

Available online at www.sciencedirect.com



Food Chemistry

Food Chemistry 107 (2008) 1538-1546

www.elsevier.com/locate/foodchem

Isomerisation kinetics and antioxidant activities of β -carotene in carrots undergoing different drying techniques and conditions

Bhudsawan Hiranvarachat^a, Peamsuk Suvarnakuta^b, Sakamon Devahastin^{a,*}

^a Department of Food Engineering, King Mongkut's University of Technology Thonburi, 126 Pracha u-tid Road, Bangkok 10140, Thailand ^b Department of Food Science and Technology, Thammasat University, Paholyothin Road, Pathum Thani 12121, Thailand

Received 18 June 2007; received in revised form 23 July 2007; accepted 4 October 2007

Abstract

Carrots are known as a natural source of β -carotene. In order to preserve the latter, carrots must generally be processed, and drying is one of the most common methods for processing carrots. During drying β -carotene in carrots suffers degradation. β -Carotene degradation is generally due to thermal degradation and isomerisation. In this work, the drying kinetics as well as the isomerisation kinetics and antioxidant activities of β -carotene in carrots undergoing hot air drying, vacuum drying and low-pressure superheated steam drying (LPSSD) were determined within the temperature range of 60–80 °C and, in the case of vacuum drying and LPSSD, at a pressure of 7 kPa. A high performance liquid chromatography (HPLC) method was used to determine the β -carotene contents and its isomerisation kinetics, while the antioxidant activities of various combinations of all-*trans*- and *cis*-forms of β -carotene in carrots were evaluated using the Trolox equivalent antioxidant capacity (TEAC) assay.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Antioxidant activity; Degradation; Hot air drying; Low-pressure superheated steam drying; cis/trans-Isomerisation; Vacuum drying

1. Introduction

β-Carotene is one of the common carotenoid hydrocarbons that contain specific end groups or two-beta rings. It acts as provitamin A, which is converted by humans to vitamin A (Retinol) (Sergio & Russell, 1999; Patrick, 2000). Moreover, β-carotene has high antioxidant activity, by scavenging peroxyl radicals, which occur as a result of oxidation reactions, especially at low oxygen tension (Larson, 1988). Since carotene stereoisomers display different chemical properties and antioxidant activities, the knowledge of various factors affecting formation of all-*trans*and *cis*-isomers of β-carotene in foods is of interest (Marx, Stuparic, Schieber, & Carle, 2003).

Carrots (*Daucus carota* var. sativa) are one of the most important root crops. The consumption of carrots and

0308-8146/\$ - see front matter \odot 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.foodchem.2007.10.026

their related products has increased steadily, partly due to the antioxidant activity of β -carotene in carrots (Rubatzky, Quiros, & Simon, 1999). However, in the food industry, carrots must generally be processed prior to their use and drying is one of the most frequently used processes. Many techniques have been developed to dry carrots, with the goal of maintaining their nutritional value, especially β carotene, as much as possible.

Different drying techniques and conditions are known to affect the quality of a food product, either in terms of its physical properties, chemical properties or biochemical properties. In the food industry, hot air drying is widely used, although it often leads to much quality degradation, especially in terms of the nutritional properties. Several other drying techniques have therefore been proposed and studied (Devahastin, Suvarnakuta, Soponronnarit, & Mujumdar, 2004). Although there are some works that report the study of β -carotene degradation in carrots undergoing different drying techniques and conditions

^{*} Corresponding author. Tel.: +66 2 470 9246; fax: +66 2 470 9240. *E-mail address:* sakamon.dev@kmutt.ac.th (S. Devahastin).

(Suvarnakuta, Devahastin, & Mujumdar, 2005), no information is so far available on the effect of drying on the *cis/trans*-isomerisation of β -carotene in carrots.

Naturally, β -carotene exists in the all-*trans* form. After processing, however, some all-*trans* form is converted into its different *cis*-isomers (Aman, Schieber, & Carle, 2005). Heat, light and the presence of sensitisers promote isomerisation of *trans*-carotenoids to their *cis*-form (Dutta, Chaudhuri, & Chakraborty, 2005).

Lessin, Catigani, and Schwartz (1997) studied the quantification of *cis/trans*-isomers of carotenoids in canned carrots and other vegetables. They found that all-*trans*- β -carotene was lower in all processed samples, as compared to the fresh samples. Only all-*trans*- β -carotene was found in fresh carrots while 9-*cis*- β -carotene and 13-*cis*- β -carotene occurred after canning. Canning caused a 33% increase in total *cis*-isomers. This change in isomeric compositions was due to *cis/trans*-isomerisation, which occurred as a direct result of the thermal processing.

