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Inhibition of citral degradation in model beverage emulsions using micelles and reverse micelles

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ABSTRACT

Citral is a flavour component that is widely used in the beverage, food, and fragrance industries. Citral chemically degrades over time in aqueous solutions due to acid catalysed and oxidative reactions, leading to loss of desirable flavour and the formation of off-flavours. We examined the influence of surfactant micelles (Tween 80) in the aqueous phase and reverse micelles (polyglycerol polyricinoleate, PGPR) in the oil phase on the oil–water partitioning and chemical degradation of citral in medium chain triglyceride oil-in-water emulsions. The percentage of citral in the aqueous phase of the emulsions increased with increasing Tween 80 concentration, which was attributed to its incorporation within surfactant micelles. The rate of citral degradation decreased as the Tween 80 concentration was increased from 1% to 5% w/w in both aqueous solutions and in emulsions, suggesting that citral was protected from degradation once it was incorporated into micelles. The presence of reverse micelles (5% or 10% w/w PGPR) in the oil droplets decreased the percentage of citral present within the aqueous phase of the emulsions, suggesting that citral was preferentially incorporated into the reverse micelles. In addition, the presence of reverse micelles increased the chemical stability of citral, possibly because a greater fraction remained within the oil droplets. These results show that micelle or reverse-micelle structures may be used to improve the chemical stability of citral in beverage emulsions.

1. Introduction

Citral (3,7-dimethyl-2,6-octadienal) is one of the most important flavour compounds in citrus oils, which are widely used in foods and beverages, such as soft drinks and deserts. Citral is a monoterpene aldehyde that is composed of a mixture of two geometric *cis*- and *trans*-isomers, geranial and neral in a 3:2 ratio (Schieberle & Grosch, 1988a, 1988b). Citral decomposes rapidly during storage at acidic pH by a series of cyclisation and oxidation reactions (Tan, 1997; Ueno, Masuda, & Ho, 2004). Acid-catalysed cyclisation of citral decreases the level of fresh-like aroma of citral and also generates off-odour compounds that limit citral's application in foods and beverages (Kimura, Nishimura, Iwata, & Mizutani, 1983a; Peacock & Kuneman, 1985; Schieberle, Ehrmeier, & Grosch, 1988; Schieberle & Grosch, 1988a). Under acidic conditions, the formation of off-odour compounds from citral degradation is also affected by temperature, oxygen availability (Kimura, Nishimura, Iwata, & Mizutani, 1983a; 1983b, Peacock & Kuneman, 1985) and antioxidant addition (Liang, Wang, Simon, & Ho, 2004a, 2004b; Ueno, Kiyohapa, Ho, & Masuda, 2006; Ueno et al., 2003).

The rate of chemical degradation of a labile component can be altered appreciably when incorporated into a colloidal dispersion (such as a micelle solution, microemulsion or emulsion) because it and other ingredients can partition between different physicochemical environments: aqueous phase, oil phase and interfacial region (Decker & McClements, 2001; Given, 2009). If a labile component can be located within an environment where it is isolated from other components that promote its chemical degradation, then it may be possible to retard the degradation rate. Since citral degradation occurs predominantly in acidic aqueous solutions, it may be possible to alter its degradation rate by altering its partitioning between the oil and aqueous phases. For example, if citral can be located predominantly within a non-polar environment, such as the interior of a lipid droplet or surfactant micelle, then it may be possible to protect it from degradation. The incorporation of micelles and reverse micelles into oil-in-water emulsions would be expected to alter the partitioning of citral between the oil droplets and the surrounding aqueous phase, and thereby alter its stability to chemical degradation.

A number of studies have recently examined the degradation of citral in oil-in-water emulsions containing flavour oils. These studies have shown that the rate of citral degradation depends on the composition of the interfacial layer coating the lipid droplets

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(Djordjevic, Cercaci, Alamed, McClements, & Decker, 2007, 2008), as well as the composition of the organic phase, e.g., medium chain triacylglycerols to triacetin ratio (Choi, Decker, Henson, Popplewell, & McClements, 2009).

In this study, we examine the impact of micelles (Tween 80) in the water phase and reverse micelles (PGPR) in the oil phase on the partitioning and chemical stability of citral in oil-in-water emulsions.

2. Materials and methods

2.1. Materials

Citral (mixture of *cis*- and *trans*-isomer, 95% pure) and Tween 80 (HLB ≈ 15) were purchased from Acros Organics (Fair Lawn, NJ) and Sigma Chemical (St. Louis, MO). Medium chain triglycerides (MCT, NEOBEE 1053) were obtained from Stepan Company (Northfield, IL). Polyglycerol polyricinoleate (PGPR, 4150, HLB ≈ 3) was obtained from Palsgaard (Morristown, NJ). All other chemicals were reagent grade or better and were obtained from Fisher Scientific (Pittsburgh, PA).

