ARTICLES

Interfacial Phenomena in the Evaluation of Antioxidants: Bulk Oils *vs* Emulsions†

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Antioxidants have been difficult to evaluate in oils and food emulsions due in part to the complex interfacial phenomena involved. Lipophilic and hydrophilic antioxidants were evaluated with corn oil stripped of natural tocopherols in bulk and in emulsion systems. Oxidation was followed by determining formation of hydroperoxides and hexanal. The lipophilic antioxidants α-tocopherol and ascorbyl palmitate were more effective in an oil-in-water emulsion system than in bulk oil, while the opposite trend was found for the hydrophilic antioxidants Trolox and ascorbic acid. The oil-insoluble ascorbic acid was a particularly efficient antioxidant in suspension in the bulk oil system. Mixtures of α-tocopherol and ascorbic acid were more active in bulk oil, while mixtures of α-tocopherol and ascorbyl palmitate were more efficient in emulsion systems. Differences observed in the efficiency of antioxidants may be explained by their affinities toward the air–oil interfaces in bulk oil and the oil–water interfaces in emulsions.

INTRODUCTION

Much work has appeared in the current and early literature comparing the effectiveness of antioxidants with different lipid substrates, model systems, oxidation conditions, and methods to determine lipid oxidation. This diversity in oxidation conditions and methods used to determine lipid oxidation has led to considerable confusion in the literature. Natural antioxidants have been difficult to evaluate in oils and food emulsions in view of the complex interfacial affinities between air–oil and oil–water interfaces involved (Porter, 1980) and the questionable conditions and methodology used to follow oxidation (Ragnarsson and Labuza, 1977). The methodology to evaluate natural antioxidants must be carefully interpreted depending on whether oxidation is carried out in bulk oils or in emulsions and on what analytical method is used to determine the extent and end point of oxidation (Frankel, 1993). The conclusions reached in many studies may not be valid because of the choice of inappropriate methods for evaluating oxidative stability.

The antioxidant activity of Trolox C (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), a hydrophilic carboxylic acid derivative of α-tocopherol, was compared with that of several food grade antioxidants and test systems (Cort, 1975). Under a wide range of conditions and test systems Trolox C proved to be superior to α-tocopherol. Thus, with soybean oil oxidized as a thin layer at 45 °C, the comparative antioxidant activity decreased in the order *tert*-butyl hydroquinone (TBHQ) [2-bis(1,1-dimethylethyl)-4-hydroxyphenol] = Trolox > ascorbyl palmitate > *tert*-butylhydroxytoluene (BHT) [2-bis(1,1-dimethylethyl)-4-methylphenol] > *tert*-butylhydroxyanisole (BHA) > α-tocopherol. With soybean oil oxidized at 98 °C under conditions of the active oxygen method (AOM), the activity decreased as follows: TBHQ > Trolox > ascorbyl palmitate > BHT > BHA (2-/3-*tert*-butyl-4-methoxyphenol) = α-tocopherol. With a safflower oil emulsion oxidized in the presence of hemoglobin at room temperature, the activity decreased, as follows: BHA > Trolox > BHT = TBHQ > ascorbyl palmitate ≫ α-tocopherol.

In several reviews, Porter (Porter, 1980, 1993; Porter et al., 1989) postulated the general rule that in food systems of low surface-to-volume ratio (e.g., bulk vegetable oils) polar antioxidants with high hydrophilic–lipophilic balance (HLB), such as propyl gallate, TBHQ, and Trolox C, are more effective than nonpolar lipophilic antioxidants, such as BHA, BHT, and tocopherols. In contrast, in foods of high surface-to-volume ratio (e.g., emulsified oils), lipophilic antioxidants of low HLB are strongly favored. From a kinetic study, Pryor et al. (1988) concluded that rate constants for antioxidants are very sensitive to the system used for measurements, since rates obtained with a micellar system do not parallel rates obtained with a homogeneous system. More recently, Porter et al. (1989) used a polyamide fluorescence method to follow oxidation of lecithin liposome model catalyzed by hematin to evaluate a series of antioxidants. With this fluorescence method, they confirmed the so-called "polar paradox" that polar anitoxidants are more effective in nonpolar lipids, whereas nonpolar antioxidants are more active in polar lipid emulsions.

