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Formation of volatile compounds from lycopene by autoxidation in a model system simulating dehydrated foods

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ABSTRACT

Carotenoids are highly unsaturated natural pigments susceptible to oxidation during food processing and storage. Despite the recognized consequences of the oxidative degradation of carotenoids, the mechanisms involved are not well elucidated. In this work, a scheme for the study of volatiles produced by oxidative degradation of carotenoids in a model system simulating dehydrated foods was developed. Solid phase microextraction (SPME) was used for capturing the volatile compounds, which were identified by gas chromatography/mass spectrometry (GC/MS) and by comparison of Kovats indices. The scheme was applied to synthetic lycopene or lycopene isolated from watermelon. Ten volatile compounds were identified as products of the oxidative degradation of lycopene, the main volatiles formed being 6-methyl-5-hepten-2-one, citral or geranial (*trans*-3,7-dimethyl-2,6-octadienal) and neral (*cis*-3,7-dimethyl-2,6-octadienal). These compounds are often reported as volatiles of food sources of lycopene, but because lycopene was isolated in the present study, direct evidence for a precursor–product relationship is provided. Moreover, comparison of the volatile compounds generated in this study with those identified as products of enzymatic oxidation of lycopene indicates that enzymatic and non-enzymatic oxidation of lycopene may follow the same routes.

1. Introduction

Aside from being natural pigments, carotenoids are among the food constituents that continue to draw worldwide attention because of their beneficial effects on human health. However, due to a high degree of unsaturation, these compounds are susceptible to degradation during processing and storage of foods. Both isomerization and autoxidation occur, but the latter is the principal cause of carotenoid degradation, resulting in loss of color and of these valuable health-promoting compounds.

Better understanding of the reactions, influencing factors and underlying mechanisms of oxidative degradation of carotenoids is needed so that effective measures can be taken to avoid or at least minimize it during processing and storage of food. There are also important implications for human health. For example, degradation products of lycopene increased gap junctional communication, which is one of the modes of action of carotenoids against cancer (Aust et al., 2003; King et al., 1997). On the other hand, products of the cleavage of β-carotene have been reported to be potentially toxic (Sommerburg et al., 2003) and may impair mitochondrial respiration (Siems et al., 2002).

The volatile products of the degradation of carotenoids can be desirable, as in black tea (Ravichandran, 2002) and wine (Mendes-Pinto, 2009) where they become part of the characteristic aroma. In some processed foods, however, degradation/cleavage of carotenoids is undesirable because it is responsible for the appearance of off flavor, as in dehydrated carrot (Falconer, Fishwick, Lan, & Sayer, 1964) and in certain types of wine (Rapp & Marais, 1993).

Unlike lipid oxidation for which the mechanisms had been well elucidated, including the identification of nonvolatile and volatile degradation products and the establishment of the sequence of reactions, knowledge of carotenoid oxidation is limited and fragmentary. Fortunately, there has been a resurgence of interest on this topic in recent years, with the dicyclic β-carotene as the most investigated carotenoid.

Several studies have also been carried out with acyclic lycopene, but the focus has been on the nonvolatile oxidation products investigated by HPLC–MS (Caris-Veyrat, Schmid, Carail, & Bohm, 2003; Khachik, Pfander, & Traber, 1998; Kim, Nara, Kobayashi, Terão, & Nagao, 2001; Rodriguez & Rodriguez-Amaya, 2009), although Caris-Veyrat et al. did identify three compounds that are considered volatiles. Investigating the thermal degradation of lycopene, Kanasawud and Crouzet (1990) identified by GC/MS eight volatile compounds in an aqueous model system and Rios, Fernández-García, Mínguez-Mosquera, and Pérez-Gálvez (2008), six volatiles in tomato oleoresin.

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Aside from the very low levels, the identification of volatile compounds generated by the oxidation of carotenoids in food is difficult because of the presence of numerous volatiles formed from other food constituents. Model systems are therefore used, allowing easier monitoring of the products of carotenoid oxidation. Extrapolation of the results to food, however, should be done with caution and the model system should mimic food as much as possible.

