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Polyphenolic Chemistry of Tea and Coffee: A Century of Progress

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Tea and coffee, the most popular beverages in the world, have been consumed for thousands of years for their alluring flavors and health benefits. Polyphenols, particularly flavonoids and phenolic acids, are of great abundance in tea and coffee and contribute a lot to their flavor and health properties. This paper reviews the polyphenol chemistry of tea and coffee, specifically their stability, and scavenging ability of reactive oxygen species (ROS) and reactive carbonyl species (RCS). During the manufacturing and brewing process, green tea and black tea polyphenols undergo epimerization and oxidation, respectively. Meanwhile, the lactonization and the polymerization of chlorogenic acid are the major causes for the degradation of polyphenols in coffee. Tea catechins, besides having antioxidant properties, have the novel characteristic of trapping reactive carbonyl species. The A ring of the catechins is the binding site for RCS trapping, whereas the B ring is the preferred site for antioxidation.

KEYWORDS: Polyphenol chemistry; stability; scavenging ability; tea; coffee

INTRODUCTION

Tea and coffee, the most popular beverages in the world, have been consumed for thousands of years. Tea is produced by brewing the dried leaves and buds of the plant *Camellia sinensis*, which was first cultivated in China and then in Japan. With the opening of ocean routes to the East by European traders during the 15th to 17th centuries, commercial cultivation gradually expanded to Indonesia and then to the Indian subcontinent, including what is now Sri Lanka (*1*). In 1657, tea first reached Britain. Tea is now second only to water in worldwide consumption. Annual production of about 1.8 million tons of dried leaf provides world per capita consumption of 40 L of beverages (*2*). Tea is generally classified into three types based on different processing methods, specifically, green tea (nonfermented tea), oolong tea (partially fermented tea), and black tea (fully fermented tea) (*3*).

The coffee plant was first cultivated in Africa in an Ethiopian region (Kaffa) and was then introduced into Yemen, Arabia, and Egypt, where it developed and entered into daily life. Muslims are generally credited with first importing coffee into Europe via Italy, whereas the French are responsible for introducing coffee to the Americas through its colonization of many continents with coffee plantations. Coffee is the third most consumed beverage in the world, after water and tea (*4*). Coffee berries are dried once ripe, roasted at various temperatures to the desired flavor, and then ground and brewed. The two most common species of coffee berries are *Coffea robusta* and *Coffea arabica*.

Many studies have shown the relationship between the consumption of tea and coffee and their potential disease prevention properties, which might be due to their polyphenol contents (*5*,*6*). Polyphenols are secondary metabolites of plants that are used in their defense system against severe environments such as ultraviolet radiation and pathogens. These compounds are generally classified into flavonoids, phenolic acids, lignans, and stilbenes. Flavonoids, the most ubiquitous polyphenols, are benzo-γ-pyrone derivatives consisting of phenolic and pyrane rings and are classified into flavanols, flavones, flavonols, flavanones, isoflavones, and anthocyanidins. Phenolic acids are divided into two subclasses: derivatives of benzoic acid and derivatives of cinnamic acid.

The major polyphenols in tea and coffee are flavonoids, particularly flavanols (i.e., catechins), and phenolic acids. Green tea infusion (200 mL) contains up to 200 mg of catechins (*7*). Black tea contains very few flavanol monomers, which are easily oxidized into dimers (theaflavins) and polymers (thearubigins). Tea is also an important source of gallic acid, which is a hydroxybenzoic acid. Chinese pu-er teas contain the highest level of gallic acid ($\sim$15 g/kg of dry weight) compared to other types of tea (*8*). However, the hydroxycinnamic acids are greater in coffee relative to hydroxybenzoic acids in tea. Caffeic acid and its derivative chlorogenic acid (a caffeic acid ester of quinic acid) are the most abundant polyphenols in coffee. A single cup of coffee contains 70−350 mg of chlorogenic acid (*9*).

Here we review the history and progress of the polyphenolic chemistry of tea and coffee, as well as their stability and the trapping activity of reactive oxygen species (ROS) and reactive carbonyl species (RCS).