The classical studies of Cort et al. (Cort, 1974; Cort et al., 1975), Scott et al. (1974) and Porter et al. (Porter, 1980, 1993; Porter et al., 1989) comparing the activities of antioxidants are difficult to interpret in view of the multitude of test conditions used: oxidation varying from room temperature to 98 °C, with and without heme catalyst; lipid substrates ranging from vegetable oils to chicken fat, emulsified tocopherol-stripped safflower oil, or soy lecithin liposome; a multitude of methods to determine oxidation varying from peroxide values, oxygen

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analyzer, and fluorescence; and a diversity of oxidation endpoints ranging from peroxide values of 70 mequiv/kg for vegetable oils and 20 mequiv/kg for animal fats, removal of oxygen as percent of a standard compound such as nordihydroguaiaretic acid, and induction periods for fluorescence formation. The many difficulties and pitfalls in interpreting comparative data from the literature on antioxidants under a diversity of test conditions and methodology was discussed recently (Frankel, 1993). Valid comparisons of antioxidants require careful interpretation of the methodology used depending on conditions of oxidation and on what analytical method is used to determine the extent and endpoint of oxidation.

This paper reports a study aimed at testing two lipophilic antioxidants (α-tocopherol and ascorbyl palmitate) and two hydrophilic antioxidants (Trolox and ascorbic acid) with the same tocopherol-stripped corn oil, in bulk and in an oil-in-water emulsion system, both oxidized at the same temperature of 60 °C to avoid the difficulties of high-temperature stability tests (Ragnarsson and Labuza, 1977; Frankel, 1993). Oxidation was followed by two methods: conjugated diene hydroperoxides determined spectrophotometrically and hexanal determined by static headspace capillary gas chromatography. Mixtures of α-tocopherol and ascorbic acid or ascorbyl palmitate were tested also to clarify the mechanism of antioxidant synergism.

MATERIALS AND METHODS

Materials. Corn oil stripped of tocopherols was obtained commercially (Eastman Chemical Co., Rochester, NY). Samples were found to be free of tocopherols by HPLC, and the peroxide values were less than 2. Fatty acid composition determined by gas chromatography (GC) of the methyl esters was as follows: 10.5% 16:0, 2.1% 18:0, 25.5% 18:1, 60.8% 18:2, and 1.1% 18:3. α-Tocopherol and Tween 20 (polyoxyethylene sorbitan monolaurate) were purchased from Sigma Chemical Co., St. Louis, MO. Trolox C, L-ascorbic acid, and L-ascorbic acid 6-palmitate were from Aldrich Chemical Co., Milwaukee, WI.

Preparation of Oil and Emulsion Samples. Stripped corn oil with no antioxidant was compared with samples containing α-tocopherol, Trolox C, ascorbic acid, or ascorbyl palmitate added at two levels. The concentrations of antioxidants used were 232 and 1161 μM, which are equivalent to 100 and 500 ppm of α-tocopherol, respectively. Although ascorbic acid was insoluble in corn oil, it produced a cloudy colloidal suspension that was homogeneous during shaking. Ten percent stripped corn oil-in-water emulsions (25 mL) were made with 2.5 g of control oil with no additive and oils containing added antioxidants, made up with distilled water in a 50-mL Erlenmeyer flask and emulsified with 0.25 g of Tween 20. Emulsions were then sonicated for 6 min in an ice bath at high power using a sonicator (Model W-10, Heat Systems, Ultrasonics Inc., New York). These oil-in-water emulsions were physically stable during oxidation at 60 °C.

The effect of pH on oxidative stability of corn oil emulsions was checked. In comparisons of α-tocopherol and Trolox, the same stabilizing effect was obtained with buffered (25 mM phosphate, pH 7.3) as with unbuffered corn oil emulsions. To avoid the metal chelating effect of phosphate and other polybasic acid buffers, all oxidations were conducted with unbuffered emulsions. The effect of metal chelators on oxidative stability of emulsions will be the subject of another publication.

