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Degradation, under Non-Oxygen-Mediated Autooxidation, of Carotenoid Profile Present in Paprika Oleoresins with Lipid Substrates of Different Fatty Acid Composition

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A heat-induced degradation was carried out over two crude paprika oleoresins diluted with high oleic or high linoleic oil. Occurrence of oxygen was avoided, and changes in individual carotenoids were followed over time. Degradation rate constants were not significantly different, so that carotenoid stability was not linked with unsaturation degree of the oily system. A parallel reaction to degradation, trans to cis carotenoid isomer conversion, was also denoted during the thermal treatment, and it initially showed a higher rate than degradation of cis-isomers. Both processes (isomerization and cis-isomers degradation) were finally compensated, and their development was also unaffected by the nature of the lipid profile. Under the reaction conditions, oleic and linoleic fatty acids showed the same reactivity and induced degradative reactions, equally affecting the carotenoid profile. An enhanced stability of carotenoid content and provitamin A value was not achieved with a decrease in the unsaturation level of the oily system.

KEYWORDS: Paprika oleoresins; carotenoids; stability; fatty acids; provitamin A; unsaturation; oil

INTRODUCTION

Food fatty acids oxidation is the cause of general food deterioration by development of undesirable off-flavors, which counteract food quality and even can make it detrimental to health (*1*, *2*). Additionally, degradation of fatty acids affects the rest of the lipophilic components, which in some cases are the most valuable compounds of food. This is the case of several essential oils and oleoresins, where minor lipophilic substances make the food attractive to both producer and consumer. Some common examples are ginger, coriander, rosemary, turmeric, and paprika oleoresins that enhance flavor or color properties of food.

Paprika oleoresin is obtained by solvent extraction of dehydrated red pepper fruits, a process that generates a highly concentrated carotenoids oil, mainly used in food industry as a coloring agent, although it is applied in cosmetic products and pharmaceutical applications (*3*). The lipophilic extract is valuable because of its pigment profile, composed by a wide variety of carotenoids with different levels of oxygenation. The profile includes simple hydrocarbons and diverse hydroxylated and oxo carotenoids, although all of them present the same polyene chain with alternated double and single bonds. This distinctive structure is responsible for their physical and chemical properties, which provide this group of natural compounds with their coloring properties, antioxidant activities, and biological functions (*4*, *5*). However, the carotenoid structure also makes them very sensitive to heat, light, and prooxidant conditions reacting very easily with free radicals generated from different degradative processes such as fatty acids oxidation (*6*, *7*). As the carotenoid content of paprika oleoresins is both the quality and the economical standard, producers try to minimize all those processing conditions that could induce damage to the coloring matter. Therefore, raw and processed materials are protected from light, oxygen, and extreme heating, factors that trigger either direct degradation of carotenoids and indirect one, through fatty acids autoxidation.

Processing of paprika oleoresin includes a very severe thermal stage to remove organic solvent used during the extraction to satisfy statutory requirements of maximum solvent residue levels in food additives. Detrimental effects caused by that stage have been reduced by using flash evaporation or replacing organic solvents by supercritical fluids (*3*). Occurrence of oxygen plays a main role in fats and oils stability studies, as promoter of degradative reactions of the lipid substrate, and it is a limiting factor in autoxidation of lipophilic compounds. Several processing and storage techniques are employed to avoid or reduce those factors such as oxygen and light, which promote carotenoid degradation (*8*).

Addition of natural antioxidants is a common procedure applied to control free radicals progress and food deterioration. In the case of paprika oleoresins, rosemary extracts are added to enhance oxidative stability, as they prevent degradation caused by light, heat, and oxygen (*9*). However there is a trend of minimizing the use of food additives, so that an enhanced stability is reached by preventing endogenous food oxidation,

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that is, removing prooxidants naturally present in food or replacing compounds sensitive to oxidation with more stable ones.