POLYPHENOLS IN TEA AND COFFEE

The major polyphenols in tea and coffee are flavonoids and phenolic acids. Due to differences in manufacturing, the types of polyphenols in the three major types of teas, green tea, black tea,

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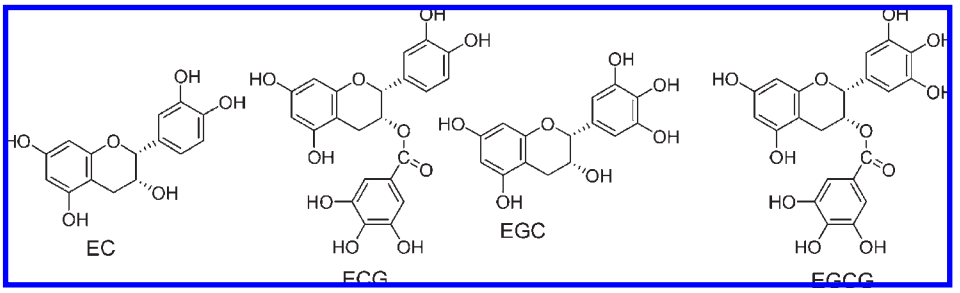

Figure 1. Polyphenols in green tea.

and oolong tea, are very different. Similarly, commercial processing greatly changes the polyphenols in coffee beans during roasting.

In the processing of green tea, the tea leaves are either first steamed, in the case of Japanese green tea "sen-cha" or pan-fried, in the case of Chinese green tea (*10*). These heat treatments inactivate enzymes in the tea leaves. The temperature of pan-frying can reach as high as 230 °C, which is much higher than the steaming temperature of 100 °C. Steaming, therefore, results in fewer chemical changes than pan-frying. Following heat treatment, tea leaves are subjected to subsequent rolling and drying processes.

More than 75% of world tea production is black tea. The steps involved in the processing of black tea include withering, leaf disruption, fermentation, drying, and grading. All steps are designed to achieve optimal oxidation of tea catechins and produce tea products with good flavor and color. Oolong tea is prepared by frying the leaves after rolling to terminate the oxidation process. It is only partially oxidized and retains a considerable amount of the original polyphenols (*11*).

Tea polyphenols, also known as catechins, account for 30−42% of water-soluble solids in brewed green tea. There are four major tea catechins: (−)-epicatechin (EC), (−)-epicatechin gallate (ECG), (−)-epigallocatechin (EGC), and (−)-epigallocatechin-3-gallate (EGCG) (*14*). The structures of these catechins are shown in **Figure 1**. Epicatechin and epigallocatechin were isolated and identified in green tea in early 1930 (*12*). In the late 1940s Bradfield and his co-workers identified and quantified catechin, epicatechin, gallocatechin, epicatechin gallate, and gallocatechin gallate in a Ceylon green tea (*13*). The most abundant compound, gallocatechin gallate, was later proved to be epigallocatechin gallate (*14*). Catechin/epicatechin oligomers, which are procyanidins B2 and B3, were also identified, but their concentrations were found to be much lower than that of monomers (*15*, *16*). Besides the flavonoids in tea, gallic acid and theogallin (1-galloylquinic acid) were observed in Japanese green tea through sensory-guidance identification (*17*). Later, 3-galloylquinic acid, 4-galloylquinic acid, 1,3,5-trigalloylquinic acid, 4-(digalloyl)quinic acid, 5-(digalloyl)quinic acid, and either 3-galloyl-5-(digalloyl)quinic acid or 3-(digalloyl)-5-galloylquinic acid were also identified in green tea (*18*).

Most of the important chemical changes that take place in black tea occur during the fermentation process. Polyphenol oxidase and peroxidase, which are responsible for the oxidation of flavanols, oxidize pyrogallol and catechol to their *o*-quinones. Further chemical reactions then lead to various oxidation products. During fermentation, the characteristic black tea polyphenols, theaflavins and thearubigins, are generated. Four major theaflavins have been identified from black tea, including theaflavin, theaflavin-3-gallate, theaflavin-3′-gallate, and theaflavin-3,3′-digallate (**Figure 2**). The proposed mechanism of theaflavin formation is shown in **Figure 3**. Thearubigin is known as a heterogeneous mixture of pigments (*19*).