Methods. *Oxidation.* Oil samples (5 g) weighted into screw-capped 25-mL Erlenmeyer flasks and 10% oil-in-water emulsion samples (25 mL) in 50-mL flasks were oxidized at 60 °C in a shaker oven (Lab-Line Instrument, Inc., Melrose Park, IL). Oxidative stability was evaluated by analyzing samples periodically for conjugated diene hydroperoxides and for hexanal by GC headspace. All analyses were done in duplicate.

Measurement of Conjugated Diene Hydroperoxides. Weighed oil samples were dissolved in 5 mL of isooctane, and the conjugated diene absorbance was measured at 234 nm. Results were calculated as hydroperoxides in millimoles per kilogram of oil using an absorptivity of 26 000 for linoleate hydroperoxides (Chan and Levett, 1977). Samples of oil-in-water emulsions (0.10 g) were extracted with a mixture of 1 mL of methanol and 1 mL of hexane: the methanol layer was washed twice with 1 mL of hexane. The combined hexane extracts were evaporated to dryness under nitrogen and then dissolved with 5 mL of isooctane; the absorbance was measured at 234 nm. The absorbances were calculated on the same basis as the oil samples.

Measurement of Hexanal by Static Headspace GC. Oil (0.1 g) and emulsion (1 mL) samples were measured into special 6-mL-headspace vials, sealed with silicone rubber Teflon caps with a crimper. Oils were heated at 100 °C for 10 min and emulsions at 80 °C for 10 min. A procedure was developed to determine hexanal within 6 min, using a Perkin-Elmer Sigma 3B gas chromatograph with an H-6 headspace sampler (Norwalk, CT) and a capillary DB-1701 column (30 m × 0.32 mm, 1-μm thickness, J&W, Folsom, CA) heated isothermally at 65 °C. The GC conditions were as follows: helium linear gas velocity, 20 cm/s (helium head column pressure 30 psi); splitless injector temperature, 180 °C; and detector temperature 200 °C.

After heating, the bottles were pressurized for 30 s before injection. The method depends on the equilibrium between the gas and liquid with hexanal distributed between the two phases. Content of hexanal was determined by analyzing quantitatively samples of the gas phase. Peak areas for hexanal were integrated electronically and standardized with known amounts of authentic hexanal purified chromatographically (Frankel and Tappel, 1991). Results were calculated as hexanal in millimoles per kilogram of oil.

Statistical Analyses. Analysis of variance (ANOVA) was used to determine the least significant difference between mean values (Steel and Torrie, 1980) of duplicate analyses of hydroperoxides and of headspace hexanal. One-way analysis of variance was calculated on measurements taken after each day of oxidation. Significance level is $p < 0.05$ unless otherwise indicated.

RESULTS

α-Tocopherol *vs* Trolox. The effects of two lipophilic and hydrophilic antioxidants were compared in commercially available corn oil stripped of natural tocopherols to eliminate the confounding effects of natural tocopherols. Evaluations were made by oxidizing in bulk and in emulsion systems at 60 °C.

α-Tocopherol was compared with Trolox at two concentrations. On the basis of hydroperoxide formation, Trolox was significantly more active than α-tocopherol ($p < 0.05$) in bulk corn oil after 1 day of oxidation at 60 °C (Figure 1a). α-Tocopherol showed antioxidant activity after 3 days of oxidation at 232 μM concentration. However, at 1161 μM α-tocopherol showed prooxidant activity between 2 and 3 days, and antioxidant activity after 4 days of oxidation.

The relative antioxidant activities of α-tocopherol and Trolox were different when oxidation was measured on the basis of hexanal formation rather than on the basis of hydroperoxide formation. At 232 μM α-tocopherol had a significantly lower antioxidant activity ($p < 0.05$) than Trolox after 4 days of oxidation (Figure 1b). Moreover, at 1161 μM α-tocopherol had a significantly higher antioxidant activity than at 232 μM after 4 days of oxidation. No prooxidant effect was observed on the basis of hexanal formation.

