Antioxidant Activity of Tea Catechins in Different Lipid Systems

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Tea catechins showed different trends in relative antioxidant activity in different lipid systems. In corn oil triglycerides oxidized at 50 °C, epigallocatechin (EGC), epigallocatechin gallate (EGCG), and epicatechin gallate (ECG) were better antioxidants than epicatechin (EC) and catechin at 140 μM. Used as reference compounds, gallic acid (GA) was more active than propyl gallate (PG), and both were more effective than EC and catechin. However, in the corresponding corn oil-in-water emulsions, all tea catechins, GA, and PG were prooxidants at 5 and 20 μM by accelerating hydroperoxide and hexanal formation. In contrast, in soy lecithin liposomes oxidized at 50 °C, EGCG and PG were the best antioxidants, followed by EC, EGC, ECG, catechin, and GA at 20 μM. In liposomes oxidized at 37 °C with 10 μM cupric acetate, catechin and EC were better antioxidants than ECG, but EGCG, EGC, PG, and GA promoted lipid oxidation. The improved antioxidant activity observed for tea catechins in liposomes compared to emulsions can be explained by the greater affinity of the polar catechins toward the polar surface of the lecithin bilayers, thus affording better protection. The marked variation in activity among tea catechins may be partly explained by their different reducing potentials, stabilities, and relative partitions between phases in different lipid systems.

Keywords: *Antioxidants; prooxidants, tea catechins; catechin; epicatechin; epicatechin gallate; epigallocatechin; epigallocatechin gallate; gallic acid; propyl gallate; triglycerides; emulsion; liposome; antioxidant mechanism; interfacial oxidation; hydroperoxides; hexanal*

INTRODUCTION

Tea catechins are recognized as important contributors of the antioxidant activity of green tea extracts, including (+)-catechin, (+)-gallocatechin, (−)-epicatechin (EC), (−)-epicatechin gallate (ECG), (−)-epigallocatechin (EGC), and (−)-epigallocatechin gallate (EGCG) (Das et al., 1965; Matsuzaki and Hara, 1985; Balentine, 1992). The structures of some of these tea catechins are shown in Figure 1. Under conditions of the active oxygen method (AOM) at 97.8 °C, the antioxidant activities of green tea catechins increased in the order EC < ECG < EGC < EGCG, but their antioxidant activities were not evaluated at the same molar concentrations (Matsuzaki and Hara, 1985). Tea catechins inhibited the oxidation of marine oils at 60 °C in increasing order, EC < EGC < EGCG < ECG, at 200 ppm on the basis of peroxide value (Wanasundara and Shahidi, 1996).

Tea catechins were the most powerful antioxidants of the flavonoids and flavonoid-related compounds in the copper-catalyzed oxidation of mixtures of low-density lipoproteins (LDL) and very low-density lipoproteins (VLDL) at 37 °C by measuring the fluorescence of thiobarbituric acid reaction (Vinson et al., 1995). The antioxidant activity in inhibiting the oxidation of mixtures of LDL and VLDL increased in the order catechin < ECG < EGC < EGCG. However, in the oxidation of unilamellar liposomes of phosphatidylcholine initiated with a water-soluble azo compound at 37 °C, the antioxidant activities of EGCG and EGC were lower than those of EC and ECG at pH 7.4, and their depletion of EGCG and EGC was faster than that of EC and ECG (Terao et al., 1994). Catechins were considered to act as antioxidants by scavenging radicals. The antioxidant potentials of catechins against the artificial water-soluble phenothiazine radical cations increased in the order catechin ≃ EC < gallic acid (GA; Figure 1) < EGC < EGCG < ECG (Salah et al., 1995). However, the order of their effectiveness was different against lipid peroxyl radicals: GA < EGC < catechin ≃ EC ≃ EGCG ≃ ECG, which was consistent with the order of effectiveness in sparing α-tocopherol in the oxidation of LDL catalyzed by metmyoglobin. Although (+)-catechin and (−)-epicatechin had different abilities to scavenge hydroxyl radicals and superoxide anions in aqueous systems, both inhibited the oxidation of methyl linoleate similarly (Hanasaki et al., 1994). In biological systems, catechin and EC also accelerated damage to DNA in the presence of a bleomycin−iron complex (Scott et al., 1993) as well as GA and its methyl and propyl esters (Aruoma et al., 1993). Therefore, whether tea catechins act as antioxidants or prooxidants appears to be dependent on the method to evaluate oxidation and the lipid used in the test system.

