Food Research International 86 (2016) 64–73

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Carotenoid transfer to oil during thermal processing of low fat carrot and tomato particle based suspensions

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ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form 21 May 2016
Accepted 21 May 2016
Available online 29 May 2016

Keywords:
Carotenoids
Structural barriers
Thermal processing
Carotenoid transfer
Kinetics

ABSTRACT

Carotenoid solubilization in the oil phase is a prerequisite for carotenoid bioaccessibility during digestion. However, the level of bioencapsulation and the hydrophobicity of carotenoids were proven to strongly affect their transfer to oil during *in vitro* digestion. Therefore, thermal processing (95–110 °C) was exploited to favor carotenoid transfer from tomato- and carrot-based fractions to the oil before digestion. Initially, the total (all-*trans* + *cis*) carotenoid content in the oil increased quickly, thereafter, depending on the temperature applied, either a drop or a plateau was reached at longer treatment times. Treatment conditions of >100 °C for 10 min significantly favoured carotenoid transfer to oil (≥75%). The rates of transfer to oil were as follows: β-carotene ≈ α-carotene > lycopene. The results revealed that the cell wall hinders carotenoid transfer to oil during thermal processing. Overall, the results indicate that typical high temperature short time thermal processing can be sufficient to achieve maximal carotenoid transfer to oil with minimal degradation in real food systems/food emulsions and this can be crucial to improve the nutritional quality of carrot and tomato based products.

1. Introduction

The evidence for the association between adequate intake of carotenoid-rich fruit and vegetable-based foods and the reduced risk of certain degenerative diseases continues to grow. Carotenoids are a group of lipid soluble pigments present in a wide variety of fruits and vegetables. Their physiological functions are linked to their antioxidant properties and/or pro vitamin A activity (Fernández-García et al., 2012). Carotenoids are polyisoprenoid compounds and can be categorized as either carotenes (composed of carbon and hydrogen atoms) or xanthophylls (oxygenated hydrocarbon derivatives that contain at least one oxygen function such as hydroxyl, keto, epoxy, methoxy, or carboxylic acid groups) (Britton, 1995). Lycopene, α-carotene and β-carotene are the predominant members of the carotenes (Stahl & Sies, 2005). The major biochemical functions of carotenoids are determined by the extended system of conjugated double bonds which is also responsible for their color (Britton, 1995).

In fruit and vegetable tissues, carotenoids are located inside the chromoplast organelles in a specific sub-structure of crystalline, membranous or globular nature, embedded in a cellular structure (Jeffery, Holzenburg, & King, 2012). This natural localization of carotenoids has consequences for their release and stability during processing, storage, and digestion. In this context, release from the matrix, by matrix disruption (during processing or digestion) followed by solubilization into an oil phase, which can be achieved by processing fruits and vegetables in the presence of lipids (Mutsokoti, Panozzo, Musabe, Van Loey, & Hendrickx, 2015) or during digestion in the presence of lipids (Palmero, Panozzo, Simatupang, Hendrickx, & Van Loey, 2014) is necessary before carotenoids can be incorporated into mixed micelles during digestion (Castenmiller, West, Linssen, van het Hof, & Voragen, 1999; Fernández-García et al., 2012). However, the level of bioencapsulation and the hydrophobicity of carotenoids were proven to strongly affect their transfer to oil during in vitro digestion procedures (Palmero et al., 2013, 2014; Verrijssen et al., 2014). To this regard, thermal processing can be exploited to favor carotenoid transfer to the oil before digestion. In fact, previous investigations have mentioned that thermal treatments can lead to matrix structure disruption (De Belie, Herppich, & De Baerdemaeker, 2000; Sila, Smout, Vu, Loey, & Hendrickx, 2005) which can facilitate the release of carotenoids from the matrix. In fact, in vivo studies established that absorption of lycopene and β-carotene from fresh and unheated carrot and tomato juices is less compared with processed tomatoes and carrot (Agarwal, Shen, Agarwal, & Rao, 2001; Fröhlich, Kaufmann, Bitsch, & Böhm, 2007; Tydeman et al., 2010; van het Hof et al., 2000). Moreover, Schubert and Ax (2003) observed an increase in lycopene and asthaxanthin solubility in palm oil with increasing oil temperature, with temperatures of at least 100 °C required to achieve considerable (3 gL^{-1}) concentrations in the oil. This implies that thermal processing of fruit and vegetable