The objective of the present work was to establish a strategy for the study of carotenoid degradation at ambient temperature in a model system that simulates dehydrated foods, capturing the volatile compounds from the carotenoid headspace by solid phase microextraction and identifying them by gas chromatography/mass spectrometry (GC/MS). The scheme was tested with lycopene. Carotenoids in dehydrated foods are especially prone to autoxidation because of the greater superficial area, thus greater exposure to oxygen. Moreover, a lot more work is needed on carotenoid oxidation in different food simulating systems, under different conditions, before its mechanisms can be satisfactorily elucidated.

2. Materials and methods

2.1. Materials

Synthetic lycopene and microcrystalline cellulose (MCC) Sigmacell 50 were purchased from Sigma Chemical Company (St. Louis, MO, USA). SPME fibers of three types of coating were evaluated: polydimethylsiloxane (PDMS; 100 μm × 10 mm), polyacrylate (PA; 85 μm × 10 mm) and a mixed coating of divinylbenzene, carboxen and polydimethylsiloxane (DVB/Car/PDMS; 50/30 μm × 10 mm), all of Supelco brand (Sigma-Aldrich Co., Bellefonte, PA, USA).

2.2. Isolation of lycopene from watermelon

Watermelon was chosen to be the source of lycopene because a previous paper (Niizu & Rodriguez-Amaya, 2003) showed that its carotenoid composition consisted almost exclusively of lycopene.

The carotenoids of watermelon (approximately 300 g) were extracted with acetone using a mortar and pestle and mixing the fruit with celite (Hyflosupercel), based on the method of Rodriguez-Amaya (1999) and Kimura and Rodriguez-Amaya (2002). The extract was filtered through a glass sintered funnel. Extraction and filtration were repeated until the residue was devoid of color. The carotenoids were transferred to petroleum ether in a separatory funnel, the petroleum ether extract was dried with anhydrous sodium sulfate and concentrated in a rotary evaporator (T ≤ 35 °C).

Lycopene was isolated by open column chromatography, utilizing a glass column (30 cm × 2.5 cm i.d.), packed with MgO:Hyflosupercel (1:1, previously activated for 4 h at 110 °C). The column was developed with increasing proportion of ethyl ether and acetone in petroleum ether. Lycopene was eluted with about 35–50% of acetone and quantified spectrophotometrically in petroleum ether. The purity of the isolated lycopene determined by HPLC was 96%.

2.3. Preparation of the model system

The model system was prepared according to the procedure utilized by Chou and Breene (1972), Ramakrishnan and Francis (1979), and Goldman, Horev, and Saguy (1983) to simulate dehydrated foods. MCC was previously dried in a vacuum oven at 75 °C for 24 h, cooled and kept in a desiccator. Lycopene was dissolved in methylene chloride and mixed with MCC and the mixture was homogenized in a mortar and pestle. Methylene chloride and adsorbed air were removed under vacuum for 2 h. The model system had a final concentration of 1 mg of lycopene per gram of dry powder. This operation and all analytical procedures were carried out under subdued light.

Portions of approximately 1 g of the model system were put into 20 mL vials and immediately sealed with silicone septa, the internal part being PTFE (polytetrafluoroethylene). The headspace was filled with nitrogen. A chromatogram was taken before exposing the system to oxygen.

The nitrogen atmosphere was modified with the injection of a flow of oxygen (about 100 mL/min) for 5 min. The vials were stored in an oven at 32 ± 1 °C, protected from light, in a horizontal position to increase the superficial area exposed to oxygen.

2.4. Extraction of the volatile compounds by headspace-solid phase microextraction

Initially SPME fibers of three types of polymer coating with different polarities were tested. The SPME fibers were pre-conditioned according to the instructions of the manufacturer: 250 °C for 30 min for the PDMS fiber, 300 °C for 2 h for the PA fiber and 270 °C for 1 h for the DVB/Car/PDMS fiber.

The vials containing the model system were stored in an oven for 4 and 7 days. Each fiber was introduced in the vial through the septum and exposed to the headspace at 32 ± 0.5 °C for 20 min for the extraction of the volatile compounds formed. When the extraction process was completed, the fiber was removed from the vial and inserted into the injection port of the gas chromatograph for thermal desorption of the volatiles.