Chen, Peng, and Chen (1995) studied the thermal degradation of canned carrot juices. They found that canning of carrot juices at 121 °C led to the formation of 13-*cis*- isomer, which was the predominant isomer in that study. This result was consistent with that of Marx et al. (2003), who studied the effects of pasteurisation and sterilisation on *cis/trans*-isomerisation of β -carotene in carrot juices. They found that in the case of pasteurisation, only 13-*cis*- β -carotene occurred. On the other hand, in the case of sterilisation, 9-*cis*- β -carotene and 13-*cis*- β -carotene occurred. 9-*cis*- β -carotene was found at temperatures higher than 90 °C for processing times longer than 60 min.

As mentioned earlier, β -carotene has high antioxidant activity. Many investigators have thus studied the antioxidant activities of various isomers of β -carotene in different products undergoing processing. Bohm, Puspitasari-Nienaber, Ferruzzi, and Schwartz (2002), for example, studied the antioxidant activities of different geometrical isomers of β -carotene and other carotenoids using TEAC assay. They reported that all-*trans*- β -carotene had higher antioxidant activity than 13-*cis*- β -carotene.

The objectives of this study were to investigate the effects of selected drying techniques, i.e., hot air drying, vacuum drying and low-pressure superheated steam drying (LPSSD), on the isomerisation kinetics and antioxidant activities of β -carotene in carrots at different conditions. The relationship between the amount of different isomers of β -carotene, as well as their antioxidant activities, and carrot moisture content were also investigated.

2. Materials and methods

2.1. Materials

Fresh carrots (*D. carota* var. sativa) were purchased from a local market and stored at 4 °C. Before starting each drying experiment, carrots were peeled and diced (only the cortex part was used) into 1 cm³ cubes. The moisture content of fresh carrots was determined by drying the samples at 105 °C for 24 h in a hot air oven (Memmert, model 800, Schwabach, Germany).

2.2. Experimental set-up

2.2.1. Low-pressure superheated steam dryer

A schematic diagram of the low-pressure superheated steam dryer and its accessories is shown in Fig. 1. The dryer consists of a stainless steel drying chamber with inner dimensions of $45 \times 45 \times 45$ cm³; a steam reservoir, which received steam from a boiler and maintained its pressure at around 200 kPa; and a liquid ring vacuum pump (Nash, model ET32030, Trumball, CT), which was used to maintain the vacuum in the drying chamber (fixed at 7 kPa in this study). An electric heater, rated at 1.5 kW, which was controlled by a PID controller (Omron, model

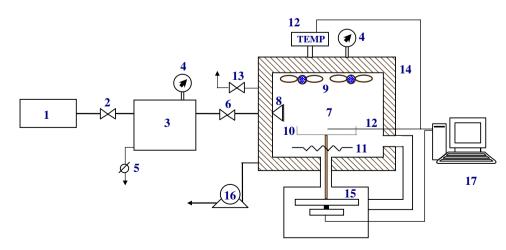


Fig. 1. A schematic diagram of the low-pressure superheated steam dryer and associated units. 1, boiler; 2, steam valve; 3, steam reservoir; 4, pressure gauge; 5, steam trap; 6, steam regulator; 7, drying chamber; 8, steam inlet and distributor; 9, electric fans; 10, sample holder; 11, electric heater; 12, on-line temperature sensor and logger; 13, vacuum purge valve; 14, insulator; 15, on-line weight indicator and logger; 16, vacuum pump; 17, PC with installed data acquisition card.

E5CN, Tokyo, Japan) was installed in the drying chamber to control the steam temperature and to minimise the condensation of steam in the drving chamber during the startup period. Two variable-speed electric fans were used to disperse steam throughout the drving chamber. The sample holder was made of a stainless steel screen with dimensions of $16.5 \times 16.5 \text{ cm}^2$. The change of the mass of the sample was detected continuously (at 60 s intervals) using a load cell (Minebea, model UCG-3 kg, Nagano, Japan). The temperatures of the steam and of the drying sample were also measured continuously using type-K thermocouples, which were connected to an expansion board (Omega Engineering, model no. EXP-32, Stamford, CT). Thermocouple signals were multiplexed to a data acquisition card (Omega Engineering, model no. CIO-DAS16Jr.) installed in a PC. Labtech Notebook software (version 12.1, Laboratory Technologies Corp., Andover, MA) was then used to read and record the temperature data.

2.2.2. Vacuum dryer

For vacuum drying experiments the same experimental set-up was used as for the LPSSD experiments without the application of steam to the drying chamber.

2.2.3. Hot air dryer

A schematic diagram of the hot air dryer used is illustrated in Fig. 2. It consists of a stainless steel drying chamber $(45 \times 45 \text{ cm}^2)$, in which the sample was placed. The inlet air that was used to dry the sample was heated up to the desired temperature by an electric heater rated at 9 kW. The sample was placed on a tray made of a stainless steel screen. The air velocity over the drying tray was fixed at 0.8 m/s.