Change of unsaturated fatty acids by saturated ones has been used as a method to enhance fats and oils stability, especially when the lipid substrate contains a high composition of polyunsaturated fatty acids very prone to autoxidation. Hydrogenation, use of saturated oils, and modification of plant desaturases enzymes activity are methods employed to change and increase the natural saturated to unsaturated fatty acids ratio. To avoid excessive presence of saturated lipids, which present an undesirable negative impact on health, modification of the monounsaturated to polyunsaturated fatty acids ratio may be enough to increase oxidation stability. Thus, sunflower and canola oils that contain 80−90% of oleic acid are commercially available, with a high oxidative stability and retention of their organoleptic qualities (*10*). A change in the usual fatty acid profile of canola oil has been applied to increase oxidative stability of β-carotene. The degradation rate of that carotenoid was related with unsaturation degree of lipid substrate: lower in the case of high oleic canola oil that was more stable under the imposed autoxidative conditions (*11*).

Fatty acids composition of paprika oleoresin consists mainly of linoleic acid that represents ca. 77% of total content (*12*). Therefore, carotenoids present in paprika oleoresins are solved in a lipid substrate where endogenous oxidation occurs very easily. As before mentioned, oxygen plays a key role in degradation of oils, but this is even more critical in the case of carotenoids-containing oils, because development of the antioxidant or prooxidant reactions that carotenoids could undergo depends on oxygen levels. It has been shown that when oxygen concentration is above 150 Torr, carotenoids degradation goes through prooxidant mechanisms, increasing the oxidative level in the substrate where they are solved (*13*). Lycopene and β-carotene displayed prooxidant activities in safflower oil exposed to heat and oxygen, decreasing the induction period (*14*). Therefore, it is unknown whether the enhanced oxidative stability provided by a change in the lipid substrate containing carotenoids is modulated by development of oxygen-mediated prooxidant reactions. The objective of the present study was to assess the carotenoid content stability of paprika oleoresin, changing the unsaturation level of its lipid substrate and avoiding those degradative reactions promoted by oxygen. The exclusion of oxygen from the reaction system allowed comparison of the stability of the carotenoid profile present in two paprika oleoresins, one with the conventional lipid substrate, and another one with a lower unsaturation level.

MATERIALS AND METHODS

Materials. The firm Extractos-Vegetales S.A (La Línea de la Concepción, Cádiz, Spain) supplied the two paprika oleoresins employed in this study. A batch of crude paprika oleoresin was subdivided in two sets that were diluted with high oleic or high linoleic refined oil, therefore obtaining a high oleic paprika oleoresin or a conventional paprika oleoresin. Fatty acids composition of the oleoresins resembled that of the refined oils used for dilution the crude extract, and they contained oleic or linoleic acid (72 or 75% of total fatty acids composition, respectively). Although the oleoresins differ on the unsaturation level of the lipid substrate, both contain the same carotenoid profile at equal concentrations. The use of the same batch implies that samples were subjected to the same processing conditions, and therefore they present the same initial degradation level.

Chemicals and Reagents. HPLC-grade acetone and methanol were supplied by Teknokroma (Barcelona, Spain). Diethyl ether containing ca. 7 ppm BHT was purchased from Microdur, S. L. (Sevilla, Spain). HPLC-grade water was obtained with a MilliQ water purifying system from Millipore (Milford, MA). All-*trans*-β-apo-8′-carotenal, used as internal standard for carotenoid determination, was purchased from Sigma (Barcelona, Spain). Other reagents were all of analytical grade.

Work Plan. Aliquots of high oleic and conventional paprika oleoresins were placed separately in 2-mL vials, which were gas-flushed with nitrogen and airtight without headspace. Afterward, samples were subjected to a heat-induced degradation process. Previous experiments indicated 80 °C as a suitable temperature. In both cases, sampling was performed at 11 time points in triplicate, to determine the quantitative carotenoid composition, using one vial for analysis at each time point and discarding it once the sample was taken. The total heating time was 600 h.

Extraction and Saponification of Carotenoid Profile. The sample (0.03 g) was dissolved directly in 100 mL of diethyl ether, and 1 mL of all-*trans*-β-apo-8′-carotenal in 40−60 °C light petroleum ether (200 μg/mL) was added as an internal standard for later quantification. Saponification of resulting solution was carried out in a 500-mL decanting funnel with 50 mL of 10% potassium hydroxide in methanol, shaking the mixture vigorously. After an hour of reaction at room temperature, 200 mL of 10% sodium chloride in water was added, and the aqueous and organic phases were left to separate. The organic phase was washed with 200-mL portions of distilled water until the washings were neutral. Organic solution containing the carotenoids was filtered through a solid bed of anhydrous sodium sulfate, evaporating the filtrate to dryness in a rotary evaporator. The residue was dissolved in acetone to a volume of 10 mL and stored at −30 °C until its analysis by HPLC.