Fig. 1 presents the proposed scheme for obtaining and identifying the volatile compounds produced by the oxidation of carotenoids.

2.5. HPLC conditions

HPLC to verify the purity of lycopene was carried out in a Waters separation module, model 2690 (Waters Corp., Milford, MA, USA) equipped with quaternary pump, automatic injector, online vacuum degasser, and photodiode array detector model 996, controlled by software Millennium (version 3.20). A monomeric C_{18}, Spherisorb ODS2, 3 μm, 4.6 × 150 mm, column was employed. The mobile phase was composed of acetonitrile (with 0.05% triethylamine), methanol and ethyl acetate (60:20:20), used isocratically at a flow rate of 0.5 mL/min.

2.6. GC/MS conditions

The volatile compounds were analyzed by GC/MS, employing two systems. One system was used to optimize the extraction conditions of the volatile compounds: a Hewlett Packard gas chromatograph (model HP 6890) coupled to a mass spectrometer (model HP 5973) (Agilent Technologies Inc., Palo Alto, CA, USA). Thermal desorption of the volatiles from the fiber was performed in the injection port (SPME liner of 0.8 mm i.d.) at a temperature of 200 °C in splitless mode, in which the split purge valve opened after 4 min (1:25). Volatile compounds were separated on a fused silica capillary column HP-5, 30 m × 0.32 mm i.d., 0.25 μm film thickness (Agilent Technologies Inc., Palo Alto, CA, USA). Helium was employed as carrier gas, at a constant flow rate of 1.0 mL/min. The oven temperature was held at 50 °C for 10 min, raised to 180 °C at 3 °C/min, and held at this temperature for 10 min. The GC/MS interface and the ionization source were maintained at 230 °C. The instrument was run in the electron ionization mode with the ion source at + 70 eV. Mass spectra were collected over a 35–350 m/z range.

The other system was a Shimadzu gas chromatograph coupled to a mass spectrometer model QP-2010Plus (Shimadzu Corporation, Kyoto, Japan), which was used to identify the volatile compounds. Thermal desorption of the volatiles from the fiber was performed at a temperature of 250 °C in a split/splitless type injector in splitless mode for 4 min. The fiber was left in the injection port for 10 min to eliminate any carry-over effect. Volatile compounds were separated on an apolar fused silica capillary column ZB-5 ms, 30 m × 0.25 mm i.d., 0.25 μm film thickness

