGCg, ECg) as well as C were identified.

2. Materials and methods

2.1. Materials

Individual catechins (−)-epigallocatechin gallate (EGCg, ⩾98%), (−)-epigallocatechin (EGC, ⩾98%), (−)-epicatechin gallate (ECg, ⩾98%), (−)-epicatechin (EC, ⩾98%), (−)-gallocatechin gallate (GCg, ⩾98%), (−)-gallocatechin (GC, ⩾98%), (−)-catechin gallate (Cg, ⩾98%), (−)-catechin (C, ⩾98%), and gallic acid (GA, ⩾98%) were purchased from Aladdin Industrial Corporation (LA, USA). The other chemical reagents used were of HPLC grade (Jinmei Biotech Corporation, Tianjin, China). The Milli-Q water was prepared by an EASYPure II UV Ultra Pure Water System (Barnstead International, Dubuque, IA, USA).

2.2. Study on the chemical conversions of catechins at different temperatures

The chemical conversions of catechins at ambient temperature, warm condition and high temperature were investigated. Two milliliter individual catechin solutions (500 μM, water) were placed in MS-100 Thermo-Shaker (Allsheng Instruments CO., Ltd., Hangzhou, China) preheated at 30, 60 and 90 °C for 8 h. The whole equipment was covered with two layers of foil in avoidance of light. The catechins samples were cooled to ambient temperature immediately under running water, and then stored at −20 °C to terminate reactions based on the method reported by Fufsler, Castelfranco, and Wong (1984). All samples were turned back to room temperature, made up to 2 mL with water and then centrifuged at 12,000 rpm for 10 min prior to HPLC analysis.

2.3. Study on the chemical conversions of catechins at different duration of heating

Two milliliter individual catechin solutions (500 μM, water) were placed in MS-100 Thermo-Shaker preheated at 90 °C for 0.5, 1, 2, 4, 8 h in avoidance of light. The catechins samples were treated according to the method in Section 2.2 before HPLC analysis.