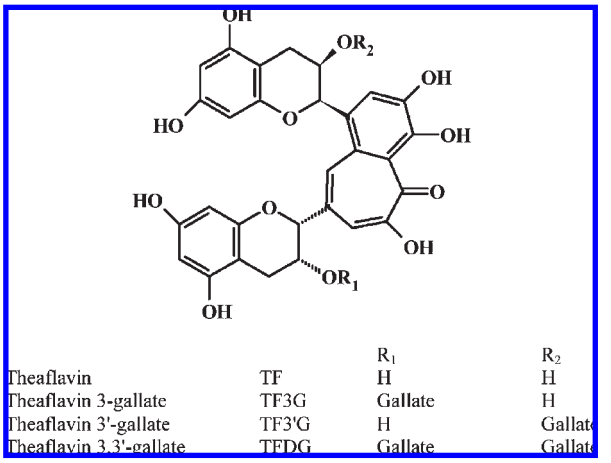

Figure 2. Structures of theaflavins.

Roberts et al. (*20*) reported fermented black tea contains polyphenolic pigments that are not found in unprocessed tea leaves. They designated the brown acidic pigments and the yellow neutral pigments as thearubigins and theaflavins, respectively. They suggested that theaflavin was the coupling oxidation product of EGC and EGCG, having benzotropolone structure. Later, Takino et al. (*21*) corrected the structure of theaflavin and revealed that theaflavin was the coupling oxidation product of EC and EGC. Theaflavin formation was confirmed by enzymatic oxidation with crude tea polyphenol oxidase and chemical oxidation with potassium ferricyanide. It was clear that theaflavins are produced by enzymatic co-oxidation of appropriate pairs of catechins, one having a *vic*-trihydroxy structure and the other having an *o*-dihydroxy group, followed by condensation.

Takino et al. (*21*) proposed a theaflavin formation mechanism based on the formation of purpurogallin from pyrogallol. The results suggested the possibility of the existence of similar pigments from the other pairs of flavanols. Bryce et al. (*22*) successfully isolated three other pigments from black tea and confirmed their parent flavanols using chemical oxidation methods. One of them, named TF1, was identical to the theaflavin reported by Roberts et al. (*20*). TF2 was identified as a mixture of TF2A and TF2B, which were produced by chemical oxidation from EGCG and EC (TF2A) and EGC and ECG (TF2B), respectively. TF3 was an identical compound that was isolated from ferricyanide oxidation of EGCG and ECG. They identified TF4 as an oxidation product from gallic acid and EC. Later, Collier et al. (*23*) confirmed the presence of four theaflavins in black tea and also the presence of epitheaflavic acid and epitheaflavic acid gallate, which are identical oxidative products from the coupling of EC and gallic acid and the coupling of ECG and gallic acid, respectively. Isotheaflavin, which was reported by Coxon et al. (*24*, *25*), was also identified to be present in black tea and was confirmed to be an oxidative coupling product of EGC and