2.3. β -Carotene analysis

Analysis of the total amount of β -carotene was performed using the methods described by Suvarnakuta et al. (2005). A sample of 5–8 g of dried carrots was ground for 2 min using a stainless steel pulveriser (Waring, model SS110, Torrington, CT). The ground sample was then placed in a flask filled with 40 ml of ethanol. 2 N potassium hydroxide (40 ml) was added, to saponify the solution, at 70 °C for 30 min. The extract was then cooled down immediately to 0 °C. β -Carotene was then extracted three times

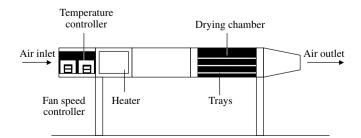


Fig. 2. A schematic diagram of hot air dryer and associated units.

with 5 ml of diisopropyl ether and the aqueous layer was discarded. The extracted solution was filtered through a 0.45 m filter before being injected into a liquid chromatograph column.

Å symmetry[®] C₃₀ 5 μm (4.6 mm × 250 mm) HPLC column (YMC, Kyoto, Japan) was used for the analysis of different isomers of β-carotene. The HPLC system consisted of a pump and a controller (Waters, model 600, Milford, MA), a tunable absorbance detector (Waters, model 486). A sample of 75% methanol and 25% methyl tert-butyl ether (MTBE) was used as the mobile phase and its flow rate was set at 2 ml/min. A UV detector, at 450 nm, was used for detecting β-carotene. The mobile phase was degassed using an ultrasonic generator.

From the preliminary experiments, it was found that only 13-*cis*- β -carotene formed as a result of isomerisation; only this *cis*-isomer was then tested for in the subsequent study. A standard of all-*trans*- β -carotene was purchased from Fluka (Buchs, Switzerland). 13-*cis*- β -Carotene was obtained by iodine-catalysed photoisomerisation of all*trans*- β -carotene as previously described by Aman et al. (2005). Briefly, all-*trans*- β -carotene was dissolved in diisopropyl ether containing two drops of 1% iodine. The solution was then exposed to ambient light for 30 min.

A typical chromatogram of β -carotene isomers of interest is shown in Fig. 3. The concentration of all-*trans*- β -carotene was calculated from the peak area of its chromatogram while the *cis*-isomer proportion was calculated from the relative peak area of the *cis*- β -carotene divided by the peak area of the *trans*- β -carotene in each sample.

Quantification of β -carotene was carried out based on a β -carotene standard curve. The standard curve was prepared daily by injecting solutions of HPLC β -carotene standard in diisopropyl ether at six concentrations (0, 2, 4, 6, 8 and 10 g/ml). All standard curves showed good linearity ($r^2 > 0.99$).

The measured all-*trans*- β -carotene content is expressed in terms of the β -carotene retention ratio, while the *cis*-proportion is reported in terms of the *cis/trans* ratio:

$$\beta\text{-Carotene retention ratio} = \frac{\beta_t}{\beta_i} \tag{1}$$

$$cis-Proportion = \frac{\beta_{cis}}{\beta_{trans}}$$
(2)

where β_i and β_t are the β -carotene contents of fresh and dried carrots (mg/100 g solids), respectively. β_{cis} and β_{trans} refer to the peak area of *cis*- β -carotene and the peak area of *trans*- β -carotene, respectively. All *trans*- and *cis*- β -carotene measurements were performed in duplicate and the data presented are an average of the two measurements.

2.4. Antioxidant activities measurement

Antioxidant activities of various combinations (or proportions) of isomers of β -carotene in carrots were determined following the TEAC procedure similar to that of

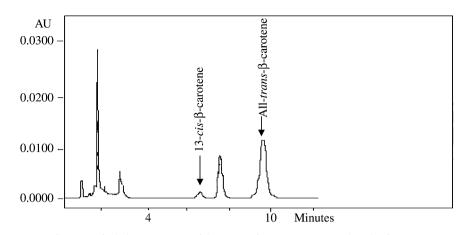


Fig. 3. Typical chromatogram of β -carotene in carrots at a wavelength of 450 nm.

Miller, Sampson, Candxias, Bramly, and Rice-Evans (1996) with some modifications. ABTS⁺⁺ radical cation was prepared by passing a 5 mM aqueous stock solution ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulof phonic acid)) through manganese dioxide on a Whatman No. 5 filter paper. Excess manganese dioxide was removed twice from the filtrate by passing it through a 0.45 µm syringe filter. This solution was then diluted with ethanol to an absorbance of 0.70 (0.02) at 734 nm and pre-incubated at ambient temperature for 1 h prior to its use. Trolox (6hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was used as an antioxidant standard. 2.5 mM Trolox was prepared in phosphate buffer saline (PBS) at pH 7.4 for use as a stock solution. $ABTS^{+}$ solution (1 ml) and 200 µl of Trolox solution were well mixed using a vortex mixer (Scientific Industries Inc., model G-560E, Bohemia, NY) for 30 s.

