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Review

Formulation challenges in encapsulation and delivery of citral for improved food quality

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ABSTRACT

Citral, one of the most important natural flavouring compound having intense lemon aroma and flavour, is widely used as an additive in foods, beverages and cosmetics with high consumer acceptance. Citral is chemically unstable and degrades over time in aqueous solutions due to acid catalysed and oxidative reactions leading to loss of desirable flavour and formation of off-flavours. Therefore, incorporation of citral into foods and beverages is a major challenge for the food industry because their chemical deterioration needs to be inhibited to minimize loss of product quality. The task to find the appropriate delivery system is most challenging for food industry. In the present review, the encapsulation and delivery techniques of citral mostly based on colloidal systems have been reviewed in detail. Moreover, the remaining technical challenges of such delivery systems like insignificant stabilization of citral, use of non-biocompatible constituents, instability to the environmental stress and difficulty of their preparation are discussed for prospective development of such formulations.

Contents

1. Introduction

Citral or 3,7-Dimethyl-2,6-octadienal is an acyclic monoterpenoid consisting of two geometrical isomers. The E-isomer is specifically referred to as geranial or citral A and the Z-isomer as neral or citral B. Citral is one of the most important flavouring compound used widely in beverages (Piorkowski & McClements, 2013), foods, and fragrances for its characteristic flavour profile (Choi, Decker, Henson, Popplewell, & McClements, 2009). It is also used commercially in the production of vitamin A, ionones and methylionones (Pihlasalo, Klika, Murzin, & Nieminen, 2007). In addition, there is an interest for the use of citral in the synthesis of menthol which is widely applied in pharmaceuticals, cosmetics, toothpastes, chewing gum and cigarettes (Pihlasalo et al., 2007). *Cymbopogon citrates* (lemongrass) and *Litsea cubeba* are cultivated

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worldwide having the major use in international markets as a raw material source for the isolation and production of citral on industrial scale (CU, 1992; Hamid & Djisbar, 1989; Juida de Carlini, 1986; Kroschwitz, 1997; Oyen & Dung, 1999; Pihlasalo et al., 2007). *Cymbopogon citratus* is cultivated in South and South-East Asia, South and Central America, Madagascar and nearby islands, and in Africa. Lemongrass is also cultivated and often naturalized throughout the tropics and warm subtropics e.g. in southern parts of the Russian Federation and northern Australia. It is very commonly cultivated throughout South-East Asia both as an industrial and as a garden crop (Juida de Carlini, 1986; Oyen & Dung, 1999). In trade statistics hardly any distinction is made between the 2 major sources of lemongrass oil: West Indian lemongrass (*C. citratus*) and East Indian lemongrass (*Cymbopogon flexuosus*) (Juida de Carlini, 1986; Oyen & Dung, 1999). In 1986 world production of lemongrass oil was estimated at 650 tonnes, valued at about 4.3 million US$, most of the oil originating from Central and South America (Argentina, Brazil, Guatemala, Honduras). In 1992–1994 average annual import of lemongrass oil in the United States was 80 tonnes and the price per kg averaged US$ 7.35 (Juida de Carlini, 1986; Oyen & Dung, 1999). East Indian lemongrass oil is mainly produced and consumed in India. *L. cubeba* oil is of Chinese origin, rich in citral (about 70 percent) and competes to a limited extent with lemongrass (CU, 1992; Hamid & Djisbar, 1989). United States, countries of Western Europe and Japan are major importers of *L. cubeba* oil, total imports are probably of the order of several hundred tonnes annually, although trade in some years is estimated at up to 500 tonnes (CU, 1992; Hamid & Djisbar, 1989).