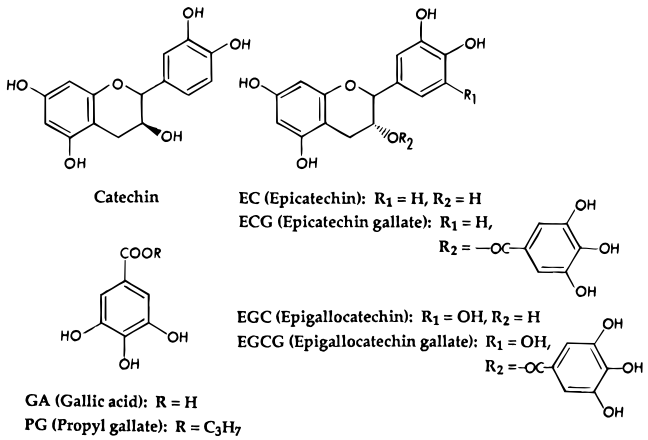

Figure 1. Structures of tea catechins, GA, and PG.

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Our previous work showed that antioxidant activity in different lipid systems was affected by their physical state (Frankel et al., 1994, 1996; Huang et al., 1994), different lipid substrates (Huang et al., 1996a; Hopia et al., 1996), and pH (Huang et al., 1996b). The methods used to evaluate lipid oxidation also affected the determination of antioxidant activity (Huang et al., 1994). The order of activity and ranking of phenolic antioxidants is dependent on the temperature and other conditions of oxidation (Frankel, 1993). Therefore, to better understand the mechanisms for antioxidant actions, it is important to use different lipid systems and more than one method to evaluate antioxidant activity.

This study was aimed at comparing the effectiveness of tea catechins in different food-related lipid systems in the presence or absence of metal ions by systematically studying the interactive effects of three variables, antioxidant concentration, physical state, and oxidation stage, on antioxidant activity in corn oil triglycerides, corn oil-in-water emulsions, and soy lecithin liposomes at 37 or 50 °C. Used as reference compounds, GA and propyl gallate (PG; Figure 1) were also evaluated to better understand the antioxidant mechanisms of catechins containing the galloyl moiety. The effectiveness of antioxidants was evaluated at different stages of oxidation by measuring both the formation of hydroperoxides (conjugated dienes) and the decomposition of hydroperoxides (hexanal).

MATERIALS AND METHODS

Materials. The same corn oil triglycerides stripped of tocopherols were used as previously (Huang et al., 1994). Soy phosphatidylcholine, (±)-catechin, gallic acid, and Tween 20 (polyoxyethylene sorbitan monolaurate) were obtained from Sigma Chemical Co. (St. Louis, MO), propyl gallate was obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI), and cupric acetate monohydrate was obtained from EM Science (Cherry Hill, NJ). (+)-Catechin, (−)-epicatechin, (−)-epicatechin gallate, (−)-epigallocatechin, and (−)-epigallocatechin gallate were special gifts from Dr. Yukihiko Hara, Mitsui Norin Co., Ltd. (Sizuoka Pref., Japan).

Preparation of Bulk Oil, Emulsion, and Liposome Samples. Corn oil samples (6 g) were prepared in screw-capped 25 mL Erlenmeyer flasks with or without added 140 μM catechins, GA, and PG. The pure compounds were added in methanol solutions and purged under nitrogen before addition of corn oil. Antioxidants and/or cupric acetate were dissolved in corn oil by heating to 50 °C for 10 min.

Oil-in-water emulsions (10%, 30 g) were prepared with or without 5 and 20 μM pure antioxidants in 50 mL Erlenmeyer flasks as described previously (Huang et al., 1996a). To avoid the effect of buffers on antioxidant activity, the emulsions and liposomes were prepared with deionized water. Emulsification was carried out by sonicating for a total of 6 min at high power (sonicator, cell disruptor, Model W-10, Heat Systems, Ultrasonics, Inc., New York). To evaluate the effect of metal ions on antioxidant activity, 10 μL of 30 mM cupric acetate was added to some of the emulsion samples to a final concentration of 10 μM. The particle sizes of emulsions were determined with a Microtrac ultrafine particle analyzer (Leeds & Northrup, North Wales, PA). The average particle size in fresh samples of emulsions was 0.19−0.25 μm. The pH of these emulsions was in the range of 3.0−3.5.

