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Inhibition of Citral Degradation by Oil-in-Water Nanoemulsions Combined with Antioxidants

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ABSTRACT: The aim of the present study was to investigate the effects of oil-in-water (O/W) nanoemulsions combined with six different natural antioxidants on the stability of citral. Acidic emulsions (lecithin-stabilized palm kernel lipid in pH 3 buffer) containing 1000 ppm citral and 1000 ppm antioxidants (black tea extract, ascorbic acid, naringenin, tangeretin, β-carotene, and tanshinone) were stored at 25 and 50 °C, respectively. The emulsions with and without antioxidants were analyzed by solid phase microextraction gas chromatography (SPME-GC) to monitor the degradation process of citral and the formation of different off-flavor compounds, such as α,*p*-dimethylstyrene and *p*-methylacetophenone. The results suggested that encapsulation of citral in emulsions and the addition of the appropriate antioxidants (β-carotene, tanshinone, and black tea extract) could greatly enhance citral's chemical stability during storage.

KEYWORDS: citral degradation, oil-in-water nanoemulsions, antioxidant

INTRODUCTION

Citral is an α,β-unsaturated aldehyde with one additional double bond. Both of its two isomers, neral and geranial, can easily undergo a series of degradation reactions, especially under low-pH condition and with the presence of oxygen.[1] Degradation of citral will lead to loss of the lemon-like aroma and the production of various off-flavor compounds,[2] which limits its application in the food and cosmetic industries. The degradation mechanism is still not completely understood. Previous studies[3−5] proposed that the reaction under acidic aqueous condition started from isomerization of geranial to neral, which then underwent cyclization to form monoterpene alcohols, such as *p*-menthadien-8-ol and/or *p*-menthadien-4-ol. Oxidation of these intermediate compounds then took place to produce *p*-cymene-8-ol and its dehydration products α,*p*-dimethylstyrene, *p*-cymene, and *p*-cresol. α,*p*-Dimethylstyrene was suggested to be responsible for the formation of another major off-odor compound, *p*-methylacetophenone.[3] Among all of these compounds, *p*-cresol, *p*-methylacetophenone, and *p*-cymene are the most potent off-odorants, with phenolic, gasoline-like and bitter almond-like odors; thus, these three molecules are often used as indicators for the assessment of citral degradation.[1]

Improving the stability of citral, especially at low-pH aqueous condition, has challenged the food industry for decades and is a long-standing industry need. Conventional methods to inhibit citral degradation are to increase the product pH values and to reduce the storage temperature and environmental oxygen. However, these methods are not always practical. Therefore, new strategies are needed to prevent citral from degrading.[6] Numerous works have been made to stabilize citral by encapsulating it in the form of an emulsion because encapsulation could isolate the active compound (i.e., citral) from the reactive species in the aqueous medium, such as protons and free radicals. For example, Choi et al.[7] encapsulated citral in both medium-chain triacylglycerols emulsion droplets and triacetin microemulsion droplets, and the results showed great improvement of citral's stability when stored at 20 °C under acidic condition (pH 3.0). Mei et al.[8] evaluated the stability of citral in oil-in-water emulsions at pH 3.0 with solid and liquid octadecane, and it was found that citral's stability could be improved in oil-in-water emulsions.

Antioxidants have also been used to inhibit citral's degradation and reduce the generation of the off-flavor compounds, such as *p*-cymene and *p*-cresol. Kimura et al.[5] attempted to inhibit the formation of undesirable off-flavors produced by citral in acidic aqueous solution by the use of butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), *n*-propyl gallate, α-tocopherol, nordihydroguaiaretic acid, and *n*-tritriacontane-16,18-dione. However, these compounds were found to be not effective in reducing the production of oxidative products from citral. In contrast, Liang et al.[9] showed that the antioxidative phenolic compounds (from grape seed, pomegranate seed, and green tea and black tea extracts, respectively) were able to inhibit the formation of *p*-cymene, *p*-cresol, *p*-methylacetophenone, and 8-hydroperoxy-*p*-cymene from citral degradation at pH 3.0. Ueno et al.[10] also discovered the inhibitory effects of black tea theaflavins on the formation of *p*-cresol and *p*-methylacetophenone for citral in acidic buffer solutions at pH 3.0. Peacock and Kuneman[4] used isoascorbic acid to inhibit the formation of α,*p*-dimethylstyrene and *p*-cymen-8-ol in a carbonated beverage system containing citral.

All of these studies were conducted in acidic aqueous buffers, and no work has been done to investigate the inhibition of citral degradation in an emulsion system by antioxidants. Therefore, the objectives of this research were to use oil-in-water (O/W) nanoemulsions to encapsulate citral and evaluate the effects of several antioxidants on the reduction of citral degradation rate.