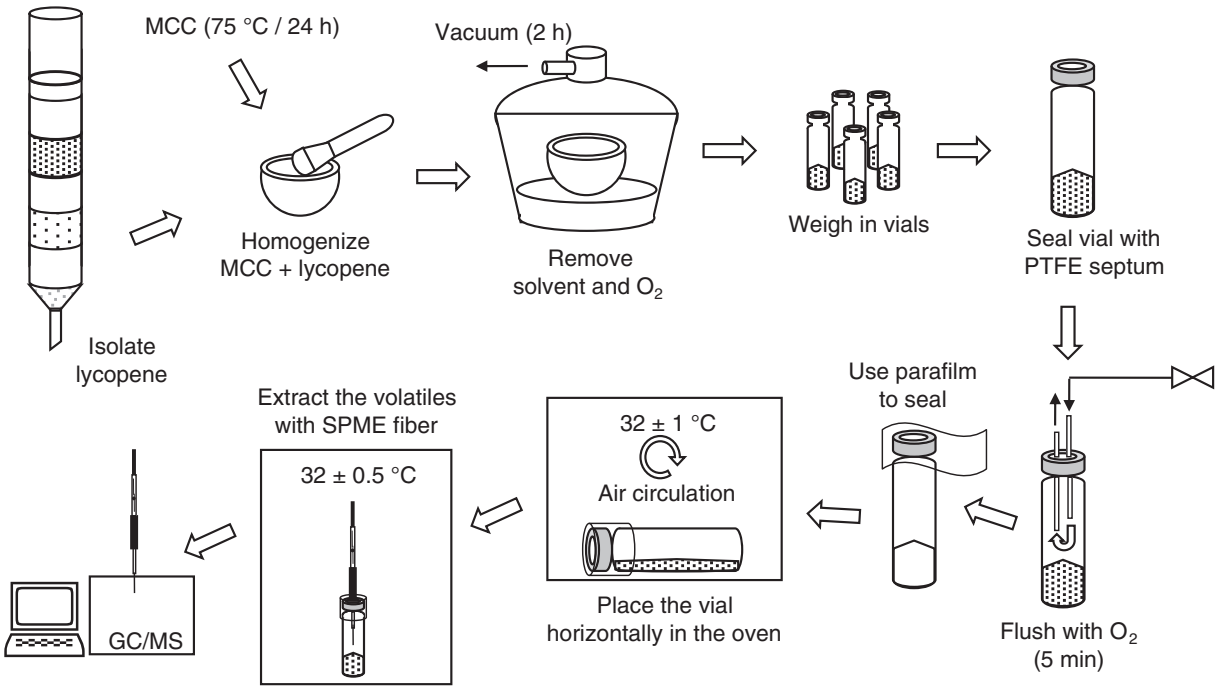

Fig. 1. Proposed scheme for obtaining and identifying volatile compounds produced by the oxidation of carotenoids.

(Phenomenex, Torrance, CA, USA). Helium was used as carrier gas, at a constant flow rate of 1.2 mL/min. The oven temperature was held at 40 °C for 2 min, raised to 150 °C at 2 °C/min, then increased to 250 °C at 25 °C/min for 10 min. The GC/MS interface and the ionization source were maintained at 240 °C. The instrument was run in the electron ionization mode with the ion source at +70 eV. Mass spectra were collected over a 30–350 m/z range.

Identification of the volatile compounds was carried out by matching the unknown mass spectra with those provided by the library mass spectra (*National Institute of Standards & Technology* library — NIST 05), comparison of the experimental and Kovats Indices (KI) from the literature (Acree & Arn, 2013; Adams, 1995; Jennings & Shibamoto, 1980) and by the elution order of compounds. A series of n-alkanes (C6–C24) was analyzed under the same conditions to obtain the KI values.

3. Results and discussion

3.1. Lycopene headspace sampling by solid-phase microextration

The total ion current (TIC) chromatograms had 6 principal peaks, regardless of which fiber was used, differing only in their relative intensities. The main difference lies in the number of peaks in the chromatogram obtained with the fiber DVB/Car/PDMS, which had 73 peaks. The chromatograms obtained with the fibers PDMS and PA had 58 and 32 peaks, respectively. Since the fiber DVB/Car/PDMS resulted in more peaks with greater intensity, it was chosen for the subsequent experiments. Beaulieu and Lea (2006) obtained 59 peaks when they studied the volatiles of 5 varieties of watermelon, using the same DVB/Car/PDMS fiber.

Thirty minute extraction, with previous 20 min of equilibrium time at 32 °C, and 10 min of thermal desorption at 250 °C in the GC/MS injection port were found sufficient to obtain chromatograms with peaks of good intensity and resolution.

3.2. Volatile compounds formed by lycopene oxidation

To confirm that the volatiles were produced by the degradation of lycopene and were not aroma compounds derived from other constituents of watermelon possibly co-eluted with the lycopene fraction during the isolation/purification step, the experiment was repeated with a lycopene standard of 94% purity. The chromatograms obtained were similar to those of lycopene isolated from watermelon.

Fig. 2 shows the TIC chromatograms of the headspace volatile compounds (a) of the control run with only MCC with oxygen, and (b) after oxidation of lycopene in the model system at 32 ± 1 °C for 24 h, and (c) the chromatogram amplified in the time interval of 5 to 35 min, the region of the chromatogram where the peaks of the oxidized products appeared. Table 1 presents the major peaks and/or those that have been tentatively identified.

Of the 73 peaks encountered in the chromatogram, 13 made up 76% of the total peak area, and 10 volatile compounds were identified. Table 1 shows that there is very good agreement between our mass spectra and those of the NIST and between KI values obtained in the present study and those taken from the literature.