Opposite trends were observed for the relative activity between-α-tocopherol and Trolox in corn oil-in-water emulsion and in bulk oil. Thus, α-tocopherol was significantly more active as an antioxidant than Trolox ($p < 0.05$) in corn oil-in-water emulsion after 1 day of oxidation, on the basis of hydroperoxide formation (Figure 2a). After 2 days of oxidation, Trolox showed a small prooxidant effect at 1161 μM, while at 232 μM it had a small antioxidant effect ($p < 0.05$). α-Tocopherol showed greater

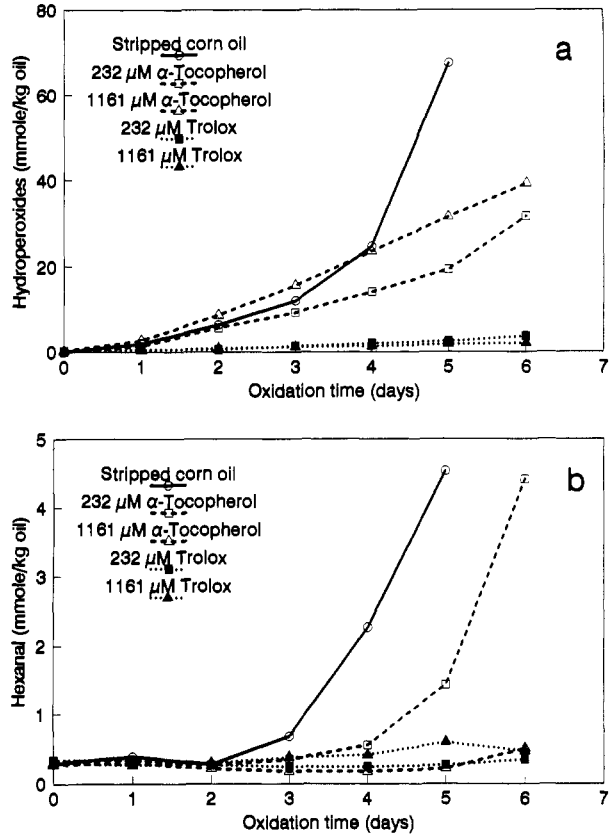

Figure 1. Effect of α-tocopherol and Trolox on the oxidative stability of stripped corn oil at 60 °C: (a) hydroperoxide formation; (b) hexanal formation.

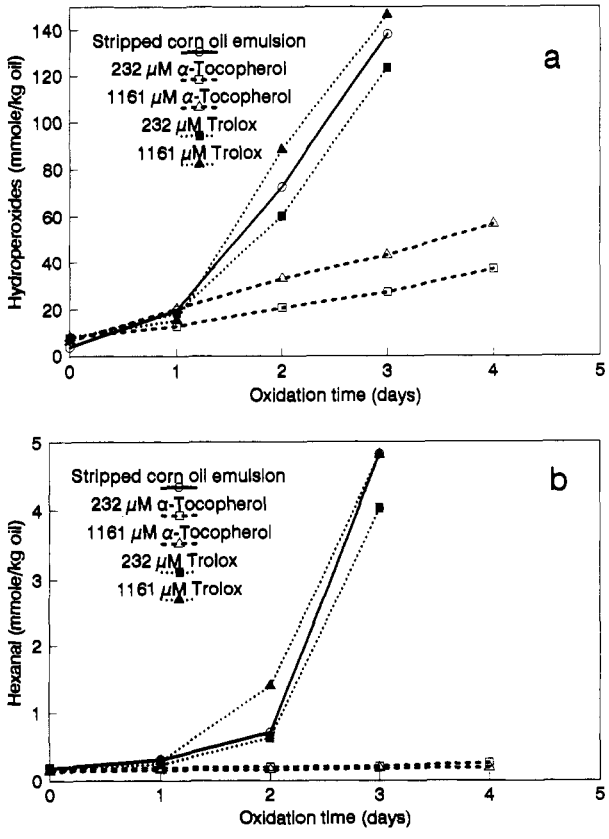

Figure 2. Effect of α-tocopherol and Trolox on the oxidative stability of stripped corn oil-in-water emulsion at 60 °C: (a) hydroperoxide formation; (b) hexanal formation.

antioxidant activity at 232 μM than at 1161 μM after 1 day of oxidation.