A number of dietary monoterpenes have shown to act effectively in chemoprevention and chemotherapy of different cancers in animal models, at cellular levels, and in human trials (Carnesecchi et al., 2001; Crowell, 1999; Mills, Chari, Boyer, Gould, & Jirtle, 1995). Furthermore, unsaturated terpenes are capable of trapping activated oxygen species *in vivo* to give intermediate epoxides which can alkylate DNAs, proteins and other bio molecules. Citral is used in traditional medicine as antispasmodic, analgesic, anti-inflammatory, antipyretic, diuretic and sedative (Saddiq & Khayyat, 2010). (Saddiq & Khayyat, 2010) showed that citral and citral-epoxide have good antifungal and antibacterial activities against *Penicillium italicum*, *Rizopussto lonifer* and *Staphylococcus aureus*. Citral possesses antifungal activity against both plant and human pathogens (Rodov, Ben-Yehoshua, Fang, Kim, & Ashkenazi, 1995; Yousef, Aggag, & Tawil, 1978) and inhibits seed germination (Dudai, Poljakoff-Mayber, Lerner, & Putievsky, 1994). It also has bactericidal (Asthana, Larson, Marley, & Tuveson, 1992; Kim, Marshall, Cornell, Preston, & Wei, 1995), insecticidal (Rice & Coats, 1994), deodorant, expectorant, appetite stimulating and spasmolytic properties, and weak diuretic and anti-inflammatory effects (Carbajal, Casaco, Arruzazabala, Gonzalez, & Tolon, 1989; Carlini, Contar, Siva-Filho, Dasilveira-Filho, & Frochtengarten, 1986). Moreover, citral produces a long-lasting inhibition of TRPV1–3 and TRPM8 channels, whereas it produces a transient block of both TRPV4 and TRPA1 channels (Stotz, Vriens, Martyn, Clardy, & Clapham, 2008). Similarly, it was demonstrated that the main constituent of the fruit essential oil of *Cinnamomum insular-imontanum* is citral, and that this compound exerted a significant inhibitory effect on the production of nitric oxide in lipopolysaccharide-stimulated RAW 264.7 cells (Lin, Chen, Lin, Tung, & Wang, 2008). In addition, citral exhibits an anti-inflammatory effect in a test of croton oil-induced mice ear oedema (Lin et al., 2008). Ortiz, Gonzalez-Garcia, Ponce-Monter, Castaneda-Hernandez, and Aguilar-Robles (2010) evaluated anti-inflammatory and gastric damaging effects resulting from the systemic administration of citral, naproxen and combined citral–naproxen in rats and concluded that the co-administration of naproxen and citral offers benefits at the clinical level and has therapeutic advantages for the clinical treatment of inflammation. The antimicrobial action exerted by citral against yeasts and moulds in different conditions has also been demonstrated (Belletti, Kamdem, Tabanelli, Lanciotti, & FaustoGardini, 2010) resulting in microbial stability of the beverages containing citral.

Citral is highly susceptible to acid-promoted and oxidative degradations (Djordjevic, Cercaci, Alamed, McClements, & Decker, 2008). It decomposes rapidly during storage by a series of cyclization and oxidation reactions. Acid-catalysed cyclization of citral reduces the intensity of the fresh lemon flavour due to its decreased levels and hence results in the formation of variety of undesirable compounds (Fig.1) creating off-flavours that limit the shelf-life of acidic citrus-flavoured foods and beverages. Citral degradation at low pH starts with the isomerization of geranial to neral which then forms the monoterpene alcohols like *p*-menthadien-8-ol and *p*-menthadien-4-ol (Kimura, Nishimura, Iwata, & Mizutani, 1983; Peacock & Kuneman, 1985). These intermediate monoterpene alcohols oxidize to p-cymene-8-ol, which undergoes a dehydration reaction to produce stable aromatic compounds such as α-*p*-dimethylstyrene, *p*-cymene and *p*-cresol (Djordjevic, Cercaci, Alamed, McClements, & Decker, 2007; Kimura et al., 1983; Peacock & Kuneman, 1985). *p*-cresol and *p*-methylacetophenone are the most potent degradation products of citral (Djordjevic et al., 2007). Consumer demand for natural ingredients as well as for more complex and authentic aroma profiles have resulted in an increased demand for the incorporation of citrus oil and citral into different food and beverage products (Djordjevic et al., 2008). However, the major challenges associated with incorporation of citral into foods and beverages through variety of encapsulation techniques include the following:

- Citral must be encapsulated into such kind of delivery system which makes it readily dispersible in aqueous-based food products, such as beverages, sauces etc. because it has a very low aqueous solubility.
- Citral delivery system should be compatible with the food matrix so that product appearance, texture, stability or flavour is not adversely altered.
- Citral should maintain its flavour and potential bioactivity within the food product during its preparation, storage, transport and utilization since it is chemically labile and its activity is adversely affected by the pro-oxidants, protons, metal ions etc.
- Citral delivery system should be bio-compatible, physiologically relevant and biodegradable so as to be effective for food and medical applications.

In this endeavour following encapsulation and delivery techniques have been reported in literature for the stabilization and delivery of citral and other lemon oil derivatives in food, cosmetics and pharmaceutical industries, most of them being based on the soft colloidal systems.

- Spray drying
- Oil-in-water emulsions
- Multilayer emulsions
- Nanoemulsions
- Molecular complexes
- Self-assembly delivery systems

However, such microencapsulation leads to physical, sensory, and nutritional changes in a number of flavours and therefore should generally not be seen as a first option while designing food formulations (Furuta et al., 2010). In case of citral where the simple options like decrease in temperature, alteration of pH etc fails one may consider encapsulation.