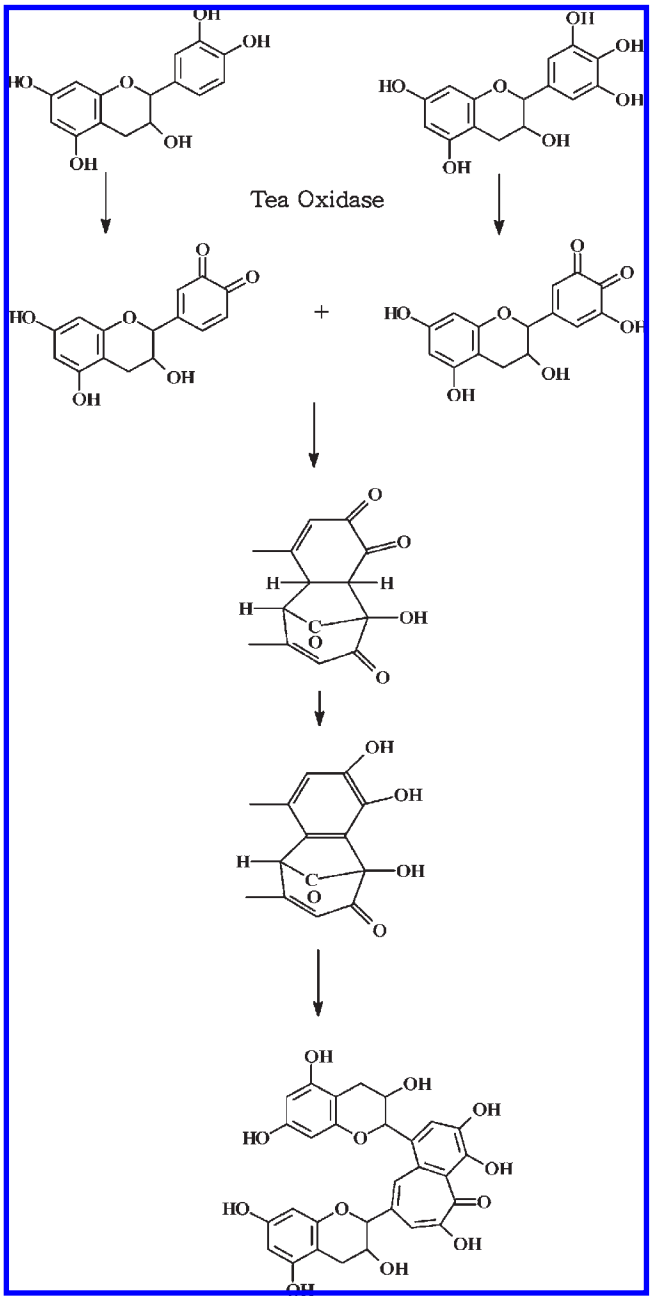

Figure 3. Proposed mechanism of theaflavin formation.

catechin. Compared to theaflavins, epitheaflavic acid, theaflavic acid, and epitheaflavic acid gallate occur at a much lower level. The relative proportions of the theaflavins in black tea were theaflavin (18%), theaflavin-3-gallate (18%), theaflavin-3′-gallate (20%), and theaflavin-3,3′-digallate (40%), and the proportions of theaflavic acids, along with isotheaflavin, were approximately 4% (*26*). Several other minor pigments have also been reported from black tea, such as theaflavate A, theaflavate B, isotheaflavin-3′-*O*-gallate, and neotheaflavin-3-*O*-gallate (*27*, *28*).

Recently, it has been reported that the galloyl ester group of theaflavin 3-gallate is as reactive as the B ring (*vic*-trihydroxy) of EGCG or EGC and the galloyl ester group of ECG, and can further react with EC to form the new theaflavin type tea catechin trimer, theadibenzotropolone A, which was characterized from the ethyl acetate fraction of black tea extract by LC-ESI-MS/MS (**Figure 4**) (*29*).

Thearubigins account for ∼10−20% of the dry weight of black tea. However, because of their hot water solubility, they account

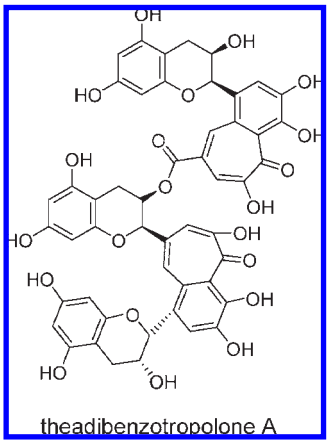

Figure 4. Structure of theadibenzotropolone A.

for ∼30−60% of the solids in black tea infusion (*20*). Even though thearubigins are suggested further oxidation products of theaflavins and catechins, their formation mechanism and chemical structures are not clear. Thearubigins have a wide range of molecular masses, ∼700−40000 Da, and are regarded as polymeric compounds. Brown et al. (*30*) reported that thearubigins are a polymeric mixture of proanthocyanidin containing flavonoids residue, and they proposed its formation mechanism through the creation of a C−C bond. Later, Berkowitz et al. (*31*) suggested that formation of epitheaflavic acid from EC and gallic acid plays an important role in the formation of thearubigins. They found that when EC was added into a tea fermentation system with epitheaflavic acid, both compounds disappeared rapidly, whereas thearubigin content increased. Interestingly, when it was reacted with only epitheaflavic acid in a tea fermentation system, no reaction occurred. The exact chemistry of thearubigins remains unclear.