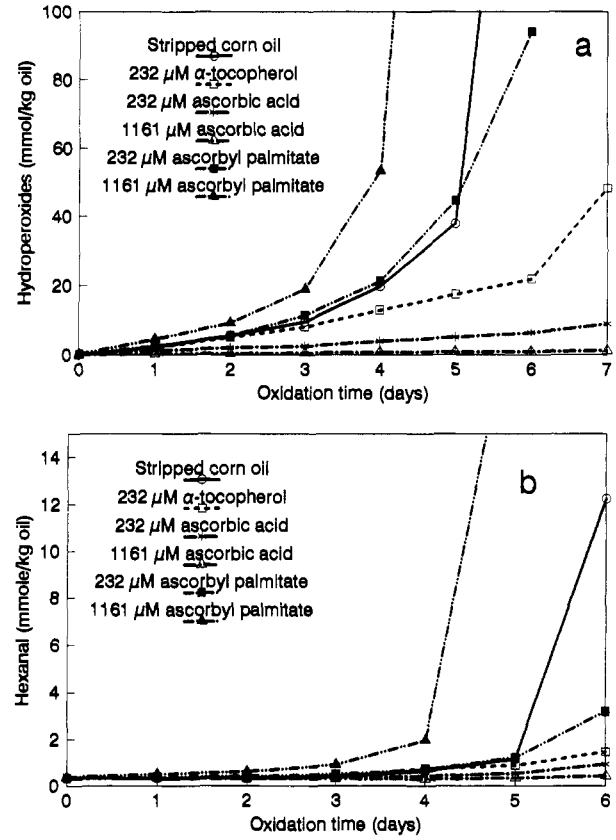

Figure 3. Effect of α-tocopherol, ascorbic acid, and ascorbyl palmitate on the oxidative stability of stripped corn oil at 60 °C: (a) hydroperoxide formation; (b) hexanal formation.

On the basis of hexanal formation, α-tocopherol was also much more effective than Trolox in emulsion than in the corresponding oil (Figure 2b). At the two concentrations tested, α-tocopherol showed the same strong antioxidant activity, while Trolox showed no significant activity.

Ascorbic Acid *vs* Ascorbyl Palmitate. The antioxidant activities of ascorbic acid and ascorbyl palmitate were compared at two added concentrations using α-tocopherol as reference. Although ascorbic acid was present in suspension in corn oil, it was significantly more active as an antioxidant than ascorbyl palmitate ($p < 0.05$) on the basis of hydroperoxide formation (Figure 3a). Moreover, ascorbic acid was significantly more active than α-tocopherol as an antioxidant after 3 days of oxidation at the same added concentration. In contrast, ascorbyl palmitate showed a prooxidant effect at both concentrations tested between 2 and 5 days of oxidation and an antioxidant effect at 232 μM after 6 days of oxidation ($p < 0.05$).

On the basis of hexanal formation, ascorbic acid was also much more active as an antioxidant than ascorbyl palmitate (Figure 3b). At the two concentrations added ascorbic acid had the same antioxidant activity as 232 μM α-tocopherol. Ascorbyl palmitate had significant prooxidant activity at 1161 μM after 4 days of oxidation and antioxidant activity at 232 μM after 6 days of oxidation ($p < 0.05$).

