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Green tea catechins during food processing and storage: A review on stability and detection

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ABSTRACT

Green tea catechins can undergo degradation, oxidation, epimerization and polymerization during food processing. Many factors could contribute to the chemical changes of green tea catechins, such as temperature, pH of the system, oxygen availability, the presence of metal ions as well as the ingredients added. Several detection methods have been developed for tea catechin analysis, which are largely based on liquid chromatography (LC) and capillary electrophoresis (CE) methods for getting a good separation, identification and quantification of the catechins. Stability of green tea catechins is also influenced by storage conditions such as temperature and relative humidity. The stability of each catechin varies in different food systems and products. Pseudo first-order kinetic model has been developed and validated for the epimerization and degradation of tea catechins in several food systems, whereas the rate constant of reaction kinetics followed Arrhenius equation.

1. Introduction

Stability of green tea catechins, the phytochemical product produced from tea leaf (*Camellia sinensis*), has been under study for several decades to determine their chemical changes during food processing. Tea catechins contained in green tea are higher than black tea and oolong tea because there is no fermentation process occurring during the manufacture of green tea (Toschi et al., 2000). During fermentation of black tea, polyphenol oxidase in the tea leaves catalyzes the oxidation of the majority of catechins into theaflavin, hence reduces its catechins content (Friedman, Levin, Choi, Lee, & Kozukue, 2009).

Scientific evidences to support the health benefits of green tea consumption begin to appear. Those benefits include improving blood flow, preventing cardiovascular disease, eliminating various toxins and improving resistance to various diseases (Afaq, Adhami, Ahmad, & Mukhtar, 2004). These might be due to green tea containing catechins which have anti-oxidative, anti-carcinogenic, anti-microbial, anti-viral, anti-inflammatory and anti-diabetic properties (Khan & Mukhtar, 2007; Lakenbrink, Lapczynski, Maiwald, & Engelhardt, 2000; Zaveri, 2006). In addition, green tea catechins have other pharmaceutical activities such as antihypertensive and hypolipidemic (Chan et al., 1999; Henry & Stephens-Larson, 1984). Owing to the health benefits, green tea consumption is increasing, which is reflected by its annual growth rate of ca. 4.5% (FAO, 2008).

The major nutraceutical compounds in green teas are tea catechins, which are flavonols. Flavanols are a class of flavonoids which are polyphenols. Green tea is rich in flavanols (300–400 mg/g) which are of interest to human health (Dubick & Omaye, 2007). Tea catechins have the most effective antioxidant activity compared to other tea polyphenols. The major green tea catechins are (−)-epigallocatechin gallate (EGCG), (−)-epicatechin gallate (ECG), (−)-epigallocatechin (EGC) and (−)-epicatechin (EC). These epicatechins can change to their epimers that are non epicatechins, i.e. (−)-gallocatechin gallate (GCG), (−)-catechin gallate (CG), (−)-gallocatechin (GC) and (±)-catechin (C) (Fig. 1). EGCG is the most abundant and active catechin and it is usually used as a quality indicator (Lakenbrink et al., 2000; Wang & Helliwell, 2000; Wang, Zhou, & Jiang, 2008a). In addition, green tea contains other polyphenols such as gallic acid, quercetin, kaempferol, myricetin and their glycosides, but at lower concentration than EGCG (Dubick & Omaye, 2007; Sakakibara, Honda, Nakagawa, Ashida, & Kanazawa, 2003).

Tea catechins are an efficient free radical scavenger due to their one electron reduction potential. Antioxidant activity as hydrogen or electron donors is determined by this reduction potential of free radicals. A lower reduction potential has a tendency to lose electron or hydrogen (Higdon & Frei, 2003). The rate of reaction with free radicals and the stability of the resulting antioxidant radicals contribute to the reactivity of antioxidant. Guo et al. (1999) reported the scavenging ability of tea catechins on superoxide anions ($O_2{\bullet}^-$), singlet oxygen ($^1O_2$), the free radicals generated from 2,2P-azobis(2-amidinopropane) hydrochloride (AAPH) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) radicals. They suggested that the scavenging ability of EGCG and GCG was higher than that of EGC, GC, EC and C due to their gallate group at 3

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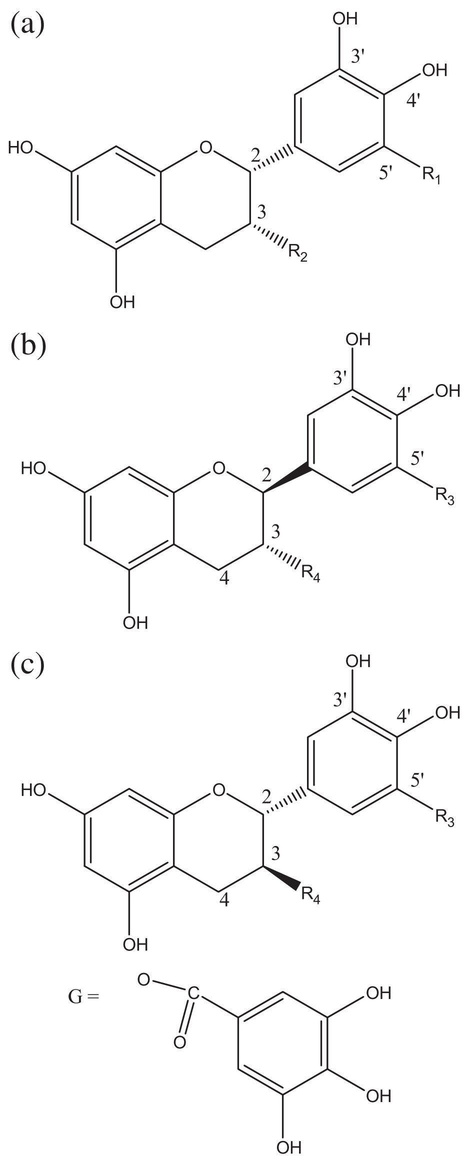