UV–Vis scanning spectrophotometer (Shimadzu, model UV-2101PC, Nagoya, Japan) was used for the determination of antioxidant activity. The absorbance was taken at 734 nm exactly at 1 min after initiation of vortex mixing. A standard curve of Trolox was prepared by measuring solutions of Trolox standard in PBS at five concentrations (0, 25, 50, 75 and 100 μ M). The standard curves showed good linearity ($r^2 > 0.99$).

To determine the antioxidant activities of various combinations of isomers of β -carotene, β -carotene was diluted in diisopropyl ether (1:9). ABTS⁺⁺ solution (1 ml) and 200 ml of the isomers solution were mixed for 30 s using the vortex mixer. The absorbance was then measured at the above wavelength.

The measured antioxidant activities of various combinations of all-*trans*-form and *cis*-form of β -carotene are expressed in terms of % relative inhibition:

% Relative inhibition
$$=\frac{\% \text{ inhibition of dried carrots}}{\% \text{ inhibition of fresh carrots}}$$
(3)

where % inhibition of dried carrots and fresh carrots refer to the % inhibition of $ABTS^{+}$ by the combinations of various isomers of β -carotene in dried and fresh carrots, respectively. To calculate % inhibition the following equation was used:

% inhibition =
$$\frac{(A_{\text{solvent}} - A_{\beta\text{-carotene}}) \times 100}{A_{\text{solvent}}}$$
 (4)

where A_{solvent} and $A_{\beta\text{-carotene}}$ are the absorbance of diisopropyl ether and the combinations of various isomers of all-*trans*-form and *cis*-form of β -carotene in carrots, respectively. All measurements were performed in duplicate and the data presented are an average of the two measurements.

2.5. Statistical analysis

The experiments were completely randomised. All data were analysed using the analysis of variance (ANOVA). Differences between mean values were established using Duncan multiple range test at a confidence level of 95% (p = 0.05). SPSS (version 13; SPSS Inc., Chicago, IL) was used to perform all statistical calculations.

3. Results and discussion

3.1. Drying kinetics of carrots

Since the results of the isomerisation of β -carotene in carrots undergoing different drying techniques and conditions were compared at the same moisture content, the drying curves of carrots undergoing different drying treatments and conditions were first constructed. Carrots that had an initial moisture content in the range of 9–11 kg/kg dry weight basis, (d.b.) were dried to a final moisture content of around 0.1 kg/kg (d.b.).

The drying curves and temperature profiles of carrots undergoing hot air drying, vacuum drying and LPSSD are shown in Figs. 4 and 5, respectively. Three different drying temperatures (60, 70 and 80 $^{\circ}$ C) were employed in each set of experiments.

As can be seen in Fig. 4, although vacuum drying was a faster drying process than LPSSD and hot air drying, the differences between the drying times of LPSSD and vacuum drying were smaller at higher drying temperatures.

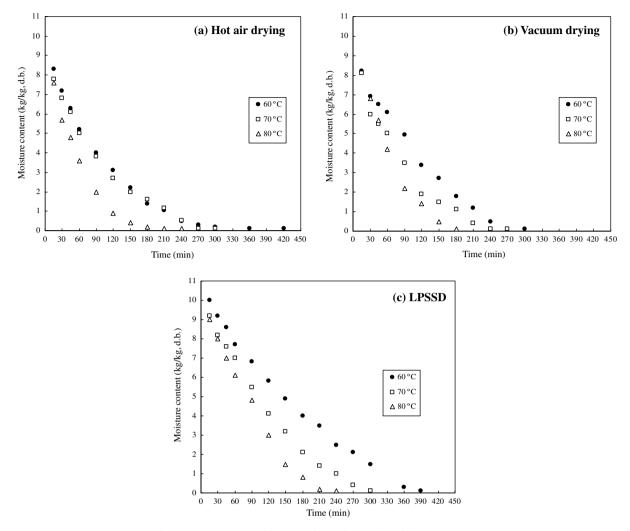


Fig. 4. Drying curves of carrots subjected to various drying treatments.

In the case of hot air drying, it took as much time to dry carrots to the final desired moisture content as did LPSSD. This is because the falling rate period of hot air drying was longer than that of LPSSD. The drying behaviour was characterised as follows: the drying rates increased with an increase in the drying temperature, due to an increased driving force for heat transfer, which is obviously related to mass transfer. Moisture diffusivities are also higher at higher temperatures.