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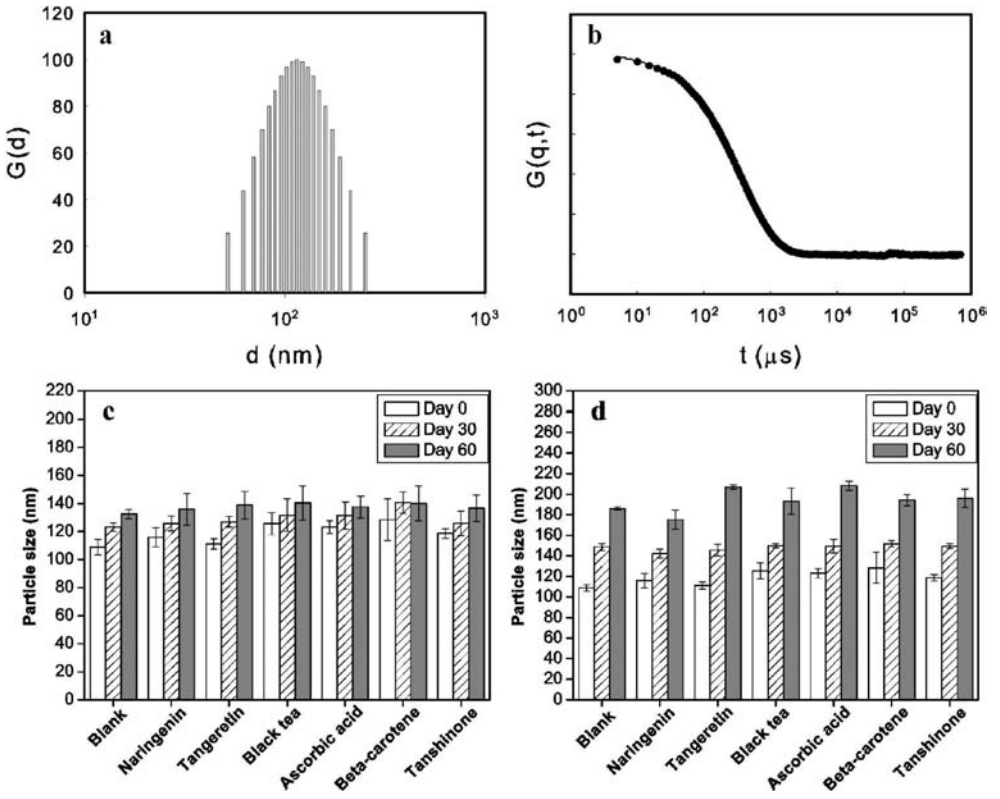

Figure 1. Representative photon correlation spectroscopy (PCS) results of emulsions analyzed by (a) cumulant analysis and (b) single stretched exponential fit method as well as the mean particle diameter changes for citral-loaded emulsions with and without antioxidants stored under (a) 25 °C and (b) 50 °C. Data represent the mean ± standard deviation (n = 3).

In this research, six commercially available antioxidants were selected (black tea extract, ascorbic acid, naringenin, tangeretin, β-carotene, and tanshinone) on the basis of their excellent oxygen and/or free radical scavenging activities.[4,10−13]

MATERIALS AND METHODS

Materials. Palm kernel fat was a gift from Firmenich (Princeton, NJ). Alcolec PC 75 soy lecithin containing 75% phosphatidylcholine was a gift from American Lecithin Co. (Oxford, CT). Narigenin, tangeretin, and tanshinone were purchased from Quality Phytochemicals, LLC (Edison, NJ). Black tea extract standardized to 30% theaflavins was a gift from Wellgen (New Brunswick, NJ). All other chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification.

Emulsion Preparation. The oil-in-water (O/W) nanoemulsion was prepared according to a hot homogenization method.[14] Ten weight percent palm kernel fat was heated to 45 °C when completely melted into liquid; 0.1 wt % citral and 0.01 wt % undecane (as the internal standard) were dissolved in the lipid phase and mixed with 5 wt % lecithin aqueous buffer solution (10 mM citric acid/sodium hydroxide/sodium chloride, pH 3.0, buffer) at the same temperature by using an Ultra-Turrax T-25 homogenizer (IKA Works Inc., Wilmington, DE) for 5 min to obtain a coarse emulsion. The coarse emulsion was then homogenized by using a high-pressure homogenizer (EmulsiFlex-C3, Avestin Inc., Ottawa, Canada) for six cycles at the pressure of 150 MPa. The temperature was kept at 45 °C during the whole sample preparation process to avoid lipid crystallization.

Incorporation of Antioxidants with Citral in Emulsions. Due to the antioxidants' different solubility, they were encapsulated in the emulsions with citral together as follows: 0.1 wt % ascorbic acid was dissolved in the surfactant aqueous buffer solution before mixing with the lipid phase; 0.1 wt % beta-carotene and tanshinone were dissolved in the melted palm kernel fat with citral, respectively; 0.1 wt % naringenin, tangeretin and black tea extract were dispersed in 2 wt % polyether glycol by vortex for 5 min and then mixed with the melted lipid with citral together, respectively. Then high speed and high pressure homogenizers were used to produce homogeneous emulsions as described above. Citric acid was added when necessary to maintain the pH value (pH 3.0) of all the samples (citral loaded emulsions with and without antioxidants). Ten mL of each emulsion sample was stored in a 20 mL amber glass vial with 10 mL headspace. All the samples were divided into two groups, with one group stored at 25 °C and the other group stored at 50 °C.