The identified volatiles, predominantly unsaturated, can be classified into aldehydes (6), ketones (2), alcohol (1), furan (1) and pyran (1). Several other peaks were detected in the chromatogram (Fig. 2b). However, these peaks besides having low arbitrary areas also had possible coelutions, which made comparison of spectra with those of the library difficult. Among these minor peaks, isomers of unsaturated hydrocarbon were the most common. These peaks should be the subject of further investigation.

Interaction of oxygen with the lycopene molecule is manifested by a high abundance of the compounds 6-methyl-5-hepten-2-one, geranial, 2,3-epoxy-geranial and rose oxide (Fig. 2b). The increase of these compounds in foods during processing and storage can be important markers of lycopene oxidation. Other compounds, such as hexanal, nonanal, octen-1-al and 1-pentanol, cannot be seen as good markers because they can also originate from lipid oxidation. In fact, only three compounds identified in this study have been previously reported as degradation products of lycopene: 6-methyl-5-hepten-2-one, geranial and neral (Caris-Veyrat et al., 2003; Kanasawud & Crouzet, 1990; Stevens, 1970).

In the experimental intervals (1, 2, 4 and 7 days) used for monitoring the degradation, it was not possible to detect intermediate compounds, which could have helped in elucidating the formation of the volatiles identified. The fact that they were not detected by the adopted method