3.2. Overall degradation kinetics of β -carotene

The β -carotene contents of fresh carrots varied slightly in the range of 68–76 mg/100 g (d.b.). The ratio of the β -carotene content of dried carrots to the fresh (β -carotene retention ratio) is therefore used to report the results in this study.

The β -carotene retention in carrots during hot air drying, vacuum drying and LPSSD is shown in Figs. 6–8, respectively. The β -carotene retention, in the case of hot air drying (Fig. 6), decreased continuously. It was observed, however, that the β -carotene retention at different temperatures was only slightly different. The falling rate of β -carotene started at the moisture content around 5.5 kg/kg (d.b.), which corresponded to a carrot temperature of 45–60 °C (see also Figs. 4a and 5a). This is due to the fact that lipoxygenase, which is an aerobic catalyst of oxidation reactions, is activated at around 60 °C (Cui, Xu & Sun, 2004).

β-Carotene retention in the cases of vacuum drying and LPSSD (Figs. 7 and 8) was not significantly higher than that in the case of hot air drying. In the case of LPSSD, only slight changes, over the moisture content range of 3–8 kg/kg (d.b.), of β-carotene occurred due to the fact that the activities of lipoxygenase and peroxidase, which are responsible for the oxidative degradation of β-carotene, were reduced due to many effects, including the absence of oxygen in the drying chamber and the lower product temperature (Fig. 5a, b, c). At moisture contents below 3 kg/kg (d.b.), β-carotene content started to decrease continuously. This is because the temperature of the carrots started to rise again (Fig. 5c); thermal degradation thus started to be significant.

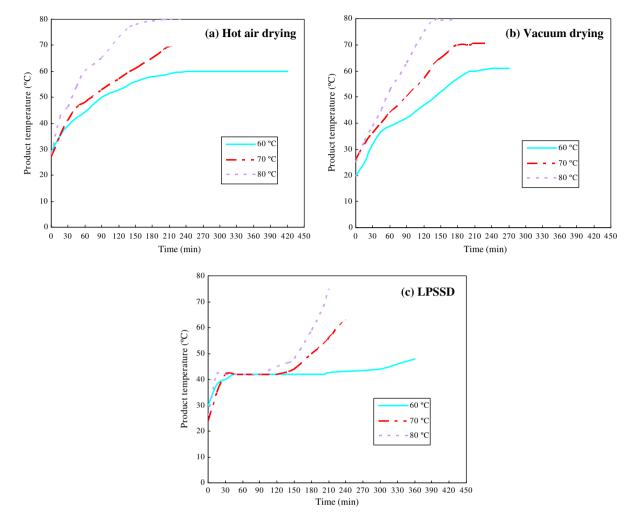
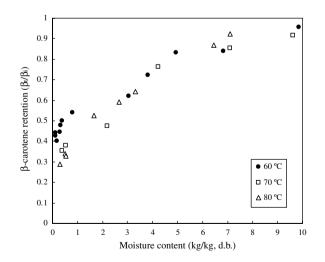


Fig. 5. Temperature profiles of carrots subjected to various drying treatments.



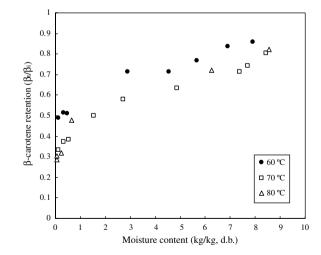


Fig. 6. Relationship between β -carotene retention and moisture content of carrots undergoing hot air drying.

In the case of vacuum drying, the trend of β -carotene degradation was similar to that of LPSSD. However, because the level of vacuum pressure used in this study was not too low (7 kPa absolute), there still existed

Fig. 7. Relationship between β -carotene retention and moisture content of carrots undergoing vacuum drying.

some oxygen that could participate in oxidation reactions. Higher temperatures, in comparison with the case of LPSSD (Figs. 5b and c) also led to more degradation.

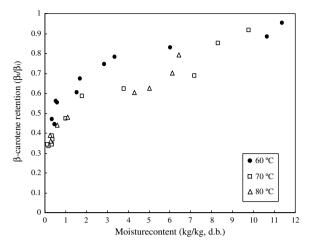


Fig. 8. Relationship between β -carotene retention and moisture content of carrots undergoing LPSSD.

3.3. Isomerisation kinetics of β -carotene

β-Carotene can be degraded either by thermal degradation or isomerisation degradation and it is known that thermal treatment promotes the formation of *cis*-isomers from all-*trans*-β-carotene in carrots (Sergio & Russell, 1999; Aman et al., 2005). In all dried (and drying) samples of this study, 13-*cis*-β-carotene was the only isomer detected by HPLC, as previously mentioned.