Physical Stability of Emulsions. The physical stability of all samples was evaluated by measuring their particle size changes at different storage temperatures (25 and 50 °C) with time. The particle sizes were measured by a photon correlation spectroscopy (PCS)-based BIC 90 plus particle size analyzer equipped with a Brookhaven BI-9000AT digital correlator (Brookhaven Instrument Corp., New York). The light source of the particle size analyzer is a solid state laser operating at 658 nm with 30 mW power, and the signals were detected by a high-sensitivity avalanche photodiode detector. All measurements were made at a fixed scattering angle of 90° and a temperature of 25.0 ± 0.1 °C. Two methods were used to analyze the autocorrelation function $G(q, t)$ data obtained from the PCS measurements. The first one was the cumulant analysis method, where $G(q, t)$ was decomposed into a distribution of the decay rate $\Gamma = 1/\tau$ given by

$$G(q,t) = \int G(\Gamma) \exp(-\Gamma t)\, d\Gamma \quad (1)$$

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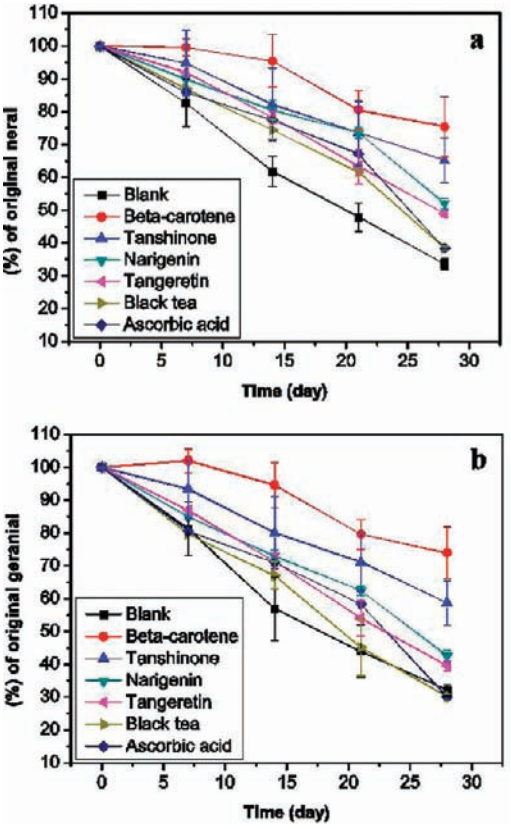

Figure 2. Degradation of (a) neral and (b) geranial in emulsions with and without different antioxidants stored at 25 °C.

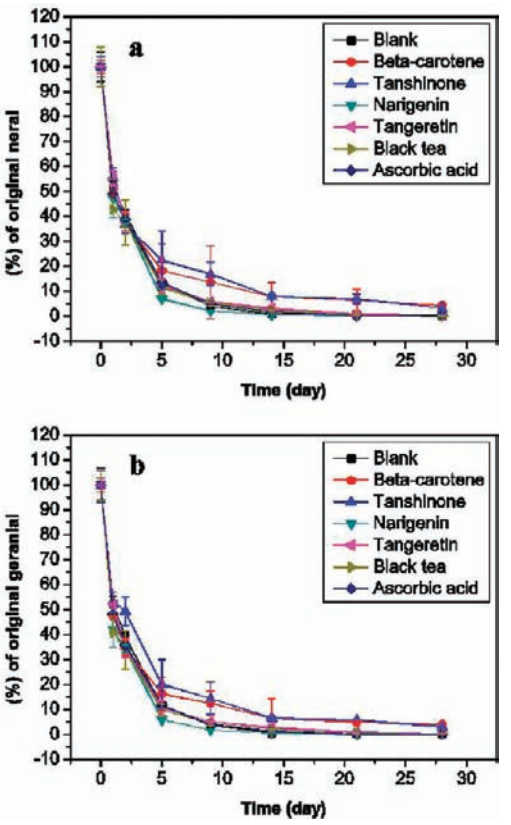

Figure 3. Degradation of (a) neral and (b) geranial in emulsions with and without different antioxidants stored at 50 °C.

The second method was the William−Watts (WW) single stretched exponential function given by

$$G(q,t) = \exp[-(t/\tau)^{\beta}] \quad (2)$$

where τ is the relaxation time and β is the distribution parameter.

Then the particle diffusion coefficient D could be calculated as

$$D = 1/\tau q^2 \quad (3)$$

where q is the amplitude of scattering vector defined as

$$q = (4\pi n/\lambda)\sin(\theta/2) \quad (4)$$

where n is the solution refractive index, λ is the laser wavelength, and θ is the scattering angle. The diffusion coefficient D can be converted into mean particle diameter d using the Stokes−Einstein equation

$$d = kT/3\pi\eta D \quad (5)$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity.

Measurement of Citral. Analyses of citral and its degradation products were conducted on an Agilent 6850 gas chromatography equipped with a J&W DB-5MS capillary column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) and a flame ionizing detector (FID). The oven temperature was increased from 60 to 150 °C at 4 °C/min, then increased to 230 °C at 20 °C/min, and held at 230 °C for 5 min. The gas flow was controlled as follows: hydrogen flow at 40.0 mL/min, air flow at 45.0 mL/min, and helium as carrier gas flow at 45.0 mL/min. FID detector temperature was 250 °C.