The hydroxycinnamic acids are more abundant in coffee than are the hydroxybenzoic acids in tea. Caffeic acid and its derivative chlorogenic acid are the most abundant polyphenols in coffee. A single cup of coffee contains 70−350 mg of chlorogenic acid (*9*). Recently, the *N*-phenylpropenoyl-L-amino acids have been observed in roasted coffee (*32*). The *N*-phenylpropenoyl-L-amino acids are the key contributors to the astringent taste of cocoa beans and cocoa nibs, and they are also very good phytoalexins and plant antioxidants (*33*−*35*). By means of HPLC-MS/MS, (−)-*N*-[4′-hydroxy-(*E*)-cinnamoyl]-L-tyrosine, (−)-*N*-[3′,4′-dihydroxy-(*E*)-cinnamoyl]-L-tyrosine, *N*-[4′-hydroxy-3′-methoxy-(*E*)-cinnamoyl]-L-tyrosine, (+)-*N*-[3′,4′-dihydroxy-(*E*)-cinnamoyl]-L-aspartic acid, (+)-*N*-[4′-hydroxy-(*E*)-cinnamoyl]-L-aspartic acid, *N*-[3′,4′-dihydroxy-(*E*)-cinnamoyl]-L-tryptophan, *N*-[4′-hydroxy-(*E*)-cinnamoyl]-L-tryptophan, and *N*-[4′-hydroxy-3′-methoxy-(*E*)-cinnamoyl]-L-tryptophan, respectively, have been detected in coffee beverages. *N*-[3′,4′-Dihydroxy-(*E*)-cinnamoyl)-L-tryptophan was found to be the quantitatively predominating *N*-phenylpropenoyl-L-amino acid, accounting for up to 84% of the total amino acid amides in the regular and decaffeinated coffee samples, whereas the other *N*-phenylpropenoyl-L-amino acids were present in significantly smaller amounts ranging from 0.01 to 0.55 mg/kg. Moreover, *N*-phenylpropenoyl-L-tryptophan and L-aspartic acid were shown to be present in higher concentration in regular coffee compared to decaffeinated coffee, which actually contains a higher *N*-phenylpropenoyl-L-tyrosine concentration.

CHEMICAL PROPERTIES OF POLYPHENOLS IN TEA AND COFFEE

Stability during Processing. Green tea and black tea polyphenols mainly undergo epimerization and oxidation during

the brewing process, whereas for coffee, the lactonization and polymerization of chlorogenic acid are the major causes of polyphenol degradation. Theanaphthoquinone has been identified as a major oxidation product of theaflavin in alkaline conditions from two different oxidant model systems, DPPH and peroxidase/hydrogen peroxide (*36*), and this compound can be generated both enzymatically and nonenzymatically from theaflavin (*37*). The oxidation of green tea is limited by inactivating the enzyme in the green tea processing. The stability of green tea catechins in water at 37 °C has been studied (*38*). EGC showed a stability similar to that of EGCG, whereas ECG and EC were more stable. The major oxidation product of EGCG is the theasinensin A (EGCG dimer), which is generated from dehydrotheasinensin A (*39*) (**Figure 5**). Dehydrotheasinensin A is generated not only by enzymatic oxidation but also autoxidation of EGCG.

If the autoxidation of (−)-EGCG was prevented by nitrogen conditions or the addition of superoxide dismutase, epimerization of (−)-EGCG to (−)-gallocatechin gallate (GCG) became appreciable (*38*). In general, epimerization is the dominant reaction of the instability; the factors influencing epimerization are temperature, heating time, pH, and ions (*40*, *41*).

The stability study of polyphenol in coffee mainly focuses on caffeic acid and chlorogenic acid; especially with the development

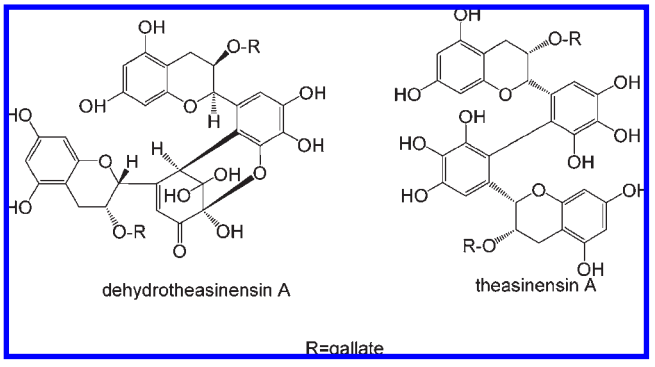

Figure 5. Structures of dehydrotheasinensin A and theasinensin A.