In the case of hot air drying (Table 1), 13-*cis*- β -carotene occurred when the product temperature, as seen in Fig. 5a, approached the drying air temperature, which was equal to or higher than 60 °C. Increased rates of isomerisation in this range of temperature are ascribed mainly to the elevated temperature, as also noted by Cui, Xu, and Sun (2004). However, the moisture contents of carrots when the formation of *cis*-isomer started were not much differ-

Table 1

Formation of 13-cis-\beta-carotene during different drying conditions

ent, i.e., 0.5, 0.4 and 0.5 kg/kg (d.b.) at 60, 70 and 80 $^{\circ}$ C, respectively. The *cis*-proportions were also not significantly different, in the range of 0.01–0.06.

For vacuum drying (Table 1), 13-*cis*- β -carotene occurred when the product temperature (Fig. 5b) was more than 50 °C. As can be seen from Table 1, the *cis*-isomer occurred at moisture contents lower than 1.8, 2.2 and 2.2 kg/kg (d.b.) at 60, 70 and 80 °C, respectively.

For LPSSD, the starting points of the formation of 13cis-isomer are reported instead in terms of the elapsed drying time. As can be seen in Table 1 the formation of 13-cis-isomer started after 150, 120 and 60 min when drying was performed at 60, 70 and 80 °C, respectively. The formation of cis-isomer, in the case of LPSSD, started much earlier than in the case of hot air drying and vacuum drying. This is probably due to the fact that carrots were held at a constant temperature corresponding to the boiling point of water at 7 kPa (around 40 °C) for an extended period of time, compared with hot air drying and vacuum drying (Fig. 5c and Table 1). Normally, if the processing temperature is maintained for a long time (like in the case of pasteurisation or sterilisation), the formation of 13-cisβ-carotene increases (Marx et al., 2003).

The formation of 13-*cis*- β -carotene in the case of LPSSD started much earlier than in the cases of hot air drying and vacuum drying. However, as can be seen in Table 1, the proportions of 13-*cis*- β -carotene at various conditions were not significantly different, in the range of 0.01-0.1.

3.4. Antioxidant activities of β -carotene

The percent relative inhibition of β -carotene in carrots undergoing hot air drying, vacuum drying and LPSSD is shown in Table 2. Percent relative inhibition, in the case

Drying time (min)	cis-Proportion (cis/trans) ^a										
	Hot air drying			Vacuum drying			LPSSD				
	60 °C	70 °C	80 °C	60 °C	70 °C	80 °C	60 °C	70 °C	80 °C		
60	n.d. ^b	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.006 ± 0.003		
90	n.d.	n.d.	n.d.	n.d.	n.d.	0.019	n.d.	n.d.	0.013 ± 0.001		
120	n.d.	n.d.	n.d.	n.d.	0.017 ± 0.012	0.030 ± 0.028	n.d.	0.005	0.026 ± 0.003		
150	n.d.	n.d.	0.03	0.016 ± 0.009	0.018 ± 0.005	0.017 ± 0.002	0.004	0.014	0.023 ± 0.004		
180	n.d.	0.017 ± 0.004	0.067 ± 0.031	0.019 ± 0.002	0.035 ± 0.012	0.055 ± 0.015	0.006	0.007 ± 0.001	0.052 ± 0.037		
210	n.d.	0.038 ± 0.029		0.014 ± 0.008	0.029 ± 0.003		0.009 ± 0.007	0.027	0.072 ± 0.036		
240	n.d.	0.036 ± 0.024		0.015	0.031 ± 0.008		0.008 ± 0.002	0.016 ± 0.007			
270	n.d.	0.034 ± 0.004		0.019 ± 0.004	0.030		0.006 ± 0.002	0.024 ± 0.005			
300	0.049	0.049		0.021 ± 0.002			0.016 ± 0.002	0.032 ± 0.016			
330	0.047						0.01 ± 0.002	0.028 ± 0.005			
360	0.036						0.021 ± 0.001				
390	0.024 ± 0.021						0.023 ± 0.012				
420	0.026 ± 0.018						0.011 ± 0.001				
450	0.009										
480	0.016										

^a Mean \pm SD of two replicates.

^b n.d. = not detectable; *cis*-isomers calculated as percentage of all-*trans*- β -carotene.