A 0.75 mm i.d. solid phase microextraction (SPME) injection sleeve was employed to minimize the broadening effect compared to a 2.0 mm injection glass liner. For SPME analysis, 10 mL of each emulsion sample was stored in a 20 mL amber glass vial containing a magnetic stir bar under stirring. The glass vial was sealed with a polytetrafluoroethylene (PTFE)/silicone speta and a screw cap. The 65 μm PDMS−DVB (polydimethylsiloxane−divinylbenzene) SPME fiber was exposed to the sample headspace manually for 30 min at 25 °C (for the 25 °C storage samples) and at 50 °C (for the 50 °C storage samples), respectively. After the absorption process, the fiber was inserted immediately into the injection port of the GC and held for 5 min to ensure a complete thermal desorption. The quantification of citral and the degradation products was analyzed by computing their peak areas versus the internal standard (undecane) peak area.

GC−Mass Analysis of Citral's Degradation Products. An Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass detector and a J&W DB-5MS capillary column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) was used. The gas flow was controlled as follows: hydrogen flow at 40.0 mL/min, air flow at 45.0 mL/min, and nitrogen flow 45.0 mL/min. The injection port was kept at 230 °C. The oven temperature was increased from 60 to 150 °C at 4 °C/min, then increased to 230 °C at 20 °C/min, and held at 230 °C for 5 min. The ionization voltage was held at 70 eV, and the ion temperature was 280 °C.

Statistical Analysis. All experiments were conducted twice in duplicate, and all data were expressed as the mean ± standard deviation. When appropriate, data were analyzed using t-test and analysis of variance ($P < 0.05$) by SPSS software (SPSS, Inc., Chicago, IL).

RESULTS AND DISCUSSION

Physical Stability of Citral-Loaded Emulsions with and without Antioxidants. Particle sizes of the citral-loaded emulsions (with and without antioxidants) were measured at days 0, 30, and 60 during storage under 25 and 50 °C, respectively. The

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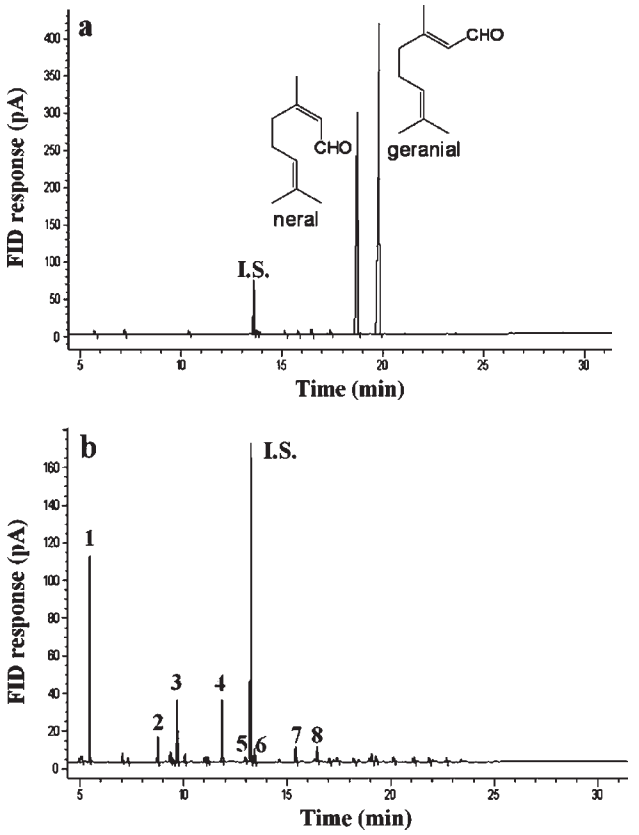

Figure 4. Representative gas chromatogram of encapsulated citral under acidic condition (pH 3.0) stored under 50 °C (a) at day 0 and (b) at day 28. Numbers correspond to those in Table 1. Undecane was used as the internal standard (I.S.).

representative PCS cumulant analysis and single stretched exponential fit results are shown in panels a and b, respectively, of Figure 1. Comparable particle sizes could be obtained from both data analysis methods (difference < 10%); therefore, particle sizes calculated from the cumulant method were used for different emulsion formulations during storage as shown in Figure 1c,d. Freshly made emulsions had particle sizes between 109 and 129 nm at day 0, whereas samples without antioxidant had the smallest size and the incorporation of different antioxidants increased the particle size. Due to the density difference between the lipid phase and the aqueous medium, lipid particles showed the tendency to grow due to creaming or sedimentation.[15] In this study, the particle sizes increased slightly during storage. The particle size for the emulsions stored at 25 °C showed an increment between 10 and 20 nm; because the particles moved more rapidly at higher temperature, the size increment for samples stored at 50 °C was ~70−80 nm. No obvious phase separation or creaming was observed for any of the emulsion samples, even at high storage temperature (50 °C). Therefore, the results proved that very small particles possessed kinetic stability,[16] especially at relatively lower temperature (25 °C in this study), and the emulsion formulations in this study showed excellent physical stability to avoid creaming.