of the sensory-guided analysis, many tastants derived from caffeic acid or chlorogenic acid during roasting were well identified (*42*−*44*). The chlorogenic acid in the raw coffee bean is converted during roasting into chlorogenic acid lactones such as 3-*O*-caffeoyl-γ-quinide, 4-*O*-caffeoyl-γ-quinide, 5-*O*-caffeoyl-epi-δ-quinide, and 3-*O*-caffeoyl-epi-γ-quinide. 3-*O*-Caffeoyl-γ-quinide is the most abundant lactone in *C. arabica* and *C. canephora*, and 4-*O*-caffeoyl-γ-quinide is the second most abundant (*45*). 3-*O*-Caffeoyl-γ-quinide and 4-*O*-caffeoyl-γ-quinide undergo transesterification and lactonization reactions, among which the carbonyl group of the caffeoyl moiety can form an intermediate five-membered orthoformate ring with the hydroxyl group in the 3-position of the quinide (**Figure 6**). The relative levels of 3-*O*-caffeoyl-γ-quinide and 4-*O*-caffeoyl-γ-quinide in roasted coffee were the reverse of those of their precursors in green coffee, indicating isomerization of chlorogenic acids prior to the formation of lactones.

Caffeic acid can be degraded into tetraoxygenated 1,3-*cis*- and 1,3-*trans*-phenylindane isomers under mild pyrolysis (228 °C, 15 min) (*46*). Very recently, 1,3-bis(3′,4′-dihydroxyphenyl)butane, *trans*-1,3-bis(3′,4′-dihydroxyphenyl)-1-butene, and eight multiply hydroxylated phenylindanes have been identified (*42*). The hydrolysis of chlorogenic acid can produce caffeic acid, which can generate the important intermediate 4-vinylcatechol via thermal decarboxylation. Alternatively, 4-vinylcatechol can be formed directly from the chlorogenic acid. The electrophilic and nucleophilic vinylcatechols dimerize to form 1,3-bis(3′,4′-dihydroxyphenyl)butane, which can react further to generate other phenylindanes.

ROS and RCS Scavenging Abilities. More and more epidemiological studies have demonstrated that the consumption of polyphenols may decrease the occurrence of oxidative-related diseases such as cancer, cardiovascular diseases, and aging (*47*, *28*). Antioxidant or oxidative stress studies of tea and coffee have been attracting more attention in recent years, and the number of publications in this field increases every year. All of these publications include discussion of antioxidant capacity assays, comparison of antioxidant activity of different polyphenols, and the chemistry mechanism of scavenging ROS by

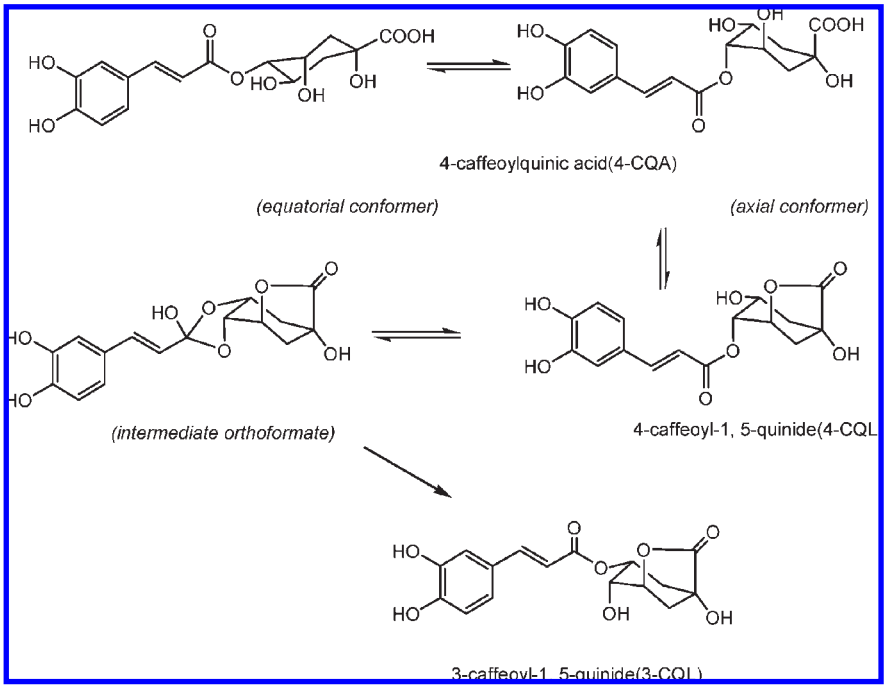

Figure 6. Formation of 3-*O*-caffeoyl-γ-quinide from 4-*O*-caffeoyl-γ-quinide (*45*).

polyphenol (*48*, *49*). Many critical review papers on antioxidant activity have been published, so the antioxidant activity of polyphenols in tea and coffee is not a major point of discussion in this paper.