Liposome samples containing 10% lecithin were prepared with or without 5 and 20 μM pure antioxidants and 10 μM cupric acetate. Lecithin (2.4 g) was suspended in deionized water at a concentration of 8 mg/mL by stirring with a glass rod and sonicating for 5 min (Bransonic bath-type sonicator, Model 12, Branson Ultrasonic Corp., Danbury, CT). The particle size of liposome was between 0.03 and 0.1 μm (Microtrac ultrafine particle analyzer, Leeds & Northrup). The procedures used for addition of antioxidants were the same as described in the preparation of oil samples. All liposome samples (30 mL) were sonicated for 2 min, and then 10 μL of 30 mM cupric acetate was added. The pH of these liposome samples ranged between 4.3 and 4.6.

Oxidation. The oxidation of oil, emulsion, and liposome samples was carried out at 50 °C in a shaker oven (Lab-Line Instrument, Inc., Melrose Park, IL). The liposome samples were also oxidized with copper ions in a 37 °C shaker water bath (New Brunswick Scientific Co., Inc., Edison, NJ). The oxidative stability of these samples was determined by measuring conjugated diene hydroperoxides spectrophotometrically and hexanal by headspace gas chromatography (GC). All oxidations and analyses were done in duplicate.

Measurement of Conjugated Diene Hydroperoxides. Measurements of conjugated dienes in oil samples were carried out according to the same procedures described previously (Frankel et al., 1994). For emulsions and liposomes, samples (0.1 g) were dispersed in 5 mL of methanol and then diluted with more methanol to a measurable absorbance. The absorbance was measured at 234 nm and calculated as hydroperoxides in millimoles per kilogram of oil.

Measurement of Hexanal by Static Headspace GC. Hexanal, one of many important volatile products of lipid hydroperoxide decomposition, is a useful marker for the decomposition of *n*−6 polyunsaturated fatty acids (PUFAs) (Frankel, 1982). The procedures used for hexanal measurements were those described previously (Frankel et al., 1994), except that all oil and emulsion samples were equilibrated at 60 °C for 15 min before GC injection.

RESULTS

Bulk Corn Oil Triglycerides. *Formation of Hydroperoxides.* Tea catechins were tested at varying concentrations in corn oil oxidized at 50 °C. Preliminary tests of (±)-catechin at different concentrations showed that hydroperoxide formation was inhibited about 50% with 40 ppm of (±)-catechin, corresponding to 140 μM in corn oil. At 50 °C, all tea catechins, GA, and PG inhibited hydroperoxide formation at 140 μM (Figure 2a). Both (+)-catechin and (±)-catechin were weak antioxidants in inhibiting hydroperoxide formation. PG was a better antioxidant than EC but less effective than GA, ECG, EGC, and EGCG. The rate of hydroperoxide formation decreased in the order GA > ECG > EGCG > EGC.

Formation of Hexanal. In contrast to hydroperoxide formation, EC and EGCG promoted initial hexanal formation slightly during the first 6 days of oxidation but inhibited hexanal formation after 6 days (Figure 2b). EGCG decreased hexanal formation more effectively than EC during the first 12 days of oxidation but was less active than the other antioxidants tested. (+)-Catechin, (±)-catechins, and PG inhibited the formation of hexanal similarly. The amount of hexanal formed was lowest in the presence of EGC followed by GA and ECG.

Oil-in-Water Emulsions. *Formation of Hydroperoxides and Hexanal.* At 50 °C, all tea catechins, GA, and PG were prooxidant and accelerated the formation of hydroperoxide and hexanal at 5 and 20 μM during 4 days of oxidation (Figures 3 and 4). After 2 days of oxidation, all of these antioxidants promoted hydroperoxide formation more strongly at 20 μM than at 5 μM except ECG (Figure 3). EGC had lower prooxidant activity than the other compounds tested at 5 and 20 μM. On the basis of hexanal formation, EC, ECG, EGC, and EGCG were less prooxidant at 20 μM than at 5 μM after 2 days of oxidation (Figure 4). Only GA was a stronger promoter of hexanal formation at 5 and 20 μM.