The reverse trend in antioxidant activity was observed between ascorbic acid and ascorbyl palmitate in corn oil-in-water emulsion compared to that in corn oil. Thus, ascorbyl palmitate had antioxidant activity after 3 and 4 days of oxidation, whereas ascorbic acid has prooxidant activity at the two concentrations added after 1 day of oxidation (Figure 4a). At the same added concentration, ascorbyl palmitate was as active as α-tocopherol after 3

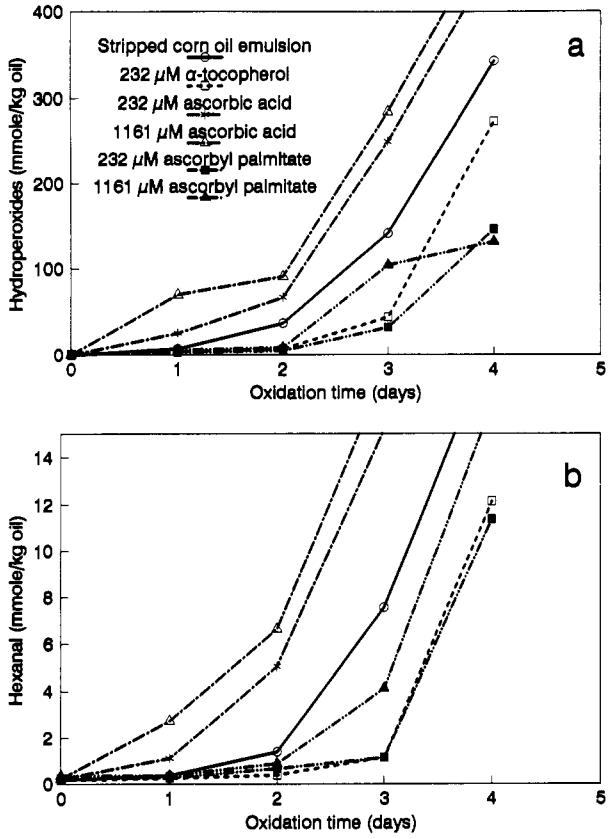

Figure 4. Effect of α-tocopherol, ascorbic acid, and ascorbyl palmitate on the oxidative stability of stripped corn oil-in-water emulsion at 60 °C: (a) hydroperoxide formation; (b) hexanal formation, same legend as (a).

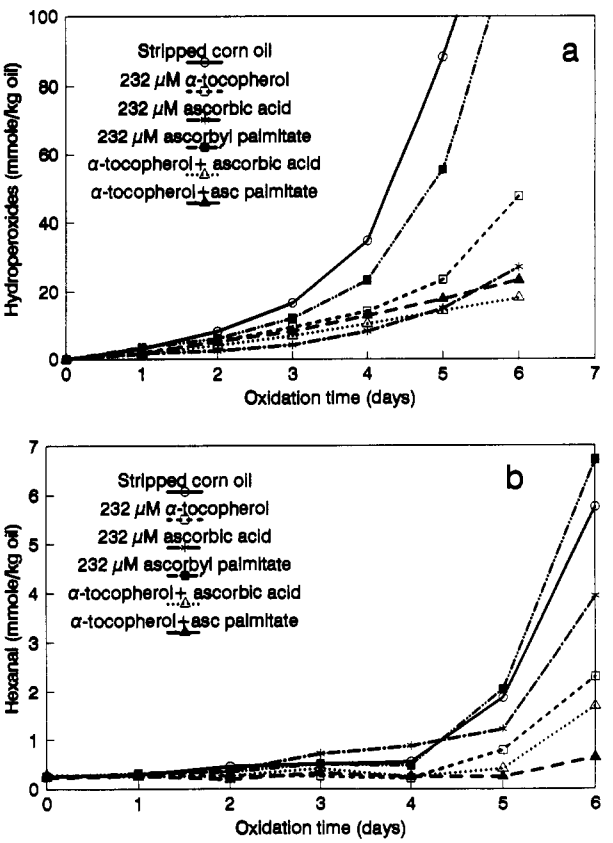

Figure 5. Effect of α-tocopherol, ascorbic acid, ascorbyl palmitate, and mixtures of α-tocopherol and ascorbyl palmitate on the oxidative stability of stripped corn oil at 60 °C: (a) hydroperoxide formation; (b) hexanal formation.

days of oxidation and more active as an antioxidant after 4 days of oxidation. On the basis of hexanal formation, similar trends were obtained in antioxidant activity for ascorbyl palmitate and in prooxidant activity for ascorbic acid (Figure 4b). However, the antioxidant activity of ascorbyl palmitate was superior at 232 μM compared to that at 1161 μM.