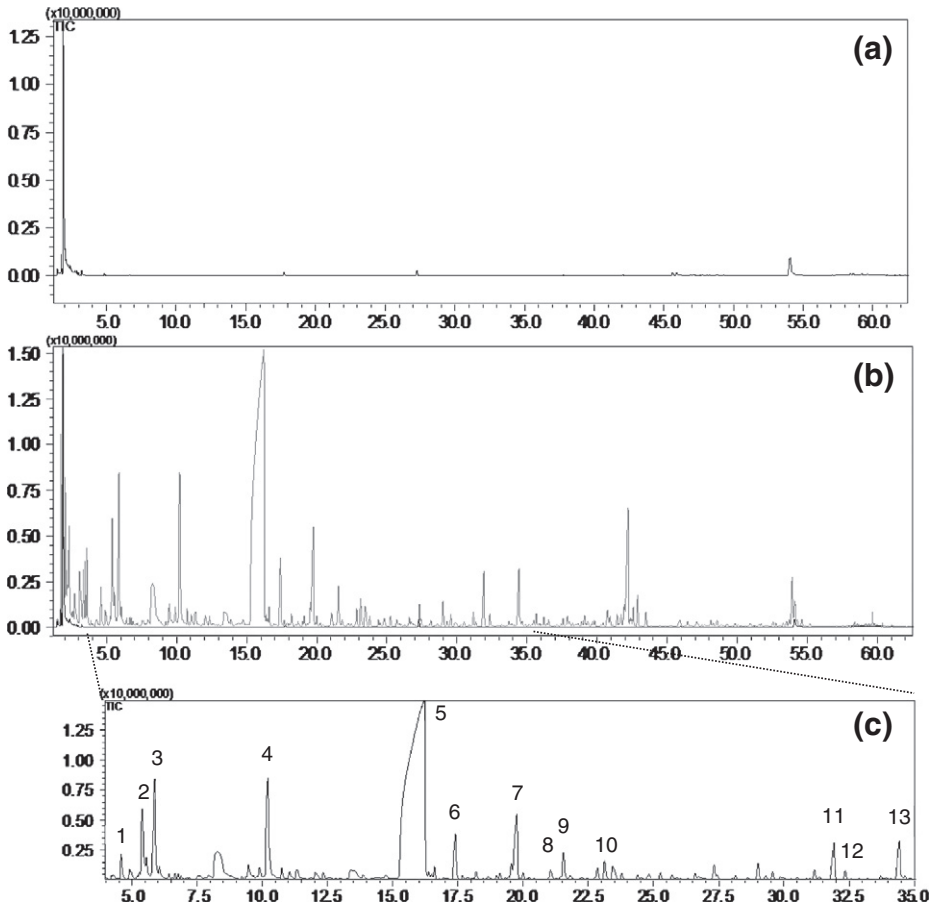

Fig. 2. TIC chromatograms of the headspace volatile compounds obtained with the SPME fiber DVB/Car/PDMS: (a) the control run with only MCC with oxygen, (b) after oxidation of lycopene in the model system at 32 ± 1 °C for 24 h, and (c) amplified oxidized product region. Peak identification: (1) 1-pentanol, (2) hexanal, (3) 2-pentanone, hydroxy-4-methyl, (4) not identified, (5) 6-methyl-5-hepten-2-one, (6) and (7) not identified, (8) (E)2-Octen-1-al, (9) rose oxide, (10) nonanal, (11) 2,3-epoxy-geranial, (12) neral, and (13) geranial.

under the conditions used would not necessarily mean that they were not formed. Once generated, they could have been rapidly transformed, thus not accumulating at levels that could be detected by the method employed. Instead of monitoring the degradation in terms of days, shorter periods (hours or minutes) might have been more appropriate.

The main compounds identified in the present study can be intense contributors to food flavor. The most abundant compound identified as 6-methyl-5-hepten-2-one can be described as mushroom, earthy, vinyl and rubber (Jodan, Margaria, Shaw, & Goodner, 2002). On the other hand, geranial and neral are frequently associated with a floral/lemon and citrus/musty note, respectively (Pherobase, 2013).

Table 1
Major volatile compounds formed by lycopene oxidation.

Peak	Volatile compound	Q	KI-MS$_{exp}$	KI$_{lit}$
1	1-Pentanol	98	771	776
2	Hexanal	97	803	801
3	2-Pentanone, 4-hydroxy-4-methyl	90	848	845
4	Not identified	–	904	–
5	6-Methyl-5-hepten-2-one	95	984	981
6	Not identified	–	1024	–
7	Not identified	–	1060	–
8	(E)2-Octen-1-al	93	1064	1056
9	Rose oxide	86	1079	1068
10	Nonanal	95	1107	1104
11	2,3-Epoxy-geranial	95	1238	1215
12	2,6-Octadienal, 3,7-dimethyl-, (z) (Neral)	92	1245	1240
13	2,6-Octadienal, 3,7-dimethyl (Geranial)	93	1276	1270

Q, quality of agreement of the mass spectrum with that of the NIST 02 library; KI-MS$_{exp}$, experimental Kovats index obtained with capillary column ZB-5 ms (30 m × 0.25 mm × 0.25 μm of film thickness); KI$_{lit}$, Kovats index from the literature.

The chromatograms of the volatile compounds derived from lycopene in the model system exposed to oxygen at 32 ± 1 °C for 1, 2, 4 and 7 days were similar, differing only in the relative proportion or intensity of the peaks. The amount of volatiles was greater on the first day, the intensity decreasing thereafter without the formation of new peaks. The trends for 6-methyl-5-hepten-2-one, geranial and neral are shown in Fig. 3. Although decreasing with time, 6-methyl-5-hepten-2-one was always the principal compound. Geranial was the volatile that showed greater reduction, decreasing 78% after 7 days.

Kanasawud and Crouzet (1990) reported a similar finding in investigating the degradation of lycopene in an aqueous model system at a temperature of 30 °C to 97 °C in the presence of air or oxygen for 3 h. However, neral was formed only at temperatures above 50 °C. Under mild conditions (temperature below 50 °C), only 6-methyl-5-hepten-2-one, geranial and pseudoionone were found. Aside from neral, 5-hexen-2-one, hexane-2,5-dione, 6-methyl-3,5-heptadien-2-one and geranyl acetate were generated at higher temperatures. Rios et al. (2008) reported, aside from 6-methyl-5-hepten-2-one, toluene, *m*-xylene, 6-methyl-3,5-heptadien-2-one, ethanone and β-citronellol in tomato oleoresin after thermal degradation at 50 °C, 100 °C and 150 °C, temperatures higher than those employed in the present work. Thermal degradation would be expected to generate more volatile compounds than the ambient oxidation carried out in the present study. Kanasawud and Crouzet (1990) isolated the volatile compounds by gas stripping with nitrogen and trapping on Tenax and by direct extraction with dichloromethane of the filtrate obtained by elimination of