However, besides having reduction potential, polyphenols in tea have been shown in the past two years to have a trapping activity for RCS, revealing a new chemistry characteristic of polyphenol (*50*−*52*, *56*). RCS such as glyoxal (GO), methyglyoxal (MG), and 3-deoxyglucosone (3-DG), which are generated from the Maillard reaction, are extremely reactive and readily modify lysine, arginine, and cysteine residues of proteins, forming advanced glycation end products (AGEs). Epidemiological and large prospective clinical studies have confirmed that AGEs are related to chronic and age-related diseases such as diabetes and diabetes complications. The ability to prevent diabetic-related complications by using tea and its polyphenols has been tested in several studies. However, detailed mechanisms for the prevention of diabetic complications by tea and its polyphenols have not been elucidated. Many studies have shown that those effects could partially be due to the inhibition of AGEs formation. Rutter et al. reported that green tea extract was able to delay collagen aging in C57Bl/6 mice by blocking AGEs formation and collagen cross-linking. Meanwhile, tea polyphenols may inhibit the formation of AGEs by trapping RCS (*53*). A recent study explored the inhibitory effect of tea polyphenols, such as catechins, EC, ECG, EGC, and EGCG, on different stages of protein glycation, including MG-mediated protein glycation. EGCG exhibited a significant inhibitory effect of 69.1% on MG-mediated protein glycation (*54*).

Trapping effects of four major catechins in green tea and three major theaflavins in black tea were compared under physiological conditions (pH 7.4, 37 °C). All of the tested compounds could efficiently trap MG with theaflavin 3,3′-digallate (TF3) in theaflavins; (−)-epigallocatechin (EGC) in tea catechins showed the highest trapping activity (*50*). The 1:1 adduct formation between EGCG and MG has been identified, and the addition reaction dominantly occurs at either the C8 or C6 position in the A ring of EGCG, whereas the gallate ring did not play an important role in the trapping of reactive dicarbonyl species (*50*, *51*, *57*). Because of their high contents of high fructose corn syrup, soft drinks are potential sources of MG, and it was found that EGCG could decrease the MG level significantly during storage (*55*).

RCS are important intermediates in the Maillard reaction as they are precursors of flavor and color generation. Trapping RCS by polyphenols can alter Maillard reaction pathways. Some flavor compounds generated in the Maillard reaction, such as pyrazine, methylpyrazine, 2,5-dimethylpyrazine, and trimethylpyrazine, can be inhibited when epicatechin is added into a glucose−glycine system because pyrazines are generated from sugar fragments that can be trapped by epicatechin (*56*). The trapping efficiencies of flavan-3-ol (EC, ECG, and EGCG) and phenolic compounds (1,3,5-trihydroxybenzene, 1,2,3-trihydroxybenzene, and methyl gallate) were compared through pyrazine generation (*57*). For EC, ECG, and EGCG similar significant reductions of pyrazine formation have been reported in a glucose−glycine model. Methyl gallate followed by 1,2,3-trihydroxybenzene was the least reactive, whereas 1,3,5-trihydroxybenzene was reported as the most reactive, suggesting that the mechanism is carbonyl trapping reaction on the A ring and not the alteration of the reaction reduction potential. By calculating the electron density of each carbon on the A ring, it was found that the higher the electron density, the higher the trapping efficiency (unpublished data). In conclusion, the scavenging ability, antioxidant properties, and carbonyl-trapping effect of polyphenols are different in the mechanism. The B ring of catechins is the preferred site for oxidation (*38*, *58*); however, the A ring of catechins is the site for carbonyl trapping (*57*).

CONCLUSION

The polyphenolic chemistry of tea and coffee is discussed in this overview of their formation, stability, and scavenging ability. Epimerization and oxidation are the major reactions occurring during tea processing. The oxidation products of tea, particularly black tea and oolong tea, still need further study. Lactonization and polymerization of chlorogenic acid are the major causes of the degradation of polyphenols in coffee. The trapping effect of tea catechins is a different characteristic from antioxidant.

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