Separation and Quantification of Carotenoid Pigments by HPLC. HPLC analyses were performed with a Waters 600E quaternary pump equipped with a Waters PDA 996 diode array detector (Waters, Barcelona, Spain) and controlled with a Millennium data acquisition station. Chromatographic separation was verified on a Spherisorb C-18 ODS2 reversed-phase column (250- × 4-mm, particle size, 5 μm) following a method described previously (*15*). The eluent phase employed was a binary gradient: acetone−water in an initial proportion of 75−25, respectively, at a constant flow rate (1.5 mL/min) to 95−5 in 5 min, and kept at this proportion for 7 min. At the end of the analysis, the column was washed with pure acetone for 3 min and returned to the initial conditions. The volume of sample injected was 20 μL, and spectrophotometric detection was performed at 450 nm. All-*trans*-β-apo-8′-carotenal was used as internal standard for calibration and quantification. Standards isolation, chromatographic separation, and carotenoid quantification are described in detail in a previous publication (*15*).

Kinetic Study. The data of carotenoid changes (individually, grouped as red or yellow isochromic pigment fractions, and total carotenoids) were analyzed by the integral method to deduce the kinetic parameters of reaction, order n and degradation rate constant k. This method uses a procedure of trial and error, in which the order of reaction in the rate equation is initially assumed.

$$-\frac{dC_P}{dt} = k \times (C_P)^n$$

The equation is then integrated, obtaining a linear expression that relates C_P (pigment concentration expressed in terms of percentage of retention) with time (t). From the expression best representing the change in the experimental data with reaction time, the order (assumed ab initio) was verified and used to obtain the degradation rate constant (k).

Statistical Analysis. Data were analyzed parametrically, and degradation rates were compared to test for significant differences (Duncan test). Significance was set at $p < 0.05$. A polynomial fit was used to follow the changes of data during the thermal treatment. The statistical analysis was performed with a statistical software package (STATISTICA for Windows, 5.5, 1999; Statsoft, Inc., Tulsa, OK).

RESULTS AND DISCUSSION

Table 1 shows initial carotenoid composition of conventional and high oleic paprika oleoresins, describing it individually and

Table 1. Initial Carotenoid Content (mg/kg of Sample; Mean Values ± SD) of Conventional (CPO) and High Oleic (HOPO) Paprika Oleoresins[a]

carotenoid	CPO	HOPO
capsorubin	2037 ± 38.3	1989 ± 49.0
violaxanthin	2381 ± 76.0	2439 ± 36.9
capsanthin epoxide	1827 ± 113	1895 ± 30.2
capsanthin	24595 ± 443	24377 ± 172
cis-capsanthin	10409 ± 285	10828 ± 230
curcurbitaxanthin A	4249 ± 30.0	4404 ± 51.8
zeaxanthin	5291 ± 33.7	5111 ± 14.7
cis-zeaxanthin	1109 ± 21.4	1161 ± 48.2
β-cryptoxanthin	4237 ± 64.2	4109 ± 25.6
β-carotene	6227 ± 79.1	6246 ± 6.31
cis-β-carotene	ND[b]	ND
red[c]	38869 ± 261	39091 ± 418
yellow[d]	23496 ± 199	23472 ± 134
total[e]	62365 ± 63.2	62563 ± 544

[a] Individual pigments, grouped by chromatic fraction (red and yellow), and total pigments are shown. [b] ND, not detected. [c] Red = capsorubin + capsanthin + capsanthin epoxide + *cis*-capsanthin. [d] Yellow = violaxanthin + cucurbitaxanthin A + zeaxanthin + *cis*-zeaxanthin + β-cryptoxanthin + β-carotene + *cis*-β-carotene. [e] Total = red + yellow.