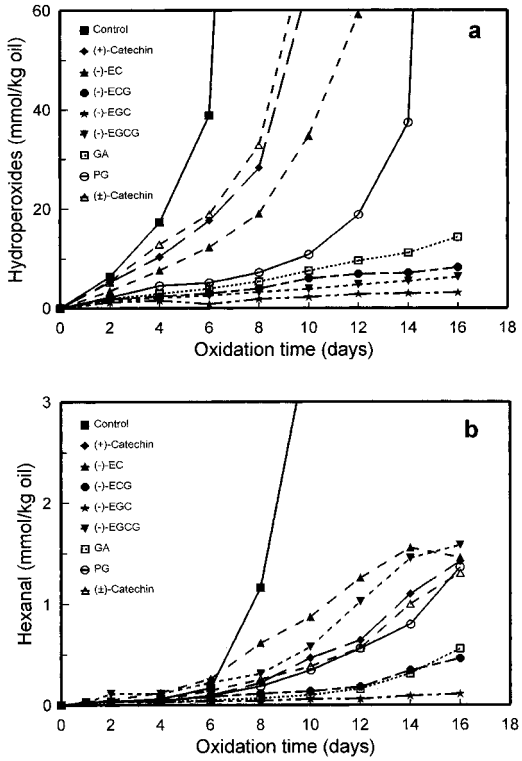

Figure 2. Effect of 140 μM tea catechins, GA, and PG on oxidative stability of bulk corn oil triglycerides at 50 °C: (a) hydroperoxides and (b) hexanal.

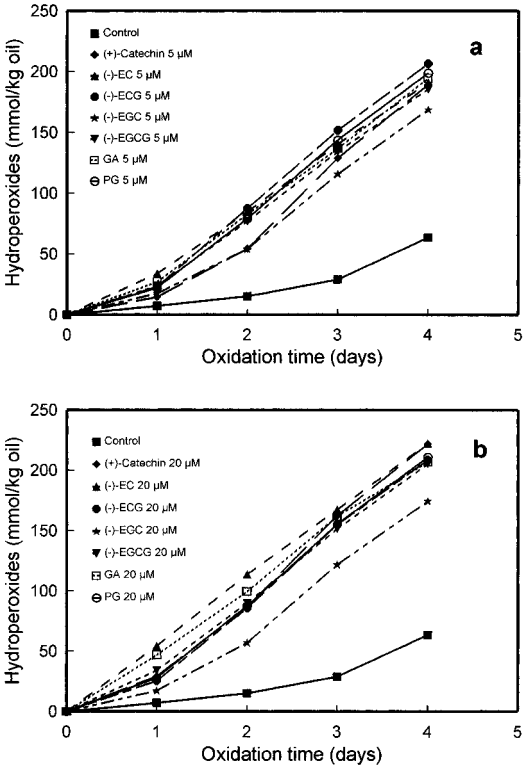

Figure 3. Effect of tea catechins, GA, and PG on oxidative stability of corn oil-in-water emulsions by measuring hydroperoxide formation at 50 °C: (a) 5 μM and (b) 20 μM.

Soy Lecithin Liposomes. In contrast to oil-in-water emulsions prepared with neutral Tween 20 as surfactant, lecithin liposomes are charged polar substrates and provide more suitable models than emulsions to study the activities of hydrophilic antioxidants. The greater affinity of hydrophilic antioxidants such as tea