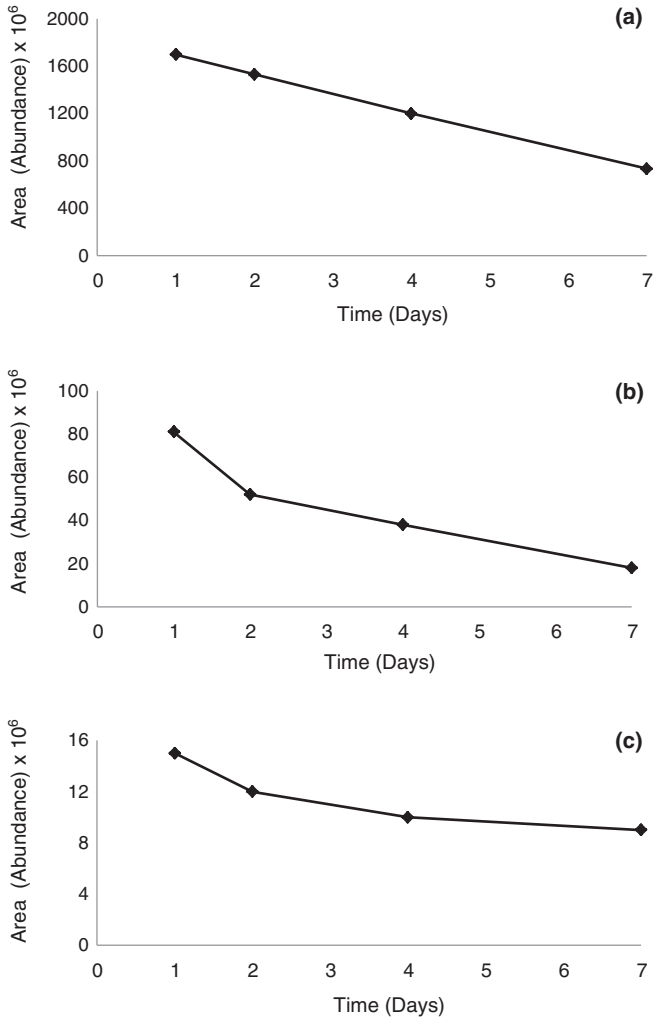

Fig. 3. Volatile compounds obtained with SPME fiber DVB/CAR/PDMS after oxidation of lycopene in model system at 32 ± 1 °C for 1, 2, 4 and 7 days: (a) 6-methyl-5-hepten-2-one, (b) neral, and (c) geranial.

undissolved compounds of the reactive medium. Rios et al. (2008) used headspace SPME with DVB/CAR/PDMS fiber.

Of the 10 volatile compounds identified in the present study, seven (1-pentanol, hexanal, 6-methyl-5-hepten-2-one, (E)2-octen-1-al, nonanal, neral, and geranial) were also found by Beaulieu and Lea (2006), also using DVB/Car/PDMS fiber for SPME extraction of the volatile compounds, in five varieties of watermelon. 6-Methyl-5-hepten-2-one was the most abundant ketone in the five varieties and hexanal was the most abundant volatile in one variety. Since Beaulieu & Lea used fresh watermelon juice as sample, the volatile compounds that they identified were obviously generated by oxidative cleavage of lycopene, catalyzed by carotenoid cleavage oxygenases that cleave specific double bonds of the polyene chain (Giuliano, Al-Babili, & von Lintig, 2003; Walter, Floss, & Strack, 2010). The results of our study and that of Beaulieu & Lea therefore indicate the similarity of enzymatic biodegradation and nonenzymatic autoxidation of carotenoids.