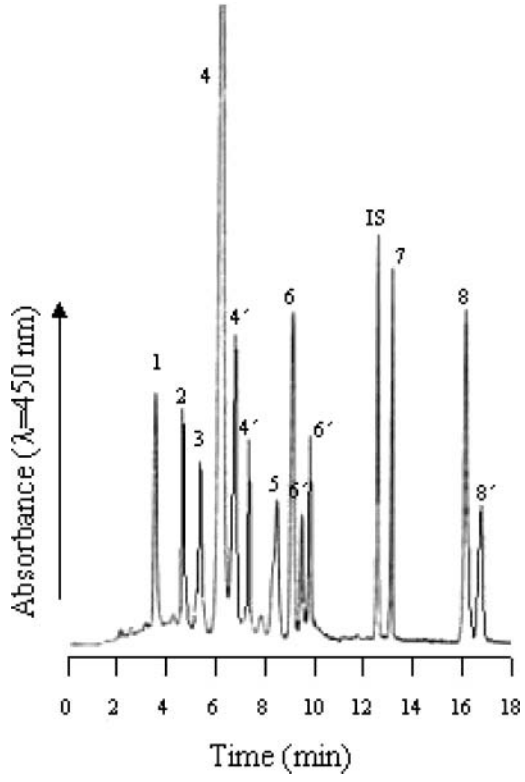

Figure 1. HPLC chromatogram of the conventional paprika oleoresin after 168 h of thermal treatment at 80 °C. Peak identification: 1, capsorubin; 2, violaxanthin; 3, capsanthin-5,6-epoxide; 4, capsanthin; 4′, *cis*-capsanthin; 5, cucurbitaxanthin A; 6, zeaxanthin; 6′, *cis*-zeaxanthin; 7, β-cryptoxanthin; 8, β-carotene; 8′, *cis*-β-carotene. IS, internal standard.

grouped in red, yellow, and total carotenoids fractions. The profile is that normally found in paprika oleoresins with capsanthin as the main carotenoid, quantitatively. Individual carotenoid composition was comparable, even isomer distribution, so both oleoresins showed very similar total carotenoid content (ca. 62.5 g/kg) and red to yellow pigments ratio (ca. 1.66). **Figure 1** shows the chromatogram corresponding to the HPLC analysis of the conventional paprika oleoresin after 168 h of thermal treatment. The method allows cis-isomers separation as may be observed in **Figure 1**, which also shows the occurrence of cis-β-carotene that was not initially detected (**Table 1**).

Table 2. Degradation Rate Constants (Mean Values ± SD) of Carotenoid Fractions (Red, Yellow, and Total) and Major Carotenoids of Each Isochromic Group for the Thermal Process Applied in Conventional (CPO) and High Oleic (HOPO) Paprika Oleoresin

	rate const ($k \pm SD$) × 10^{-4} h^{-1}		corr coeff r^2	
carotenoids	CPO	HOPO	CPO	HOPO
red[a]	15.54 ± 0.8	16.25 ± 0.7	0.964	0.969
yellow[b]	13.89 ± 0.6	14.14 ± 0.7	0.973	0.973
total[c]	14.88 ± 0.7	15.41 ± 0.7	0.970	0.974
capsorubin	14.18 ± 0.9	15.39 ± 0.9	0.869	0.908
capsanthin	18.95 ± 1.1	19.76 ± 0.9	0.954	0.956
zeaxanthin	14.35 ± 0.4	14.54 ± 0.6	0.974	0.979
β-carotene	20.28 ± 1.0	18.64 ± 1.0	0.962	0.941

[a] Red = capsorubin + capsanthin + capsanthin epoxide + *cis*-capsanthin. [b] Yellow = violaxanthin + cucurbitaxanthin A + zeaxanthin + *cis*-zeaxanthin + β-cryptoxanthin + β-carotene + cis-β-carotene. [c] Total = red + yellow.