Table 2

Antioxidant activities of various combinations (or proportions) of isomers of β -carotene in carrots (during different drying conditions) in terms of % relative inhibition

Drying time (min)	% Relative inhibition ^a									
	Hot air drying			Vacuum drying			LPSSD			
	60 °C	70 °C	80 °C	60 °C	70 °C	80 °C	60 °C	70 °C	80 °C	
15	0.896 ± 0.039	0.813 ± 0.139	0.806 ± 0.014	0.806 ± 0.101	0.715 ± 0.085	0.784 ± 0.098	0.938 ± 0.008	0.787 ± 0.074	0.798 ± 0.038	
30	0.849 ± 0.018	0.842 ± 0.052	0.787 ± 0.054	0.718 ± 0.085	0.560 ± 0.045	0.639 ± 0.056	0.857 ± 0.158	0.908 ± 0.011	0.742 ± 0.153	
45	0.853 ± 0.058	0.795 ± 0.027	0.547 ± 0.245	0.814 ± 0.105	0.643 ± 0.008	0.613 ± 0.070	0.869 ± 0.075	0.814 ± 0.079	0.719 ± 0.096	
60	0.864 ± 0.011	0.852 ± 0.179	0.693 ± 0.062	0.739 ± 0.060	0.680 ± 0.183	0.606 ± 0.038	0.824 ± 0.175	0.930 ± 0.029	0.712 ± 0.167	
90	0.775 ± 0.042	0.682 ± 0.266	0.489 ± 0.235	0.631 ± 0.008	0.450 ± 0.057	0.534 ± 0.152	0.789 ± 0.267	0.832 ± 0.084	0.678 ± 0.169	
120	0.776 ± 0.032	0.685 ± 0.239	0.473 ± 0.039	0.698 ± 0.011	0.566 ± 0.195	0.589 ± 0.145	0.777 ± 0.109	0.757 ± 0.017	0.578 ± 0.253	
150	0.723 ± 0.154	0.706 ± 0.277	0.735 ± 0.268	0.527 ± 0.080	0.501 ± 0.108	0.507 ± 0.162	0.766 ± 0.174	0.762 ± 0.045	0.597 ± 0.109	
180	0.633 ± 0.142	0.643 ± 0.040	0.585 ± 0.100	0.544 ± 0.006	0.570 ± 0.100		0.779 ± 0.122	0.770 ± 0.070	0.539 ± 0.225	
210	0.709 ± 0.214	0.580 ± 0.269	0.433 ± 0.146	0.561 ± 0.099	0.587 ± 0.197		0.683 ± 0.152	0.692 ± 0.191	0.562 ± 0.027	
240	0.788 ± 0.113	0.494 ± 0.459		0.589 ± 0.109	0.509 ± 0.145		0.647 ± 0.203	0.642 ± 0.072		
270	0.725 ± 0.085	0.492 ± 0.116		0.556 ± 0.035			0.634 ± 0.138	0.647 ± 0.024		
300	0.630 ± 0.062	0.482 ± 0.398					0.654 ± 0.148	0.595 ± 0.154		
330	0.638 ± 0.157						0.684 ± 0.066	0.676 ± 0.036		
360	0.656 ± 0.097						0.621 ± 0.149			
390	0.685 ± 0.087						0.647 ± 0.131			
420	0.591 ± 0.011						0.621 ± 0.038			
450	0.587 ± 0.169									
480	0.323 ± 0.025									

^a Mean \pm SD of two replicates.

of hot air drying, decreased continuously with decreasing moisture content. A significant drop in the % relative inhibition started at a moisture content around 1 kg/kg (d.b.), which corresponded to a β -carotene retention (Fig. 6) of about 55%. This early drop in antioxidant activities (as compared with the cases of vacuum drying and LPSSD, as will be discussed shortly) is due to the fact that the antioxidant activity of β -carotene depends on the oxygen tension presented in the system and hot air drying is the most obvious aerobic process in the present study (Burton & Ingold, 1984; Stahl & Sies, 2003).

For vacuum drying and LPSSD (Table 2), % relative inhibition remained almost constant over the moisture ranges of 1–10 and 2–12 kg/kg (d.b.), respectively. However, in the case of vacuum drying, a drop in the activities could be observed at moisture contents lower than 1 kg/kg (d.b.). As can be seen also from Fig. 7 over the moisture content range of 0.1–1 kg/kg (d.b.), a dropping period of % relative inhibition started when the β -carotene retention was around 30%. In the case of LPSSD (Table 2), a dropping period started when the moisture content was around 2 kg/kg (d.b.), which corresponded to a β -carotene retention of around 35% (Fig. 8).

In the case of vacuum drying and LPSSD (Table 2), the % relative inhibition at low moisture content was higher than in the case of hot air drying. At the final moisture content of 0.1 kg/kg (d.b.), the losses in the % relative inhibition were about 50% and 45% in the case of vacuum drying and LPSSD, respectively, while in the case of hot air drying the loss was about 70%. This is due to the low oxygen contents in the cases of vacuum drying and LPSSD.

Percent relative inhibition in the case of hot air drying implied lower antioxidant activities at the final moisture content of 0.1 kg/kg (d.b.) than in the cases of vacuum drying and LPSSD. This result corresponded to the previously mentioned results of the isomerisation kinetics of β -carotene, in which LPSSD and vacuum drying could better preserve β -carotene than hot air drying by partially converting all-*trans*- β -carotene into 13-*cis*- β -carotene. In the present study, however, the formation of 13-*cis*- β -carotene in all cases did not much affect the antioxidant activities of various combinations of isomers of β -carotene. It can be seen from Table 1 that the relative amounts of 13-*cis*- β -carotene at various conditions were not significantly different, in the range of 0.01–0.1.