Synergism between α-Tocopherol and Ascorbic Acid or Ascorbyl Palmitate. The anitoxidant activities of ascorbic acid and ascorbyl palmitate were compared, individually and in combination with α-tocopherol at the same molar concentration. In bulk oil, both mixtures of ascrobic acid and ascorbyl palmitate with α-tocopherol had strong antioxidant activity. This activity was significantly better than that of α-tocopherol alone after 5 and 6 days of oxidation (Figure 5a). The ascorbyl palmitate–α-tocopherol mixture showed a strong synergistic effect compared to ascorbyl palmitate alone. However, the ascorbic acid–α-tocopherol mixture was not significantly better than ascorbic acid alone.

On the basis of hexanal formation, the two mixtures of ascorbic acid and ascorbyl palmitate with α-tocopherol showed the best antioxidant activity after 6 days of oxidation, followed by α-tocopherol alone and ascorbic acid (Figure 5b). Ascorbyl palmitate alone was not significantly different in activity than the control corn oil.

In corn oil emulsion, the same trends were observed with the mixtures as with the individual antioxidants tested alone. The α-tocopherol–ascorbyl palmitate mixture was more effective than the α-tocopherol–ascorbic acid mixture after 4 days of oxidation (Figure 6a). Both mixtures were better than α-tocopherol alone. Ascorbic acid alone showed the same prooxidant effect as observed previously (Figure 4a). The same order of activity was observed on the basis of hexanal formation as with hydroperoxide formation (Figure 6b).

Conclusions. The hydrophilic antioxidants Trolox and ascorbic acid were more effective in corn oil than the corresponding lipophilic α-tocopherol and ascorbyl palmitate. The reverse trend was evident in corn oil-in-water emulsions. On the basis of hydroperoxide formation, 232 μM α-tocopherol was more effective than 1161 μM α-tocopherol in both bulk oil and oil emulsion. However, on the basis of hexanal formation, the reverse trend was observed. On the basis of hydroperoxide formation, ascorbic acid was more effective and ascorbyl palmitate was less effective than α-tocopherol at the same molar concentration in corn oil. The reverse trend was observed in emulsified corn oil. However, on the basis of hexanal formation, the effectiveness of these antioxidants in corn oil decreased in the order α-tocopherol, ascorbic acid, ascorbyl palmitate. In emulsified corn oil, ascorbyl palmitate was as effective as α-tocopherol, and both were more effective than ascorbic acid.

DISCUSSION

The results of this study may be largely explained on the basis of interfacial phenomena having a significant effect on oxidative stability of lipid systems. The mechanism of this process may be related to the affinities of the antioxidants toward the air–oil interfaces in bulk oil and the water–oil interfaces in emulsions. Thus, in the corn oil system, the hydrophilic antioxidants may be more protective against oxidation by being oriented in the air–oil interface. The lipophilic antioxidants are apparently less protective by remaining in solution in the oil. Our observation that ascorbic acid in suspension is particularly active as an antioxidant in bulk oil is remarkable, but not