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http://dx.doi.org/10.1016/j.foodres.2016.05.019
0963-9969/

matrices in the presence of oil can be a valuable tool to facilitate carotenoid release and their subsequent solubilization into the oil phase. This can be an alternative approach to elaborate new functional foods.

However, due to their highly unsaturated structure, carotenoids are prone to isomerization and degradation during thermal processing (Achir, Randrianatoandro, Bohuon, Laffargue, & Avallone, 2010). Oxidation is reported to be by far the major cause of carotenoid degradation and has been postulated to be a free radical process (Chen, Shi, Xue, & Ma, 2009; Xu et al., 2013). Previous investigations have shown that carotenoid degradation reactions are more pronounced in the presence of oil (Colle, Lemmens, Van Buggenhout, Van Loey, & Hendrickx, 2011; Knockaert et al., 2012). Moreover, Colle et al. (2013) reported that lycopene degradation in an olive oil/tomato emulsion primarily takes place in the oil phase. It is also known that the thermal degradation and isomerization products of carotenoids that are formed in food products can result in an alteration of the nutritional (e.g. reduction or loss of provitamin A and antioxidant activity) and sensory quality (e.g. color changes). Therefore, in the context of improving the nutritional quality of tomato and carrot based products, by facilitating the carotenoid transfer to oil during processing, thermal processing conditions should be carefully selected to maximize carotenoid transfer to the oil phase and at the same time minimize carotenoid degradation.

In the past decade, in the context of predicting carotenoid changes during thermal processing, many studies have been conducted in which lycopene and β-carotene degradation, assuming first order kinetics in both model and real food systems was described. However, the transport kinetics of carotenoids from the food matrix to the oil phase and their degradation therein during thermal processing has so far not been described in the literature. Therefore, the aim of the present work was to evaluate the main factors governing the transfer to oil of α-carotene and β-carotene from carrot and lycopene and β-carotene from tomato particle based suspensions during thermal processing. In this study, materials with different levels of carotenoid bioencapsulation were included. In addition, the kinetics of carotenoid transfer to oil and degradation during thermal processing were considered in order to determine the relevant temperature/time conditions required to maximize carotenoid transfer to oil and this can be important for process design and optimization.

2. Materials and methods

2.1. Materials

All chemicals and reagents used were of analytical or HPLC-grade. All-*trans* lycopene, all-*trans* β-carotene, all-*trans* α-carotene (≥90%, ≥95%, ≥95%, purity by HPLC assay, respectively) and *L*-α-phosphatidylcholine were purchased from Sigma-Aldrich (Borne, Belgium). 5-*cis* lycopene, 9-*cis*, 13-*cis* and 15-*cis* β-carotene (96.8%, 99%, 96%, 96%, purity by HPLC assay, respectively) were purchased from CaroteNature (Lupsingen, Switzerland). Olive oil (extra virgin) was kindly donated by Vandemoortele (Ghent, Belgium). Red tomatoes (*Lycopersicon esculentum* cv Prunus) and orange carrots (*Daucus carota cv* Nerac) were obtained fresh from a local shop in Belgium and stored at 4 °C for 1 day prior to use.

2.2. Sample preparation

2.2.1. Oil-in-water emulsion

Oil-in-water emulsion was prepared by mixing 5% olive oil to 1% L-α-phosphatidylcholine in deionized water at 9500 rpm for 10 min (UltraTurrax, IKA-Werke GMBH & CO·KG, Staufen, Germany). The mixture was then immediately homogenized at 100 MPa for one cycle (Panda 2 K, Gea Niro Soavi, Parma, Italy).