4. Conclusions

The isomerisation kinetics of β -carotene in carrots undergoing hot air drying, vacuum drying and LPSSD were investigated in this study. It was found that vacuum drying and LPSSD led to more conversion of all-*trans*- β carotene to 13-*cis*- β -carotene, while total degradation, vacuum drying and LPSSD led to less total degradation of β carotene than hot air drying.

Antioxidant activities of various combinations (or proportions) of isomers of β -carotene in carrots undergoing different drying techniques were determined using the TEAC assay. It was found that carrots undergoing LPSSD had higher antioxidant activity than those subjected to the other drying treatments. It could thus be concluded that, at the final moisture content of 0.1 kg/kg (d.b.), LPSSD at 60 °C was the best treatment to preserve β -carotene and antioxidant activities of carrots.

Since the drop in the total β -carotene retention at various drying conditions tended to occur more significantly

than the formation of 13-*cis*- β -carotene, the thermal degradation was noted to be more important than isomerisation degradation.

Acknowledgements

The authors express their sincere appreciation to the Commission on Higher Education, the Thailand Research Fund (TRF), and the International Foundation for Science (IFS) in Sweden for supporting this study financially.

References

- Aman, R., Schieber, A., & Carle, R. (2005). Effects of heating and illumination on *trans-cis* isomerization and degradation of β-carotene and lutein in isolated spinach chloroplasts. *Journal of Agricultural and Food Chemistry*, 53, 9512–9518.
- Bohm, V., Puspitasari-Nienaber, N., Ferruzzi, M. G., & Schwartz, S. J. (2002). Trolox equivalent antioxidant capacity of different geometrical isomers of α-carotene, β-carotene, lycopene and zeaxanthin. *Journal of Agricultural and Food Chemistry*, 50, 221–226.
- Burton, G. W., & Ingold, K. U. (1984). β-Carotene: An unusual type of lipid antioxidant. *Science*, 224, 569–573.
- Chen, B. H., Peng, H. Y., & Chen, H. E. (1995). Changes of carotenoids, color and vitamin A contents during processing of carrot juices. *Journal of Agricultural and Food Chemistry*, 43, 1912–1918.
- Cui, Z. W., Xu, S. Y., & Sun, D. W. (2004). Effect of microwave-vacuum drying on the carotenoids retention of carrot slices and chlorophyll retention of Chinese chive leaves. *Drying Technology*, 22, 563–575.

- Devahastin, S., Suvarnakuta, P., Soponronnarit, S., & Mujumdar, A. S. (2004). A comparative study of low-pressure superheated steam and vacuum drying of a heat-sensitive material. *Drying Technology*, 22, 1845–1867.
- Dutta, D., Chaudhuri, U. R., & Chakraborty, R. (2005). Structure, health benefits, antioxidant property and processing and storage of carotenoids. *African Journal of Biotechnology*, 4, 1510–1520.
- Larson, R. A. (1988). The antioxidants of higher plants. *Phytochemistry*, 4, 969–978.
- Lessin, W. J., Catigani, G. L., & Schwartz, S. J. (1997). Quantification of cis-trans isomers of provitamin A carotenoids in fresh and processed fruits and vegetables. Journal of Agricultural and Food Chemistry, 45, 3728–3732.
- Marx, M., Stuparic, M., Schieber, A., & Carle, R. (2003). Effects of thermal processing on *trans-cis*-isomerization of β-carotene in carrot juices and carotene-containing preparations. *Food Chemistry*, 83, 609–617.
- Miller, N. J., Sampson, J., Candxias, L. P., Bramly, P. M., & Rice-Evans, C. A. (1996). Antioxidant activities of carotenes and xantophylls. *FEBS Letters*, 384, 240–242.
- Patrick, L. (2000). β-Carotene: The controversy continues. Alternative Medicine Review, 5, 530–545.
- Rubatzky, V. E., Quiros, C. F., & Simon, P. W. (1999). Carrots and related vegetable umbelliferae. CABI: Oxon.
- Sergio, A. R. P., & Russell, M. R. (1999). β-carotene and other carotenoids as antioxidant. *Journal of the American College of Nutrition*, 18, 426–433.
- Stahl, W., & Sies, H. (2003). Antioxidant activity of carotenoids. Molecular Aspects of Medicine, 24, 345–351.
- Suvarnakuta, P., Devahastin, S., & Mujumdar, A. S. (2005). Drying kinetics and β-carotene degradation in carrot undergoing different drying processes. *Journal of Food Science*, 70, S520–S526.