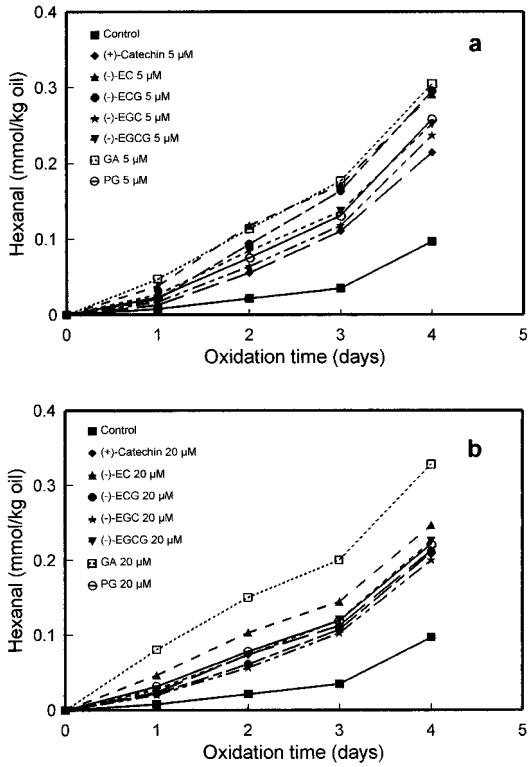

Figure 4. Effect of tea catechins, GA, and PG on oxidative stability of corn oil-in-water emulsions by measuring hexanal formation at 50 °C: (a) 5 μM and (b) 20 μM.

catechins for the polar lecithin liposome bilayers is expected to increase their antioxidant activity.

Formation of Hydroperoxides and Hexanal. Because the amount of lipid substrate in liposomes was low (0.8% phospholipids) relative to that in the emulsions (10% corn oil), the formation of hydroperoxides in the control and samples containing 5 μM GA and EGC reached a maximum after 8 days followed by a decrease (Figure 5). In the same control and samples containing 5 μM GA and EGC, hexanal formation increases when the amount of hydroperoxides formed decreases (Figure 6a). Therefore, measurement of hexanal helps to determine if hydroperoxides are analyzed at the propagation stage or at the termination stage.

At 50 °C, tea catechins, PG, and GA inhibited the formation of hydroperoxides, and their activities increased by increasing their concentrations from 5 to 20 μM (Figure 5). The order of inhibiting hydroperoxide formation was EGCG > EC ≈ PG > (+)-catechin ≈ ECG > EGC ≈ GA at 5 μM after 6 days of oxidation, but ECG was better than (+)-catechin and EC was better than PG after 8 days of oxidation (Figure 5a). At 20 μM, EGCG and PG were the best antioxidants among these compounds after 6 days of oxidation, and EGC and ECG showed the same activity as EC (Figure 5b). Gallic acid was the weakest inhibitor of hydroperoxide formation at 20 μM, followed by (+)-catechin. The inhibition of hexanal by (+)-catechin, ECG, EGC, GA, and PG increased at higher concentrations (Figure 6). The order of hexanal inhibition at 5 μM was EGCG ≈ EC > PG > ECG > (+)-catechin > EGC > GA after 9.2 days of oxidation; at 20 μM the order was ECG ≈ EC ≈ EGC ≈ PG ≈ EGCG > GA ≈ (+)-catechin.

During oxidation at 37 °C, in the presence of copper ions, (±)-catechin inhibited hydroperoxide and hexanal formation. This antioxidant activity increased in a dose dependent way from 3.5 to 140 μM (Figure 7). At 3.5

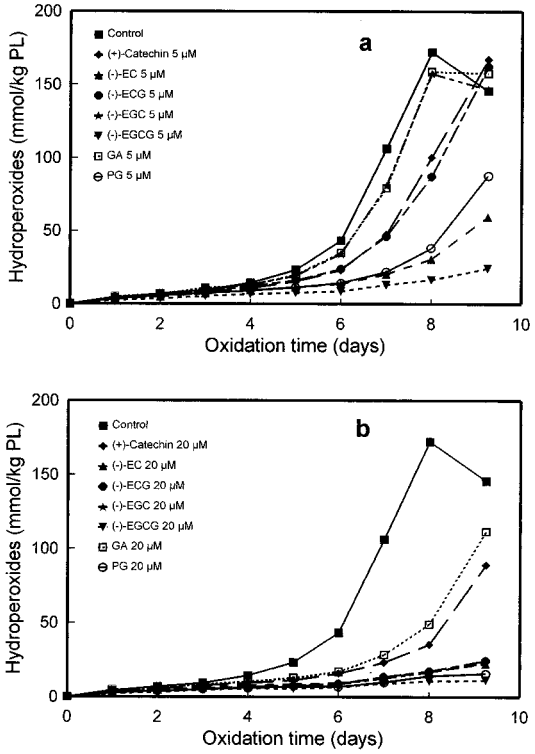

Figure 5. Effect of tea catechins, GA, and PG on oxidative stability of soy lecithin liposomes by measuring hydroperoxide formation at 50 °C: (a) 5 μM and (b) 20 μM.