Stability of Citral in Emulsions with and without Antioxidants. The stability of citral was evaluated by calculating the loss of both its two isomers (neral and geranial) during storage at different temperatures. Both neral and geranial showed similar degradation trends at 25 and 50 °C, respectively (Figures 2 and 3). At

Table 1. Degradation Products Formed from Citral-Loaded Emulsions Stored at 50 °C for 28 Days

compd no.[a]	compd name	ID method[b]
1	2-heptanone	A
2	1-octen-3-ol	A
3	δ-2-carene	A
4	*p*-cresol	B
5	α,*p*-dimethylstyrene	B
6	butanoic acid	A
7	*p*-mentha-1,5-dien-8-ol	B
8	*p*-methylacetophenone	B

[a] Numbers correspond to those in Figure 4. [b] Compounds were identified on the basis of the following criteria: A, mass spectrum agrees with that of Wiley mass spectral database and the compounds can only be considered as "tentatively identified"; B, mass spectrum and retention index agree with those of authentic compounds purchased from Sigma-Aldrich (St. Louis, MO).

25 °C, 33.5% neral and 32.1% geranial were left in the emulsion without antioxidant after 28 days, whereas 0.225% neral and 0.235% geranial were left in the same formulation at 50 °C after 28 days. It can be clearly seen that at low temperature the incorporation of certain antioxidants could slow citral (both neral and geranial) degradation. Compared to the blank sample (emulsion without antioxidant), almost 2 times the amount of citral was left in the formulations with β-carotene and tanshinone, respectively. For instance, citral degradation was not observed for the formulation with β-carotene for the first week; there were still 95.5% neral and 94.6% geranial left after 2 weeks; and 75.4% neral and 74.0% geranial remained in the sample at the end of the measurement (4 weeks). As for the emulsion with tanshinone stored at 25 °C, 65.2% neral and 58.7% geranial remained in the sample at the end of the measurement (4 weeks). Several previous studies also evaluated the capabilities of various emulsions to inhibit citral degradation. For example, Choi et al.[17] discovered the dependence of citral's degradation rates on different surfactant types, and Djordjevic et al.[18] proved the ability of whey protein isolate (WPI) as the emulsifier to inhibit the oxidative deterioration of citral. Due to different test conditions, such as GC measurement methods, storage temperatures, and pH values of the samples, it is difficult to compare different works directly. The formulations used in this research may have better performance to inhibit citral's degradation compared to other's work. For example, at similar storage conditions (pH 3.0, 20 °C, and 29 days) in the work of Mei et al.,[8] >90% of citral degraded in the sodium dodecyl sulfate (SDS) stabilized liquid octadecane emulsion, whereas >50% of citral degraded in the Brij 35 (polyoxyethylene lauryl ether) stabilized liquid octadecane. The performances of the other four antioxidants, narigenin, tangeretin, black tea extract, and ascorbic acid, were between the blank sample (emulsion without antioxidant) and the emulsions with β-carotene and tanshinone, although their effects to inhibit citral degradation were not as significant as those of β-carotene and tanshinone. Furthermore, no obvious off-flavor products produced from citral, such as *p*-cresol and α,*p*-dimethylstyrene, were detected for any of the formulations (both with and without antioxidants) stored under 25 °C for 4 weeks (data not shown).

The high-temperature (50 °C) storage samples were also measured by GC to evaluate citral's stability as well as the generation of