Stability of carotenoid content, solved in different lipid substrates, was evaluated under no occurrence of oxygen. A 1st-order model was the best fit to experimental data, a kinetic model that has also been described in the degradation of food components such as ascorbic acid in corn-soy-milk and in flour, chlorophylls in spinach, and carotenoids in freeze-dried powder during storage at different temperatures or in their heat stability studies (*16*−*18*). Comparison between degradation rate constants of red, yellow, and total carotenoids fractions, exposed in **Table 2**, allowed the determination of whether a decrease in the unsaturation level enhanced carotenoid stability. Comparable degradation rate constants for any of the before mentioned fractions were obtained without significant differences (Duncan test, $p > 0.05$). For the total carotenoid content, a degradation rate constant of ca. 15 h^{-1} was obtained either in the monounsaturated or polyunsaturated lipid surrounding. **Table 2** shows degradation rate constants for capsorubin, capsanthin, zeaxanthin, and β-carotene, which mainly contribute to the pigment profile of paprika oleoresins. Statistical comparison of degradation rate constant of those pigments in both lipid substrates indicated no significant differences. Therefore, under established reaction conditions, a change in the unsaturation level of the lipid substrate where the carotenoids were solved did not improve their stability.

The most important nutritional value of paprika oleoresins is the provitamin A content supplied by β-cryptoxanthin and β-carotene, which are important to be preserved during processing and storage. Evolution of provitamin A values and changes in β-carotene and β-cryptoxanthin concentration during thermal degradation of conventional and high oleic paprika oleoresins is shown in **Tables 3** and **4**, respectively. The thermal process applied to both oleoresins produced a continuous decrease on β-carotene and β-cryptoxanthin content and consequently a fall of the provitamin A value, with very similar losses in both oleoresins (ca. 63% at the end of thermal treatment) so changes in provitamin A content are unaffected by nature of lipid nature.

The experiment was carried out avoiding occurrence of oxygen so lipid degradation did not mainly undergo under autoxidative pathways, but through mechanisms such as those that take place during oil heating. In that case, mechanisms include polymerization reactions, thermal decomposition of fatty acids and intramolecular rearrangement. Degradation products formed in heated oils have been previously described, and they include polymers (mainly dimers), monocyclic, and bicyclic fatty

Table 3. Changes in β-Carotene and β-Cryptoxanthin Concentration (mg/kg of Sample; Means ± SD) and Provitamin A Values (I. U. of Provitamin A/kg of Sample) during Thermal Degradation at 80 °C of the Conventional Paprika Oleoresin

time (h)	β-carotene	β-cryptoxanthin	provitamin A[a]
0	6227 ± 79.1	4237 ± 64.2	13911 ± 178
48	6205 ± 3.99	4234 ± 19.2	13871 ± 10.4
96	5899 ± 185	4246 ± 71.3	13370 ± 359
168	4410 ± 88.1	3160 ± 71.8	9983 ± 201
216	3526 ± 87.3	2935 ± 380	8323 ± 365
264	3699 ± 563	3064 ± 62.3	8718 ± 988
360	3179 ± 322	2719 ± 177	7564 ± 407
408	2512 ± 323	2179 ± 255	6003 ± 747
504	2077 ± 120	1866 ± 120	5016 ± 300
552	2068 ± 132	1812 ± 94.1	4956 ± 295
600	2239 ± 231	1728 ± 78.3	5172 ± 446

[a] I. U. × 10^3= 1667 × (mg of β-carotene) + 833 × (mg of β-cryptoxanthin)/kg of sample.

Table 4. Changes in β-Carotene and β-Cryptoxanthin Concentration (mg/kg of Sample; Means ± SD) and Provitamin A Values (I. U. of Provitamin A/kg of Sample) during Thermal Degradation at 80 °C of the High Oleic Paprika Oleoresin

time (h)	β-carotene	β-cryptoxanthin	provitamin A[a]
0	6246 ± 6.31	4109 ± 25.6	13835 ± 34.1
48	6173 ± 67.5	4253 ± 78.5	13834 ± 118
96	4953 ± 357	4200 ± 129	11760 ± 547
168	3543 ± 49.3	3286 ± 131	8644 ± 162
216	3442 ± 406	3019 ± 202	8252 ± 765
264	3083 ± 79.5	2947 ± 145	7595 ± 248
360	2643 ± 312	2393 ± 354	6400 ± 816
408	2366 ± 219	2094 ± 89.2	5688 ± 433
504	2132 ± 298	1910 ± 166	5146 ± 633
552	2122 ± 69.8	1678 ± 23.6	4935 ± 133
600	2303 ± 165	1728 ± 96.7	5279 ± 356

[a] I. U. × 10^3= 1667 × (mg of β-carotene) + 833 × (mg of β-cryptoxanthin)/kg of sample.