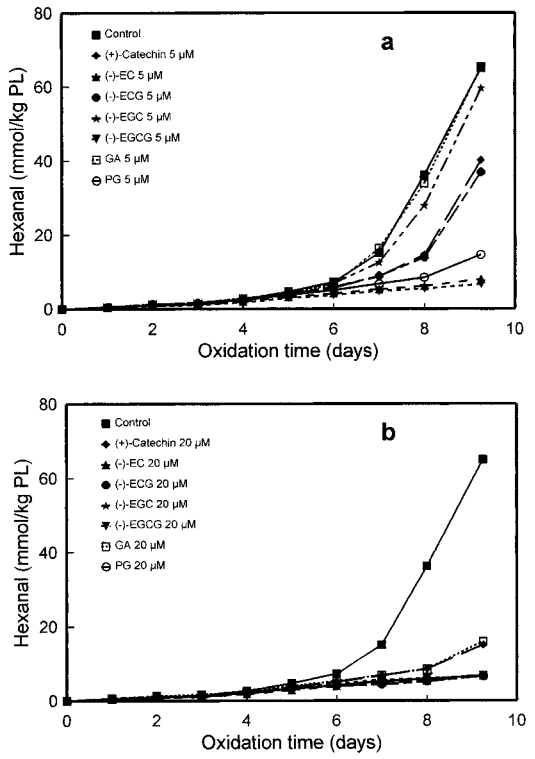

Figure 6. Effect of tea catechins, GA, and PG on oxidative stability of soy lecithin liposomes by measuring hexanal formation at 50 °C: (a) 5 μM and (b) 20 μM.

μM, (±)-catechin had no antioxidant activity in inhibiting hexanal formation after 32 h of oxidation (Figure 7b). (±)-Catechin, (+)-catechin, and EC showed similar inhibition of both hydroperoxide and hexanal formation at 20 μM (Figure 8), but (±)-catechin was slightly more active than (+)-catechin and EC in decreasing hydroperoxide formation (Figure 8a). The antioxidant ac-

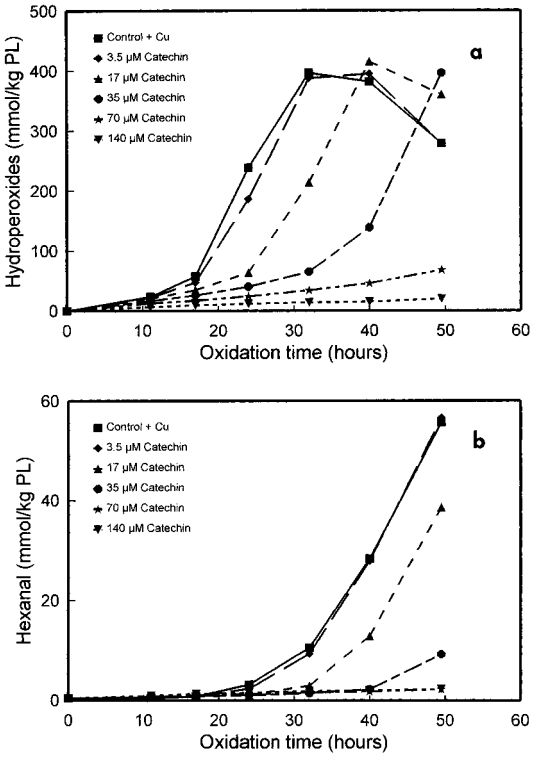

Figure 7. Effect of (±)-catechin on oxidative stability of soy lecithin liposomes in the presence of 10 μM cupric acetate at 37 °C: (a) hydroperoxides and (b) hexanal.