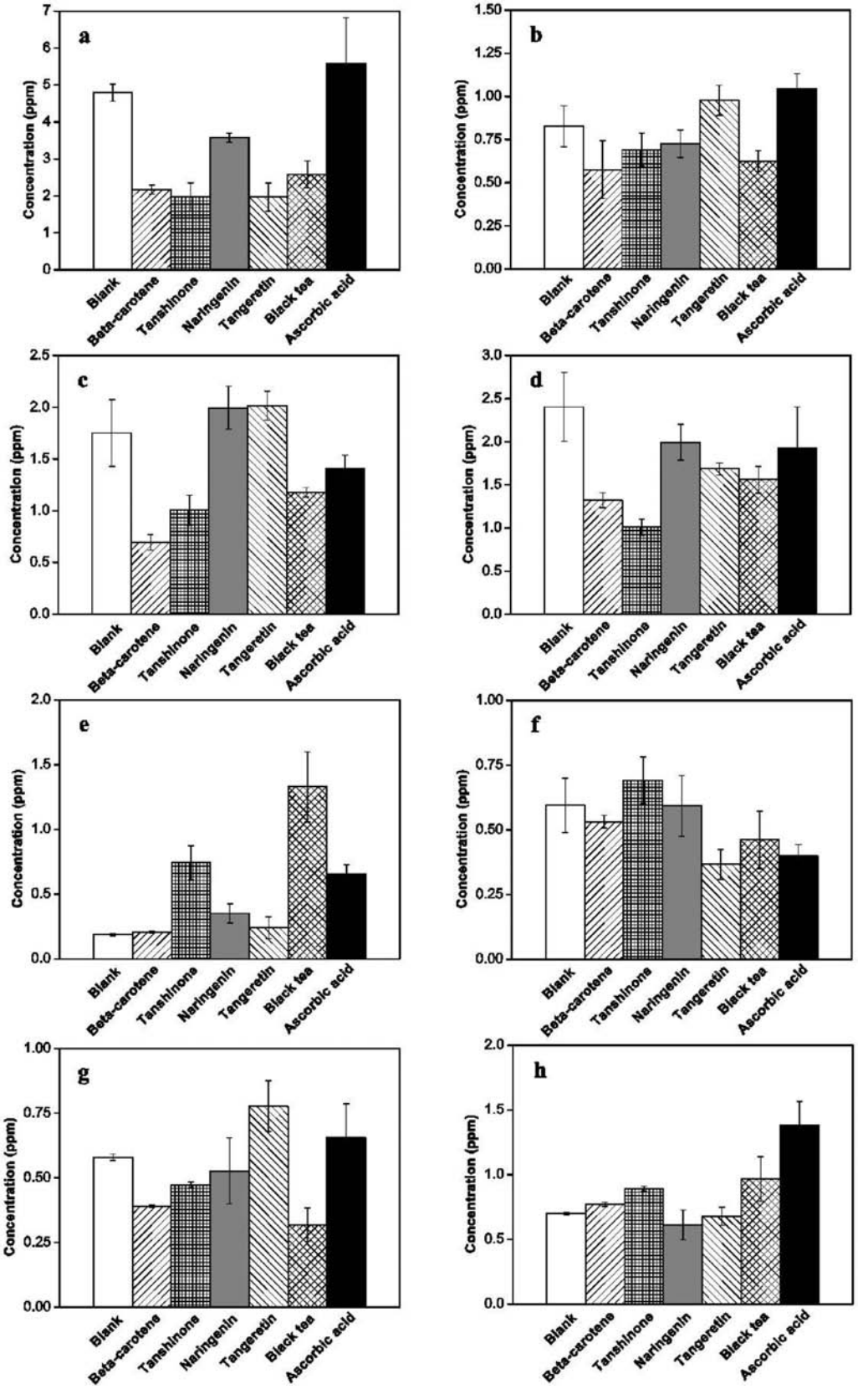

Figure 5. Concentrations of all the major degradation compounds from citral-loaded emulsions stored at 50 °C for 4 weeks: (a) 2-heptanone; (b) 1-octen-3-ol; (c) δ-2-carene; (d) *p*-cresol; (e) α,*p*-dimethylstyrene; (f) butanoic acid; (g) *p*-mentha-1,5-dien-8-ol; (h) *p*-methylacetophenone.

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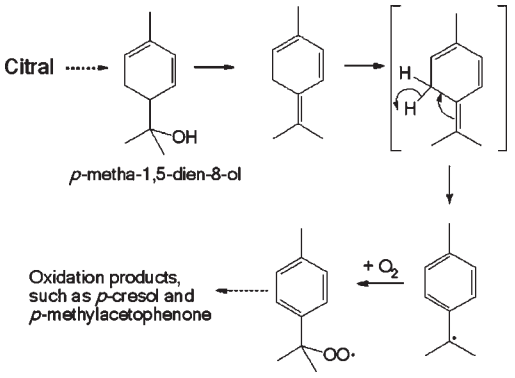
Scheme 1. Previously Proposed Free Radical and Oxidation Products Formed from Citral[2]



possible off-flavor compounds (Figure 3). As expected, citral degraded much more quickly for all of the formulations stored at 50 °C than for those stored at 25 °C; therefore, it is difficult to differentiate between various formulations. For example, about 50% of both neral and geranial was lost for all samples after only 1 day, and almost no citral was left in them after 4 weeks of storage at 50 °C. Because the purpose of the high-temperature storage measurements was to evaluate the production of off-flavor compounds from the citral-loaded emulsions, the results will be shown in the next section.

Evaluation of Off-Flavor Compounds for Citral-Loaded Emulsions. During storage at 50 °C for 4 weeks, citral was completely degraded as shown in Figure 4 and Table 1. The major products generated from citral-loaded emulsions could be divided into two groups. One was the commonly detected citral degradation products, such as *p*-cresol (peak 4), α,*p*-dimethylstyrene (peak 5), *p*-mentha-1,5-dien-8-ol, and *p*-methylacetophenone (peaks 7 and 8). The most significant point is that most of the citral degradation products[4,5,9] cannot be detected in all of the emulsion formulations, such as *p*-cymene, *p*-cymen-8-ol, 8-hydroperoxy-*p*-cymene, and many monoterpene alcohols. Besides, among four of the detected compounds mentioned above, only *p*-mentha-1,5-dien-8-ol is the acid-catalyzed reaction product, and all the others are oxidation products.[10] Therefore, the encapsulation of citral in emulsions effectively inhibited its degradation, especially the acid-catalyzed reactions. The reason is that citral could be isolated from the protons in the aqueous medium after encapsulation, which proves to be a useful way to reduce the acid-catalyzed reactions. The other group was the lipid degradation products, such as 2-heptanone, 1-octen-3-ol, and butanoic acid (peaks 1, 2, and 6) (Figure 4 and Table 1). The generation of these compounds is inevitable due to the presence of lipid and phospholipids (palm kernel fat and lecithin) in the emulsions. Although the study of lipid oxidation is beyond the scope of this research, the effects of antioxidants on the production of all the major emulsion degradation products will be discussed in this section.