2.2.2. Chromoplast fraction

The chromoplast enriched fraction from tomatoes or carrots was obtained according to the method described by Palmero et al. (2013). The vegetables were first washed in deionized water. Tomatoes or peeled carrots were cut into pieces and mixed (Waring Commercial, Torrington, CT, USA) at low speed for 5 s with 50% 0.05 M ethylenediaminetetraacetic acid (EDTA) solution. The obtained purees were gently filtrated using cheesecloth and further centrifuged (Beckman, J2-HS Centrifuge, Palo Alto, CA, USA) at 27,200 *g* for 30 min at 4 °C. The pellet was resuspended in 100 mL deionized water and represented the chromoplasts enriched fraction.

2.2.3. Cell cluster fraction

The cell cluster fraction was prepared according to the procedure described by Palmero et al. (2013). First, tomato or carrot purees were obtained. In the case of tomatoes, the pieces were mixed (Büchi B-400 mixer, Flawil, Switzerland) three times for 5 s and sieved (1 mm) to remove seeds. Carrot puree was obtained by mixing (Waring Commercial, Torrington, CT, USA) the carrot pieces with 50% deionized water for 1 min. The obtained purees were then sieved using wet sieving equipment (Retsch AS200, Haan, Germany). The fractions between 40 and 250 and 160–500 μm were collected representing the carrot and tomato cell cluster fractions, respectively (Lemmens, Van Buggenhout, Oey, Van Loey, & Hendrickx, 2009; Palmero et al., 2013).

2.3. Thermal treatments

Thermal treatments were performed by means of a microwave heating system (start E, Milestone S.r.l, Sorisole, Italy). In a first step, the relevant temperature range for the actual kinetic study was determined by screening carotenoid transfer to the oil phase (Lemmens et al., 2010). Hereto, cell clusters and chromoplast enriched fractions from carrots and tomatoes were separately mixed with the oil-in-water emulsion (1.5 g isolated fraction: 15 mL emulsion). The samples were then poured into reactor tubes, each containing a thermowell, closed with a 5 bar valve and incubated in a water bath at 40 °C for 4 min. Four other vessels were filled with 16 g of tylose solution (1.5% w/v in deionized water) to serve as thermal load. Thereafter, samples were thermally treated for 20 min in the microwave heating system at 80, 90, 110 and 120 °C. In one of the samples, the temperature was measured using a fiber optic sensor (ATC-FO, Milestone S.r.l.). The power necessary to reach the treatment (E1, Watt) within 2 min and to maintain it for a defined treatment time, (E2, Watt) was predetermined for each temperature investigated, (Table A1 and Fig. A1). Follow-up of the power assured the dynamic heating phase was limited to 1.5 min and temperature fluctuations were restricted within ±1.5 °C. During heating, the samples were stirred using magnetic stirrers to facilitate heat transfer within the samples.

In a second step, the actual kinetic experiment was performed. Samples were thermally treated at temperatures ranging from 95 to 110 °C for time intervals ranging from 0 min to 40 min. An example of a time

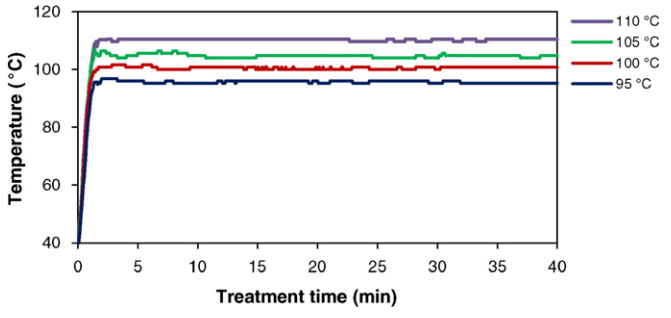

Fig. 1. Example of typical time/temperature profiles of samples microwave heated at temperatures between 95 and 110 °C.