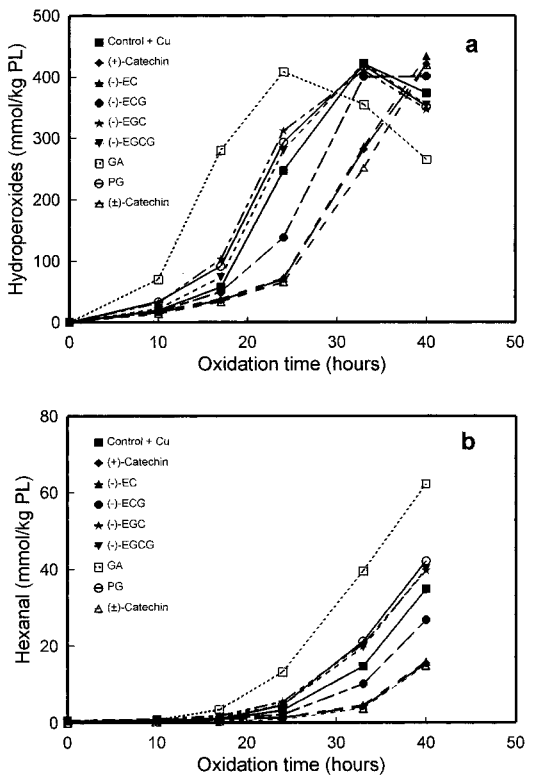

Figure 8. Effect of 20 μM tea catechins, GA, and PG on oxidative stability of soy lecithin liposomes in the presence of 10 μM cupric acetate at 37 °C: (a) hydroperoxides and (b) hexanal.

tivties of (±)-catechin, (+)-catechin, and EC toward both hydroperoxides and hexanal formation were better than that of ECG (Figure 8). However, in the presence of copper ions, EGCG, PG, EGC, and GA became promotors of hydroperoxide and hexanal formation.

DISCUSSION

To clarify the antioxidant action of tea catechins, several food-related test systems were used to evaluate their activities. This study demonstrates that whether tea catechins, GA, and PG act as antioxidants or prooxidants is dependent on the lipid system and the presence of metal catalysts. Tea catechins, GA, and PG were all antioxidants in corn oil triglycerides and in liposomes without added copper ions, whereas in oil-in-water emulsions, these compounds were all prooxidants. In liposomes with added copper catalyst, GA, EGC, EGCG, and PG were prooxidants. The order of the relative antioxidant activity of these phenolic compounds depends on the lipid system, the presence of metal catalysts, the temperature of oxidation, the antioxidant concentration, the oxidation stage, and the method used to evaluate lipid oxidation. In corn oil triglycerides oxidized at 50 °C, EGC, EGCG, ECG, and GA were better antioxidants than PG, EC, (+)-catechin, and (±)-catechin on the basis of hydroperoxide formation, but on the basis of hexanal formation, EC and EGCG were less effective than the other antioxidants. In liposomes oxidized at 50 °C without added copper ions, EGCG, EC, and PG were better antioxidants than (+)-catechin, ECG, EGC, and GA at 5 μM, but ECG and EGC were as active as EC at 20 μM. In liposomes oxidized at 37 °C with added copper catalyst, (±)-catechin, (+)-catechin, and EC were better antioxidants than ECG.

The antioxidant activity of tea catechins may be related to their hydrogen-donating ability. The lower potential and easier formation of radicals indicate the higher hydrogen-donating ability of antioxidants. On the basis of their ease of radical formation, EGCG and EGC were shown to be better hydrogen donors than ECG, and these three catechins were all better than EC (Yoshioka et al., 1991). On the basis of one-electron potential, EC was a better hydrogen donor than (±)-catechin, but a poorer donor than ethyl gallate (Steenker and Neta, 1982). In the present study, the order of antioxidant activity of tea catechins [ECG ≈ EGCG ≈ ECG > EC > (+)-catechin] in corn oil triglycerides is consistent with the order of their hydrogen-donating abilities [EGCG ≈ EGC > ECG > EC > (+)-catechin]. Alternatively, the better antioxidant activity of GA than PG in oils reported previously (Sherwin, 1976; Porter et al., 1989) may also be explained by the higher affinity of GA toward the air−oil interfaces in bulk oil (Frankel et al., 1994).