2.2. Preparation of Tween 80-stabilised emulsions

The oil-in-water emulsions were prepared by homogenising 5% w/w lipid phase (MCT) with 95% w/w aqueous phase containing (1–5% w/w Tween 80, 20 mM sodium citrate buffer, pH 3.0). These emulsions contained oil droplets stabilised by Tween 80 and micelles formed by Tween 80. Emulsions containing reverse micelles in the oil droplets were prepared by mixing 5% w/w lipid phase (5% or 10% w/w PGPR in MCT) with 95% w/w aqueous phase (1% w/w Tween 80 at pH 3.0). A coarse emulsion premix was prepared by homogenising oil and aqueous phase using a high-speed blender for 2 min at room temperature. To reduce droplet size, the premixed emulsions were sonicated (Sonic Dismembrator 500, Fischer Scientific) for 2 min at an amplitude of 70% and a duty cycle of 0.5 s at 4 °C. After preparation of both emulsions, pure citral was directly added to the emulsion to obtain a final citral concentration of 0.05% w/w and dissolved by stirring for 1 h at room temperature. The emulsions were then stored under quiescent conditions at 20 °C for up to 7 days.

2.3. Measurement of citral in oil-in-water emulsions

Citral degradation was monitored by measuring the decrease of citral isomers (neral and geranial) using a gas chromatograph (GC-17A, Shimatzu, Avondale, PA) equipped with a capillary column (DB-5, J&W Scientific, Folsom, CA; 300 mm × 0.25 mm i.d., 0.25 μm film thickness) with a glass injection splitter ratio of 5:1 and a flame ionising detector. An oven temperature programme was applied starting from 100 °C, then increasing to 145 °C at 3 °C/min, then increasing to a final temperature of 220 °C at 20 °C/min, then held at 220 °C for 10 min. The injector and flame ionisation detector were set at 250 °C. Helium (9 ml/min) was used as the carrier gas.

2.3.1. Analysis of citral in continuous phase

To determine the concentration of citral in the continuous phase, emulsions containing citral were centrifuged at 15,000*g* at 4 °C for 1 h. After centrifugation, a 3 ml disposable syringe with a 21-gauge needle was pressed against the wall of the glass tube and gently pushed down to the bottom of the tube where approximately 2 ml of the continuous phase was removed. The removed continuous phase was then filtered through a 0.45-μm membrane filter (Millipore, Bedford, MA) to remove any extraneous particles. The filtered material (0.2 ml) was dissolved in 0.8 ml reagent alcohol (ethanol) and vortexed for 15 s prior to injection into the GC. An aliquot of sample (1.0 μl) was injected into the GC and the two isomers of citral were identified by comparison to retention times with authentic standards.

2.3.2. Analysis of citral in whole emulsions

To determine the concentration of citral in the whole emulsions, the emulsions (0.1 ml) were dissolved directly in 0.9 ml reagent alcohol (ethanol) and vortexed for 15 s before injection into the GC.

2.4. Particle size measurements

Emulsions were diluted to a droplet concentration of approximately 0.006% w/w using buffer solution to avoid multiple scattering effects prior to analysis. The particle size distribution of the emulsions was then measured by laser light scattering (Mastersizer X, Malvern Instruments Ltd., Malvern, UK). This instrument determines the particle size distribution that gives the best fit between the experimental measurements and predictions made using light scattering theory (i.e. Mie theory). A refractive index ratio of 1.08 was used by the instrument to calculate the particle size distributions. Measurements are reported as the volume–surface mean diameter: $d_{32} = \sum n_i^3 / \sum n_i^2$, where n_i is the number of droplets of diameter d_i. The mean particle size of the emulsions was independent of the surfactant concentration present (1–5% w/w Tween 80 or 0–10% w/w PGPR), and did not change significantly during 7 days storage: d_{32} = 0.25 ± 0.01 μm.

3. Results and discussion

3.1. Impact of surfactant micelles on citral degradation in aqueous solutions

Initially, the impact of surfactant micelles on the chemical stability of citral was measured in aqueous solutions in the absence of oil droplets (Fig. 1). The saturation concentration of citral in an aqueous citrate buffer solution was determined to be 560 mg/l (≈0.056% w/w) at 20 °C, which is in good agreement with the value of 590 mg/l in water at 25 °C reported in the literature (United Nation Environment Programs, 2001). An initial citral concentration of 0.05% w/w was therefore used to study the influence of micelles on the chemical degradation of dissolved citral in buffer solutions,

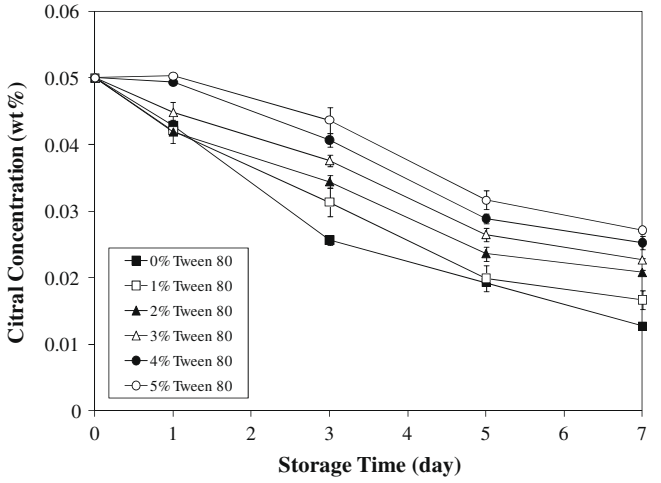

Fig. 1. Time dependence of the citral concentration remaining in aqueous buffered solutions containing different Tween 80 concentrations (pH 3, 20 °C).