



Short communication

## Citral degradation in micellar structures formed with polyoxyethylene-type surfactants

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## ABSTRACT

In a micellar solution, the chemical degradation of poorly water-soluble food flavours can be influenced by the properties of the surfactants forming the micelles in aqueous solutions. To evaluate how hydrophilic head size and hydrophobic tail length influence the chemical degradation rate of food flavour, micelles were prepared with Brij surfactants (Brij 35, 58, 78 and 700), each of which had very similar molecular structures (polyoxyethylene fatty acid ether). The chemical degradation of citral in Brij micelles was found to be highest in an acidic environment. There was no significant difference in the chemical degradation rate of citral in Brij micelles in non-acidic conditions, regardless of the hydrophilic head size or hydrophobic tail length. Brij surfactants with larger hydrophilic heads effectively retarded the chemical degradation of citral in an acidic environment. Our findings suggest that the length of the hydrophobic tail rarely influenced the micelle's ability to chemically stabilize citral.

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## 1. Introduction

Citral (3,7-dimethyl-2,6-octadien-1-al) is one of the most important natural flavour compounds in citrus oil and is widely used in foods and beverages as an additive. Citral is an acyclic monoterpene aldehyde, which is composed of a mixture of two geometric isomers, geranial (*trans*-citral) and neral (*cis*-citral), in a 3:2 ratio (Schieberle & Grosch, 1998a, 1998b). Citral decomposes rapidly by a series of cyclization and oxidation reactions during storage at acidic pHs (Tan, 2004; Ueno, Masuda, & Ho, 2004). Citral degradation at acidic pHs reduces the level of the '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, 1983b; Peacock & Kuneman, 1985; Schieberle & Grosch, 1998a). Additionally, the production of off-flavours by citral degradation is affected by temperature (Kimura et al., 1983a, 1983b; Peacock & Kuneman, 1985). The most effective ways to inhibit and retard citral degradation involve the reduction of storage temperature, alteration of pH near a neutral point, and removal of oxygen. However, considering the conditions of foods and beverages when they are consumed, these approaches are not practically

helpful for food industries to produce foods and beverages containing highly stable citral molecules (Djordjevic, Cercaci, Alamed, McClements, & Decker, 2007). Therefore, the practical proposal widely accepted in food industries is the incorporation of food flavours that are very unstable in acidic environments into colloidal dispersions, including emulsions, microemulsions, nanoemulsions and micellar solutions. Because a labile food flavour could be partitioned between different physicochemical environments, including the aqueous phase, oil phase and interfacial region (Decker & McClements, 2001; Given, 2009), the creation of a colloidal system in particular could be the best way to stabilize poorly water-soluble food flavours, such as citral. If labile food flavours can be located within an environment where they are isolated from the harsh surroundings that promote its chemical degradation, then the degradation can be effectively prevented, or reduced. Many studies have shown that the stability of citral in an acidic environment was dramatically increased by incorporating and encapsulating it into colloidal dispersions, such as emulsions and micelles (Choi, Decker, Henson, Popplewell, & McClements, 2010; Djordjevic, Cercaci, Alamed, McClements, & Decker, 2008; Maswal & Dar, 2013; Rao & McClements, 2012; Yang, Tian, Ho, & Huang, 2011, 2012). If citral can be located predominantly within the non-polar environment of surfactant micelles, then it may be possible to alter its stability against chemical degradation.

This hypothesis was examined by measuring the stability of citral against chemical degradation in Brij (polyoxyethylene alkyl

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ether) surfactant micelles and by determining the impact of the surfactant's molecular structure on the chemical stability of citral in Brij surfactant micelles.

## 2. Materials and methods

### 2.1. Materials

Citral (mixture of *cis* and *trans* isomer, 95% pure), Brij 35 (polyoxyethylene (23) lauryl ether), Brij 58 (polyoxyethylene (20) cetyl ether), Brij 78 (polyoxyethylene (20) stearyl ether), and Brij 700 (polyoxyethylene (100) stearyl ether) were purchased from Sigma Chemical Company (St. Louis, MO, USA). The molecular structures of the surfactants used are presented in Fig. 1. All other chemicals were of reagent grade and were obtained from Sigma.

### 2.2. Preparation of the Brij-micelle solution

The sample solutions were prepared by dissolving Brij 35, Brij 58, Brij 78 and Brij 700 in 10 mM phosphate buffer (pH 7) to a final concentration of 1 mM. After preparation, pure citral was directly added to the Brij micellar solution to obtain a final citral concentration of 533 mg/l and dissolved by stirring for 12 h at 4 °C. Next, the sample solution was adjusted to a final pH value in the range of 3–7 using 0.1- and 1.0-N hydrochloric acid solutions. All sample solutions were stirred at the desired pH for at least 30 min before the subsequent steps. Sample solutions were then stored under quiescent conditions at 4 °C for up to 15 days.