Trolox, a water-soluble carboxylic acid analogue of α-tocopherol, was a better antioxidant than α-tocopherol in corn oil triglycerides, whereas α-tocopherol was more active than Trolox in the corresponding emulsions (Frankel et al., 1994). In emulsions, because of its water solubility, Trolox partitioned into the water phase, oil−water interfaces, and Tween 20 micelles and became less effective in protecting lipids from oxidation (Huang et al., 1996a). Also, Trolox was less stable in water and Tween 20 micelles than in oil (Huang et al., 1996b). (±)-Catechin, GA, and PG were more hydrophilic than Trolox in the absence of buffers (Schwarz et al., 1996). Because of their hydrophilic character, tea catechins, GA, and PG may thus behave like Trolox by being less protective in emulsions. (±)-Catechin and PG were found to have a high affinity toward Tween 20, and most of GA was located in the water phase (Huang et al., 1997). In oil-in-water emulsions without added copper, EGCG, EC, (+)-catechin, GA, and PG were prooxidants and promoted lipid oxidation more strongly at higher concentrations. In contrast, under the same oxidation conditions, in liposomes, all of these tested compounds increased their antioxidant activities with concentration. These results suggest that Tween 20 used as emulsifier in the emulsion system may induce tea catechins, GA, and PG to act as prooxidants. These phenolic compounds may be also oxidized more rapidly in Tween 20 because Tween 20 can trap air, and the oxidized phenolic compounds may catalyze oxidation at oil−water interfaces. In the emulsion system trace metals present in the corn oil may also be reduced more effectively by tea catechins which become prooxidants. The greater antioxidant activities of tea catechins, GA, and PG in liposomes without added copper and (±)-catechin in the presence of copper, compared to emulsions, may be explained by their higher affinity toward the surface environment of lecithin bilayers to better protect lipids against oxidation.

In bulk corn oil, EGC and GA were better antioxidants than EC and PG, respectively, but their activities were lower than those of EC and PG at 5 μM in liposomes without added copper ions. EGC and GA, being more water soluble than EC and PG, were less effective at 5 μM in lecithin liposomes because they would have a lower affinity toward the surface of bilayers. GA was the poorest antioxidant apparently because of its highest polarity and water solubility.

In the oxidation of LDL catalyzed with metmyoglobin, GA and EGC had lower antioxidant activities than other tea catechins (Salah et al., 1995). However, in our liposome system without added copper, EGC was as good as EC in inhibiting lipid oxidation at 20 μM. According to Yoshioka et al. (1991), the hydrogen-donating ability of EGC and EGCG and the stability of their radicals were similar, but the gallyl radicals formed from EGCG may scavenge PC peroxyl radicals to stop chain reactions. In our liposomes without added copper, the higher hydrogen-donating and free radical scavenging abilities of EGCG may thus explain its better antioxidant activity relative to those of other test compounds. Athough gallate esterification of EC was expected to increase hydrogen-donating ability of EC, ECG was less active than EC at lower concentrations in liposomes without added copper. However, ECG and EC showed similar activity at higher concentrations. The lower activity of (+)-catechin than EC may be explained by its higher redox potential. Little information about the stability and polarities of EC and ECG is available to clarify their antioxidant mechanisms in liposomes.

However, in the oxidation of liposomes catalyzed with added copper, GA, PG, EGC, and EGCG were prooxidants. These results suggest that GA, PG, EGC, and EGCG may reduce copper ions to lower valence state, causing them to become prooxidants. ECG was an antioxidant but less active than (+)-catechin, (±)-catechin, and EC in liposomes with copper. The antioxidant activities of tea catechins, GA, and PG may also be related to their stability, according to Terao et al. (1994), who reported that the stability of tea catechins was related to their antioxidant activities in liposomes oxidized with a water-soluble azo initiator, and EGC and EGCG were less stable than EC and ECG.

To clarify the antioxidant or prooxidant mechanisms for tea catechins, GA, and PG in different lipid systems, more information is needed on their redox potentials, stability, metal chelation, and partition properties. The

distribution of these phenolic compounds in different lipid systems and their stability in different phases need to be measured to determine the relationship between their locations and antioxidant activity. Investigations are also needed on the effect of other surfactants on the antioxidant activities of tea catechins to better understand their behaviors in emulsions.

ABBREVIATIONS USED

EC, (−)-epicatechin; ECG, (−)-epicatechin gallate; EGC, (−)-epigallocatechin; EGCG, (−)-epigallocatechin gallate; GA, gallic acid; PG, propyl gallate; PC, phosphatidylcholine; Tween 20, polyoxyethlene sorbitan monolaurate.

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