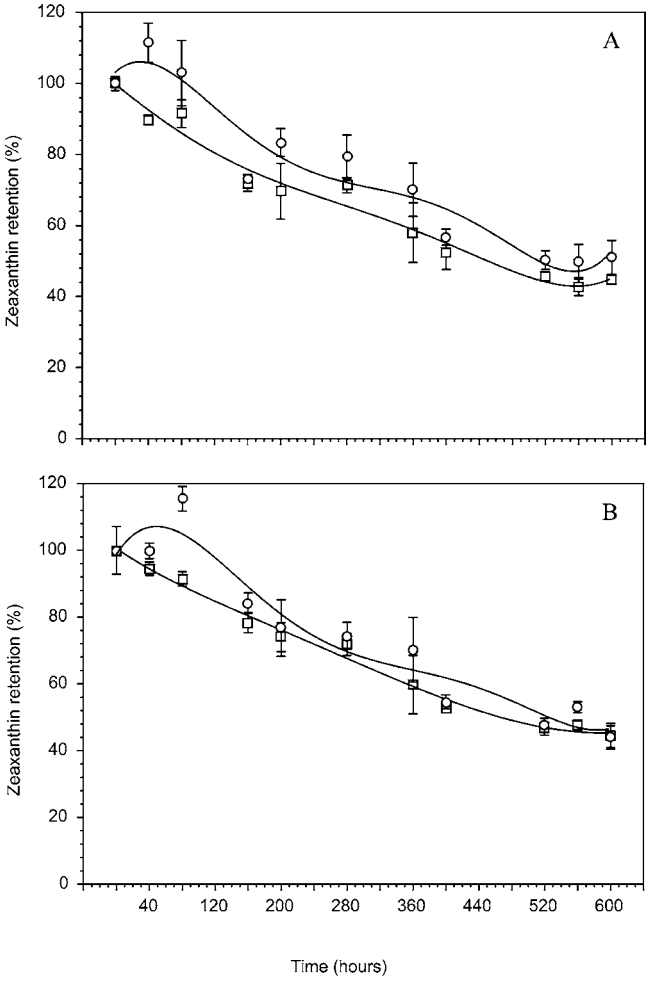

Figure 2. Evolution of *cis*- (○) and *trans*-zeaxanthin (□) retention percentage during thermal treatment of conventional paprika oleoresin (A) and high-oleic paprika oleoresin (B).

acids (*19*−*21*). Polymerization reactions and thermal decomposition mechanisms do not involve oxygen and energy provided to the samples was the driving force that produced allylic radicals, degrading fatty acids and all those lipophilic components such as carotenoids.

Direct degradation of carotenoids may have undergone the same free radical mechanisms that decompose fatty acids because the former present a central carbon chain of polyunsaturated nature (*6*, *7*, *22*, *23*). Such reaction mechanisms were also unaffected by modification of the unsaturation degree.

Another set of reactions, also denoted in the present study, was the trans to cis isomer configuration change detected for β-carotene, capsanthin, and zeaxanthin. **Figure 2** depicts evolution of retention percentage corresponding to trans and cis isomers of zeaxanthin during applied conditions in conventional (**Figure 2A**) and high oleic (**Figure 2B**) paprika oleoresins. Similar changes were observed for cis and trans isomers of β-carotene and capsanthin (data not shown). The polynomial fit obtained in both oily systems showed an initial increase on cis isomers. During the complete thermal treatment, their retention values were always higher than those corresponding to the trans isomers, which evolution showed a continuous decline. As can be deduced from polynomial fit obtained for *cis*- to *trans*-capsanthin ratio changes (**Figure 3**), transformation rate from trans to cis isomers rose continuously during a half of the thermal treatment, to finally reach an equilibrium on the final period, a similar situation to that described in the thermal-mediated isomerization of β-carotene and astaxanthin (*24*, *25*).

Such evolution displayed the significance of these processes, especially favored when carotenoids are solved in oily systems (*26*), which require low activation energy (*27*, *28*). These reactions are of significant relevance because their occurrence modifies the chemical properties, antioxidant capacity, and bioavailability and nutritional value of carotenoids in such processed foods (*4*, *29*, *30*). In food lipids, carotenoid isomerization seems to be time and temperature dependent, and the present study showed that it is also unrelated with oily system nature.