The effects of the six antioxidants on the formation of all the major degradation products showed different and complicated results (Figure 5). For example, β-carotene inhibited the production of compounds **1**−**4** and **7**, whereas similar concentration levels of compounds **5**, **6** and **8** were found; tanshinone inhibited the production of compounds **1**, **3**, **4**, and **7** and promoted the production of compounds **5** and **8**, whereas similar concentration levels of compounds **2** and **6** were found; black tea extract inhibited the production of compounds **1**−**4**, **6**, and **7**, whereas it promoted the production of compounds **5** and **8**; ascorbic acid was the worst among all of the antioxidants due to its promotion effect on compounds **1**, **2**, **5**, **7**, and **8**, and it only slightly inhibited the production of compounds **3**, **4**, and **6**. In general, β-carotene, tanshinone, and black tea extract did well to inhibit both citral and lipid degradation; the performances of the two citrus flavonoids, naringenin and tangeretin, fluctuated with the production of different compounds; although ascorbic acid is an excellent antioxidant with good metal chelating capability, it was the worst used in the emulsion formulation because it promoted the production of most of the degradation products.

Previous studies[9,10] also found that the use of antioxidants (phenolic plant extracts and pure catechins) could inhibit the generation of several citral off-odor compounds, such as *p*-methylacetophenone and *p*-cresol. However, the production of monoterpene alcohols, *p*-cymen-8-ol and α,*p*-dimethylstyrene, were greatly induced. Although details of citral degradation and how the antioxidants work are still not fully understood, it is generally accepted that there are free radicals produced during citral degradation as well as lipid oxidation, especially at high temperature. For example, it was suggested[2] that *p*-mentha-1,5-dien-8-ol produced from citral could undergo dehydration and subsequent isomerization to form an intermediate compound, *p*-mentha-1,4(8),5-triene, which soon resulted in the generation of a peroxy radical to facilitate the production of other oxidation products, such as *p*-methylacetophenone and *p*-cresol (Scheme 1). Lipid oxidation has been widely studied for many years, and it is known that the generation of highly reactive peroxyl and alkoxyl radicals and other pro-oxidants is responsible for lipid oxidation in emulsion systems.[19] It has been widely reported that the addition of antioxidants into emulsions could retard lipid oxidation through inactivating free radicals, scavenging oxygen, and other oxidative molecules.[20,21]

In this study, β-carotene and tanshinone had better performance than the others probably due to their extremely nonpolar characteristics, because it has been stated that nonpolar lipophilic antioxidants are more effective in emulsions than the polar hydrophilic antioxidants.[19] Ascorbic acid was the worst antioxidant in this study due to many possibilities: first, it is the most polar compound, with very high water solubility among the six antioxidants; when both citral and lipid oxidation happened inside or in the interfacial region of the emulsion droplet, it is within expectation that water-soluble antioxidant is much less effective to inhibit the degradation reactions. Second, the hydroxyl group in ascorbic acid behaves like an acid, which may further promote the production of *p*-menthadien-8-ols and *p*-mentha-1,4(8),5-triene and the following dehydration and/or oxidation reactions. Third, the ascorbate anion radical may have a lower reduction potential than the other antioxidants.[22] Black tea extract is rich in various theaflavins, and besides its inhibition effect on most of the citral degradation products, it greatly promoted the production of α,*p*-dimethylstyrene, which agreed well with previous study.[10] It was reported that theaflavins could produce a quinine compound (theanaphthoquinone), which might be involved in the dehydrogenation of *p*-mentha-1,4(8),5-triene. The two citrus flavonoids, naringenin and tangeretin, were not good enough to protect either citral or lipid compared to β-carotene, tanshinone, and black tea extract (Figure 5). Although they are also phenolic compounds like theaflavins, they have much simpler structures with less substituted moieties. Very little research has been done to reveal the antioxidant activities of both

naringenin and tangeretin related with citral or lipid oxidation; therefore, further study is needed to investigate the mechanisms of how the flavonoids work to influence the flavor and/or lipid degradation pathways.

In summary, oil-in-water nanoemulsions were used to encapsulate citral, and the effects of six different antioxidants (β-carotene, tanshinone, naringenin, tangeretin, black tea extract, and ascorbic acid) on citral's chemical stability under acidic condition (pH 3.0) were evaluated. On the basis of the current research results, encapsulation of citral in O/W nanoemulsions could improve its chemical stability and reduce the production of many off-flavor compounds. For example, *p*-cymene and most of the monoterpene alcohols were completely suppressed. In addition, the incorporation of the appropriate antioxidants (i.e., β-carotene, tanshinone, and black tea extract) with citral together could further inhibit citral degradation as well as lipid oxidation. Future work is needed to study the mechanisms of how encapsulation and antioxidants work to increase citral's stability. The knowledge might be promising in the design of new strategies to improve the stability for many sensitive flavor molecules as well as to reduce lipid deterioration in food emulsions.

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REFERENCES

(1) Schieberle, P.; Grosch, W. Identification of potent flavor compounds formed in an aqueous lemon oil/citric acid emulsion. *J. Agric. Food Chem.* **2002**, *36*, 797–800.