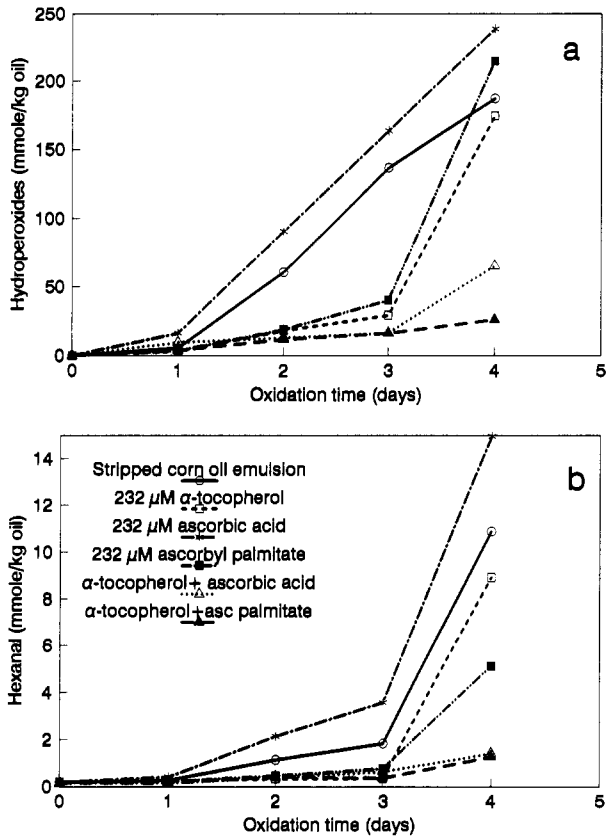

Figure 6. Effect of α-tocopherol, ascorbic acid, ascorbyl palmitate, and mixtures of α-tocopherol and ascorbyl palmitate on the oxidative stability of stripped corn oil-in-water emulsion at 60 °C: (a) hydroperoxide formation, same legend as (b); (b) hexanal formation.

new. According to Uri (1961), low solubility with a good antioxidant is no disadvantage if the rates of diffusion or dissolution are not determining factors. In the bulk oil system, the partially soluble suspended ascorbic acid may in fact be more favorably oriented at the air–oil interface where surface oxidation occurs.

In contrast, in the oil-in-water emulsion system, lipophilic antioxidants are sufficiently surface active to be oriented in the oil–water interface to better protect oil against oxidation. By moving to the water phase the hydrophilic antioxidants become diluted 10-fold and cannot adequately protect the oil in the oil–water interface. According to this mechanism, hydroperoxide formation and decomposition in emulsion systems are dependent on the effective concentrations of antioxidants in the oil and water phases and the interface. We are currently investigating these reaction parameters to provide the physical–chemical basis needed to explain the so-called polar paradox (Porter, 1980, 1993; Porter et al., 1989) that oil-soluble antioxidants are better in emulsions than in oils and water-soluble anitoxidants are better in oils than in emulsion systems.

α-Tocopherol has been shown to have a prooxidant effect at high concentrations on the basis of methods measuring hydroperoxide formation (Frankel et al., 1959; Cillard et al., 1980; Peers et al., 1981; Terao and Matsushita, 1986; Jung and Min, 1990). However, the present work showed that α-tocopherol has antioxidant activity at 1161 μM based on hexanal formation (Figure 1b), but it has prooxidant activity based on hydroperoxide formation (Figure 1a). Previously, α-tocopherol at high concentrations was shown to produce significant shifts in formation and distribution of volatile products by thermal decomposition of methyl linoleate hydroperoxides (Frankel and Gardner, 1989). Thus, in evaluations of antioxidants, further studies are needed to distinguish between their effects in inhibiting hydroperoxide formation and their effects in preventing their decomposition.

Assuming that hexanal determinations, which measure the decomposition of hydroperoxides, are more closely related to flavor deterioration than measurements of hydroperoxide formation, the results in Figure 1b imply that high concentrations of α-tocopherol may be desirable for flavor stability. In relation to flavor deterioration due to lipid oxidation, the effects of antioxidants in inhibiting hydroperoxide decomposition may have more practical implications than their effects in preventing hydroperoxide formation. The relationship of hexanal *vs* hydroperoxide formation to flavor deterioration needs, of course, to be substantiated by sensory testing.

ABBREVIATIONS USED

Trolox, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid; TBHQ, *tert*-butylhydroquinone [2-bis(1,1-dimethylethyl)-4-hydroxyphenol]; BHT, *tert*-butylhydroxytoluene [2-bis(1,1-dimethylethyl)-4-methylphenol]; BHA, *tert*-butylhydroxylanisole (2-/3-*tert*-butyl-4-methoxyphenol); AOM, active oxygen method; HLB, hydrophilic–lipophilic balance; HPLC, high-performance liquid chromatography; GC, gas chromatography; Tween 20, polyoxyethylene sorbitan monolaurate.

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