Component	Abbrev.	R_1	R_2	R_3	R_4
(-)-Epigallocatechin gallate	(-)-EGCG	OH	G	-	-
(-)-Epicatechin gallate	(-)-ECG	H	G	-	-
(-)-Epigallocatechin	(-)-EGC	OH	OH	-	-
(-)-Epicatechin	(-)-EC	H	OH	-	-
(-)-Gallocatechin gallate	(-)-GCG	-	-	OH	G
(-)-Gallocatechin	(-)-GC	-	-	OH	OH
(-)-Catechin gallate	(-)-CG	-	-	H	G
(±)-Catechin	(±)-C	-	-	H	OH

Fig. 1. General chemical structures of green tea catechins: (a) epi catechins; (b) non-epi catechins and (c) (+)-catechin.

position of C ring. While abilities to scavenge free radicals for EGC and GC were stronger than EC and C because of a hydroxyl group at the 5′ position of B ring. GCG was more stable than EGCG because it has smaller steric hindrances. In addition, the stability of GC and C was better than EGC and EC. A summary of the scavenging activity of tea catechins on different free radicals/ROS is shown in Table 1.

It is important to understand the stability of green tea catechins in foods during processing and storage in order to gain the optimum health benefits from them. The level of tea catechins could be easily reduced as a result of epimerization and degradation during processing (Wang et al., 2008a). The catechin stability in different food systems could be influenced by pH, temperature, oxygen availability, the presence of metal ions, and also concentration of other active ingredients (Guo et al., 1999; Kumamoto, Sonda, Nagayama, & Tabata, 2001; Komatsu et al., 1993; Sang, Lee, Hou, Ho, & Yang, 2005).

Table 1
Scavenging activity of tea catechins on free radicals/ROS.

Free radicals/ ROS	The order of scavenging activity	References
Singlet oxygen	EC, C>EGC, GC>EGCG, GCG.	Guo et al., 1999
	EGCG>ECG>EGC>EC>C	Mukai, Nagai, & Ohara, 2005
Hydroxyl radical	ECG>EGCG>EC>GC>EGC>C	Wiseman, Balentine, & Frei, 1997
	ECG>EC>EGCG>EGC	Guo, Zha, Li, Shen, & Xin, 1996
Lipid peroxyl radical	ECG = EGCG = EC = C>EGC	Salah et al., 1995
ABTS•$^+$ radical cation	ECG>EGCG>EGC>EC = C	Salah et al., 1995
	ECG>EGCG>EGC>EC	Higdon & Frei, 2003
DPPH• radical	EGCG = ECG>EGC>EC	Nanjo et al., 1996
AAPH	EGCG>EGC>EC	Guo et al., 1999

In this paper, the results of and mechanisms behind the chemical changes of green tea catechins in various food systems are reviewed. A summary of the detection methods of tea catechins will also be presented and discussed. The stability of catechins during processing and storage in a number of real food products will be discussed, together with kinetic modeling results.

2. Stability of catechins: epimerization and degradation

Epimerization is the conversion of tea catechins to their corresponding isomers. The identified epicatechins in green tea i.e. EGCG, EGC, ECG, and EC are in *cis* structure. They can convert to their epimers that are non-epicatechins, i.e. GCG, GC, CG, and C, respectively (Wang et al., 2008a; Chen & Chan, 1996). This epimerization between pair catechins is reversible. The chemical structures of epicatechins and non-epicatechins only differ between 2*R*, 3*R* (2, 3-*cis*, epi-form) and 2*S*, 3*R* (2, 3-*trans*, nonepiform). Fig. 2 illustrates the reversible epimerization between EGCG and GCG.

Epimerization can occur at high temperature (Wang & Helliwell, 2000). It has been recognized that catechins undergo epimerization at the C-2-position in hot aqueous solution. This epimerization can change the epistructured catechin to non-epi-structured catechin and vice versa. Wang et al. (2008a) reported that the concentration of catechins decreased while their isomers increased as the temperature increased. Degradation of catechins was evident as there was a declining trend in total catechins with increasing temperature. Many researchers have found that tea catechins could convert to their corresponding epimers in traditionally brewed tea infusion and canned tea drinks during brewing, production, and storage (Chen, Zhu, Tsang, & Huang, 2001; Zhu, Zhang, Tsang, Huang, & Chen, 1997). Tea catechins undergo many chemical changes such as oxidation and epimerization during the course of the brewing processes. As a result, epimerization of the catechins is thought to be one of the most important reactions in the manufacture of green tea (Wang & Helliwell, 2000).

2.1. Effect of pH and temperature

The stability of tea catechins is pH and temperature dependent. Tea catechins in aqueous solutions are very stable when pH is below 4, whereas they are unstable in solutions with pH>6. In addition, storage temperature affects the stability of tea catechins significantly even at ambient conditions (Chen et al., 2001; Komatsu et al., 1993; Su, Leung, Huang, & Chen, 2003; Wang & Helliwell, 2000; Wang, Zhou, & Wen, 2006). Stability studies on catechins in green tea infusion have shown that epimerization could be observed at 40 °C over prolonged storage. Therefore, not only temperature, but also heating time influenced the epimerization of catechins in green tea infusions (Wang & Helliwell,