### 2.3. Measurement of citral in Brij-micelle solution

Citral degradation was monitored by measuring the decrease in citral isomers (neral and geranial) using a gas chromatograph (7890A, Agilent Technologies, Santa Clara, CA) equipped with a capillary column (DB-5, Agilent Technologies; 300 mm × 0.32 mm i.d., 0.25 μm film thickness) with a splitless glass injection and a flame ionizing detector. An oven temperature program was applied starting at 100 °C, then increasing to 140 °C at 3 °C/min and to a final temperature of 300 °C at 10 °C/min. Finally, the temperature was held at 300 °C for 5 min. The injector and flame ionization

detector were set at 220 and 250 °C, respectively. Nitrogen was used as the carrier gas, with a column flow rate of 1.3 ml/min.

## 3. Results and discussion

The Brij series surfactants used in this study all had very similar molecular structures to each other and polyoxyethylene (*n*) fatty acid ether (Fig. 1). According to the *n* and fatty acid type, different names were assigned, such as Brij 35, Brij 58, Brij 78 and Brij 700. Although the number of oxyethylene and length of fatty acids on a molecular structure differed from each other, their hydrophilic-lipophilic balance (HLB) values were very similar in the range from 15 to 18 (17, 16, 15 and 18 for Brij 35, 58, 78 and 700, respectively), indicating that the Brij series of surfactants used in this study are suitable for use as an emulsifier in the preparation of oil in water-type emulsions. According to the literature (United Nation Environment Programs, 2001), the saturation concentration of citral in an aqueous solution is 590 mg/l at 25 °C. An initial citral concentration of about 533 mg/l was therefore used to study the influence of micelles on the chemical degradation of the dissolved citral in buffer solutions because this concentration was found to be below the saturation level. The change in the citral concentrations of Brij micellar solutions was monitored during storage at 4 °C (Fig. 2). The chemical stability of citral varied according to the pH of the Brij micellar solutions. This observation is in good agreement with a previous report (Choi, Decker, Henson, Popplewell, & McClements, 2009), which showed that citral was degraded more easily in an acidic aqueous solution than in a neutral aqueous solution. After a 15-day storage period, the amount of citral remaining in the Brij micellar solutions under neutral conditions, pH 7, (85.8%, 89.0%, 85.0% and 86.4% for Brij 35, 58, 78 and 700, respectively) and mild acidic conditions, pH 5, (86.6%, 88.5%, 88.8% and 93.4% for Brij 35, 58, 78 and 700, respectively) was higher than at acidic condition, pH 3, (67.9%, 68.9%, 67.6% and 73.7% for Brij 35, 58, 78 and 700, respectively). If the remaining amount of citral in the Brij micellar solutions was compared with those in the buffer solutions, the amounts of citral remaining in the Brij micellar solutions were slightly higher than those in the neutral and mild acidic buffer solutions but still much higher than those in the acidic buffer solution (data not shown). As described above, the reason for the rapid degradation of citral is its

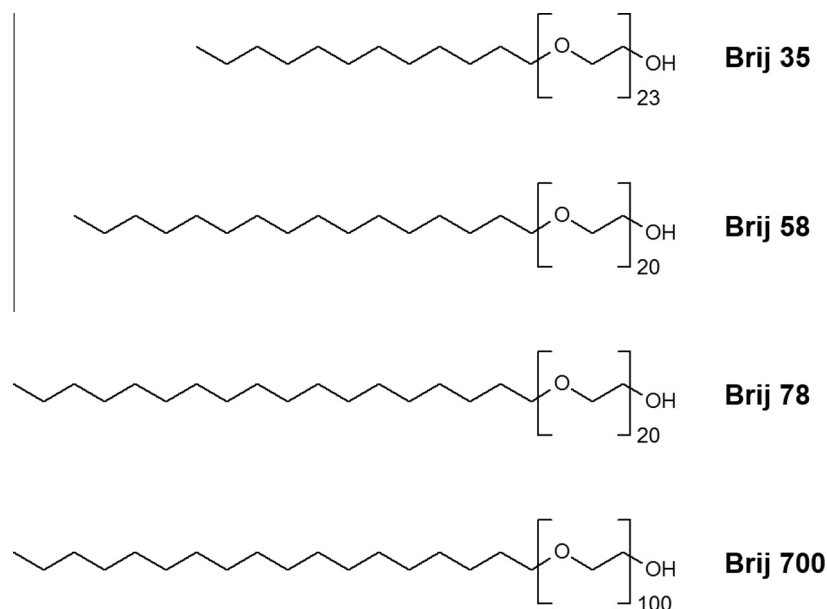


Fig. 1. The structures of the Brij series of surfactants used in this study.

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