Differences in the reactivity level between oleic and linoleic fatty acids are the grounds to improve stability of lipid substrate and that of any of the lipophilic components solved on it. Nawar reported that under autoxidative conditions, the relative reactivity of linoleic is 10-fold that of oleic acid (*31*). However those differences did not come out in the present study, and relative reactivity seems to be the same for both fatty acids (i.e., 1:1). Even Carnervale et al. found improved β-carotene stability when this carotenoid was solved in a polyunsaturated lipid system in comparison with stability provided by a monounsaturated environment (*32*). An unlinked relation between oxidative stability and unsaturation level was found in β-carotene degradation added to canola oils subjected to photooxidative conditions (*11*).

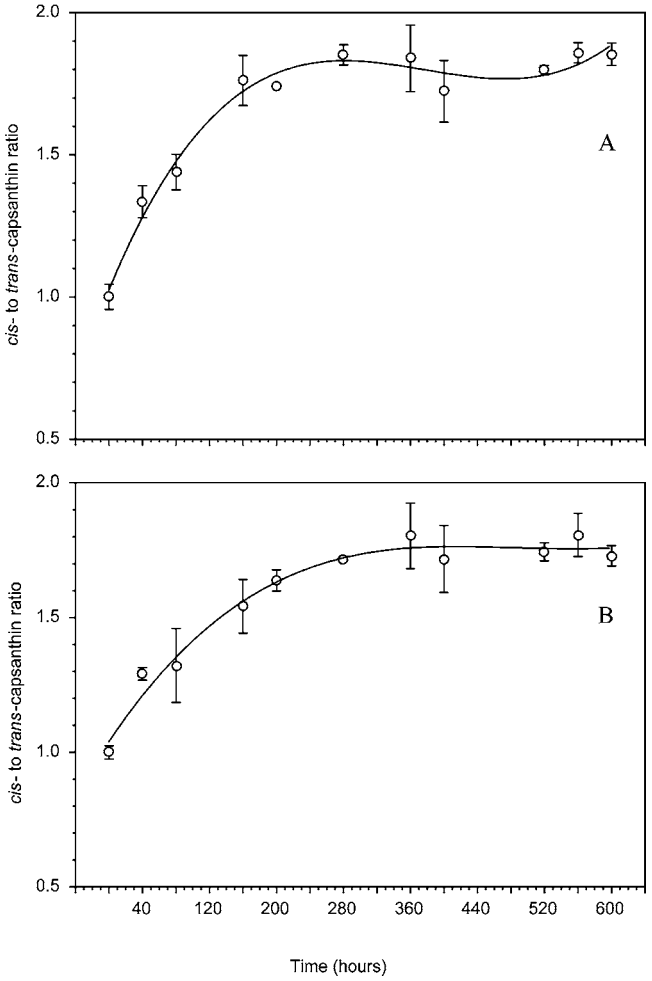

Figure 3. Changes in *cis* to *trans*-capsanthin ratio during thermal treatment of conventional paprika oleoresin (A) and high-oleic paprika oleoresin (B).

Degradation level and reactivity of lipophilic compounds in an oily system is highly related with oxygen concentration, which is a regulating factor in degradation of fats and oils (*33*, *34*). Heat-mediated deterioration of oleic and linoleic fatty acids in sunflower oil was not different at low oxygen content (2 and 4%), but when that content was increased (10 and 20%) high oleic sunflower oil showed a better stability than the conventional one (*35*).

Therefore, lipid substrates of different unsaturation degrees supply the same stability to carotenoids once occurrence of oxygen has been avoided. The degradation rate constant of the carotenoid profile is unaffected by such factors, as well as occurrence and development of carotenoid isomerization. Loss of both organoleptic (color) and nutritional (provitamin A) qualities takes place as a consequence of the temperature applied, but it is not negatively or positively modulated by oily system characteristics. A more convenient strategy, without changes in unsaturation degree of lipid substrate, to prevent carotenoid degradation in oily food additives such as paprika oleoresins should be to minimize contact of food with oxygen, applying vacuum, new packaging materials, or encapsulation techniques, avoiding oxygen-mediated autoxidation reactions.

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