(2) Ueno, T.; Masuda, H.; Ho, C.-T. Formation mechanism of *p*-methylacetophenone from citral via a *tert*-alkoxy radical intermediate. *J. Agric. Food Chem.* **2004**, *52*, 5677–5684.

(3) Schieberle, P.; Ehrmeier, H.; Grosch, W. Aroma compounds resulting from the acid catalyzed breakdown from citral. *Z. Lebensm. Unters. Forsch.* **1988**, *187*, 35–39.

(4) Peacock, V. E.; Kuneman, D. W. Inhibition of the formation of α-*p*-dimethylstyrene and *p*-cymen-8-ol in a carbonated citral-containing beverage system. *J. Agric. Food Chem.* **2002**, *33*, 330–335.

(5) Kimura, K.; Nishimura, H.; Iwata, I.; Mizutani, J. Deterioration mechanism of lemon flavor. 2. Formation mechanism of off-odor substances arising from citral. *J. Agric. Food Chem.* **1983**, *31*, 801–804.

(6) Djordjevic, D.; Cercaci, L.; Alamed, J.; McClements, D. J.; Decker, E. A. Chemical and physical stability of citral and limonene in sodium dodecyl sulfate-chitosan and gum arabic-stabilized oil-in-water emulsions. *J. Agric. Food Chem.* **2007**, *55*, 3585–3591.

(7) Choi, S. J.; Decker, E. A.; Henson, L.; Popplewell, L. M.; McClements, D. J. Stability of citral in oil-in-water emulsions prepared with medium-chain triacylglycerols and triacetin. *J. Agric. Food Chem.* **2009**, *57*, 11349–11353.

(8) Mei, L.; Choi, S. J.; Alamed, J.; Henson, L.; Popplewell, M.; McClements, D. J.; Decker, E. A. Citral stability in oil-in-water emulsions with solid or liquid octadecane. *J. Agric. Food Chem.* **2009**, *58*, 533–536.

(9) Liang, C. P.; Wang, M.; Simon, J. E.; Ho, C.-T. Antioxidant activity of plant extracts on the inhibition of citral off-odor formation. *Mol. Nutr. Food Res.* **2004**, *48*, 308–317.

(10) Ueno, T.; Kiyohara, S.; Ho, C. T.; Masuda, H. Potent inhibitory effects of black tea theaflavins on off-odor formation from citral. *J. Agric. Food Chem.* **2006**, *54*, 3055–3061.

(11) Tournaire, C.; Croux, S.; Maurette, M.-T.; Beck, I.; Hocquaux, M.; Braun, A. M.; Oliveros, E. Antioxidant activity of flavonoids: efficiency of singlet oxygen ($^1\Delta_g$) quenching. *J. Photochem. Photobiol. B: Biol.* **1993**, *19*, 205–215.

(12) Sies, H.; Stahl, W. Vitamins E and C, β-carotene, and other carotenoids as antioxidants. *Am. J. Clin. Nutr.* **1995**, *62*, 1315S–1321S.

(13) Weng, X. C.; Gordon, M. H. Antioxidant activity of quinones extracted from tanshen (*Salvia miltiorrhiza* Bunge). *J. Agric. Food Chem.* **1992**, *40*, 1331–1336.

(14) Schwarz, C.; Mehnert, W.; Lucks, J. S.; Mueller, R. H. Solid lipid nanoparticles (SLN) for controlled drug delivery. I. Production, characterization and sterilization. *J. Controlled Release* **1994**, *30*, 83–96.

(15) Sjöblom, J. *Emulsions and Emulsion Stability*, 2nd ed.; CRC Press: Boca Raton, FL, 2006; Vol. 132.

(16) Tadros, T.; Izquierdo, P.; Esquena, J.; Solans, C. Formation and stability of nano-emulsions. *Adv. Colloid Interface Sci.* **2004**, *108−109*, 303–318.

(17) Choi, S. J.; Decker, E. A.; Henson, L.; Popplewell, L. M.; McClements, D. J. Influence of droplet charge on the chemical stability of citral in oil-in-water emulsions. *J. Food Sci.* **2010**, *75*, C536–C540.

(18) Djordjevic, D.; Cercaci, L.; Alamed, J.; McClements, D. J.; Decker, E. A. Stability of citral in protein- and gum arabic-stabilized oil-in-water emulsions. *Food Chem.* **2008**, *106*, 698–705.

(19) McClements, D. J.; Decker, E. A. Lipid oxidation in oil-in-water emulsions: impact of molecular environment on chemical reactions in heterogeneous food systems. *J. Food Sci.* **2000**, *65*, 1270–1282.

(20) Decker, E. A., Antioxidant mechanisms. In *Food Lipids: Chemistry, Nutrition and Biotechnology*; Akoh, C. C., Min, D. B., Eds.; Dekker: New York, 1998; pp 397−421.

(21) Reische, D. W.; Lillard, D. A.; Eitenmiller, R. R. Antioxidants. In *Food Lipids: Chemistry, Nutrition and Biotechnology*; Akoh, C. C., Min, D. B., Eds.; Dekker: New York, 1998; pp 423−448.

(22) Williams, N. H.; Yandell, J. K. Outer-sphere electron-transfer reactions of ascorbate anions. *Aust. J. Chem.* **1982**, *35*, 1133–1144.