Hexanal, 6-methyl-5-hepten-2-one and nonanal were detected in fresh-cut watermelon slices (Saftner, Luo, McEvoy, Abbott, & Vinyard, 2007), whereas the last two volatiles were found in watermelon juice processed by high-intensity pulsed electric field or heat. Geranial, neral, 6-methyl-5-hepten-2-one and 2,3-epoxy-geranial were identified by Lewinsohn et al. (2005) in both watermelon and tomato fruits. In tomato juice treated by different technological methods, 1-pentanol, hexanal, neral and geranial were encountered (Schreier, Drawert, & Junker, 1977). 6-Methyl-5-hepten-2-one, hexanal and nonanal were among the volatiles identified in red-fleshed papaya fruit (Pino, 2014).

Studies done with lycopene-rich foods or total extracts do not eliminate the possibility that the volatiles are generated from other carotenoids or precursors other than carotenoids. In a recent study on the aroma compounds derived from thermal degradation of carotenoids in a cashew apple juice model, 33 volatiles were identified. However, since it was the total carotenoid extract that was subjected to heating, the authors could only claim that three volatiles were unquestionably formed from carotenoids because they were identified in previous studies about thermal degradation of carotenoids.

In the present study, watermelon lycopene was isolated, blanks were run, and synthetic lycopene was also subjected to oxidation, giving direct evidence that the volatile compounds were indeed generated from lycopene. Thus, possible routes for the formation of five of the

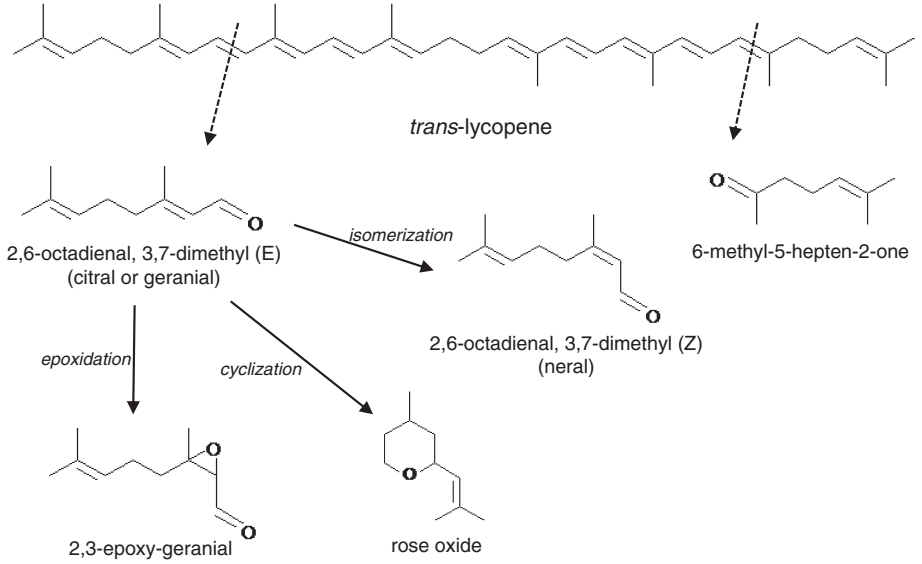

Fig. 4. Possible routes for the formation of 6-methyl-5-hepten-2-one, geranial, neral, 2,3-epoxy-geranial and rose oxide, from the lycopene.

compounds identified can be proposed (Fig. 4), based on structural considerations. The formation of geranial and its transformation to neral were previously proposed by Kanasawud and Crouzet (1990), who also used isolated lycopene (from tomato).

4. Conclusion

The proposed scheme for the study of volatiles generated by the oxidative degradation of a carotenoid, consisting of oxidation of the carotenoid adsorbed in MCC simulating dehydrated foods, solid-phase microextraction of the volatile compounds generated and identification of the volatiles by gas chromatography/mass spectrometry, provided important information about the degradation of lycopene. This scheme with small alterations in time and temperature of exposition can be used for further investigation of lycopene degradation, as well as degradation of other carotenoids, providing direct evidence of a precursor–product relationship between the carotenoid and the volatile compounds. Of the ten volatile compounds identified as products of non-enzymatic oxidation of lycopene in the present study, seven had been previously reported as products of enzymatic oxidation of lycopene.

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