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Thermal Degradation Kinetics of Carotenoids in a Cashew Apple Juice Model and Its Impact on the System Color

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The thermal degradation kinetics of the main carotenoids of cashew apple in a juice model system was studied by HPLC and related to the changes of its CIELAB color parameters. Similar isomerization equilibrium constants and activation energies were observed for both all-*trans*-β-carotene and all-*trans*-β-cryptoxanthin. The curves for the decay of the main carotenoids and color changes showed a biphasic behavior that was best fitted by a biexponential equation. For the same heating conditions (60 or 90 °C), similar rate constants for the fast (γ_1) and slow (γ_2) decays were obtained for both the chemical (carotenoids) and physical (color) parameters monitored in the present research. This fact indicates that color parameters, such as ΔE^*, are good predictors of both all-*trans*-β-cryptoxanthin and all-*trans*-β-carotene thermal degradation. A mechanism for thermal carotenoid degradation was proposed, involving parallel irreversible and reversible coupled reactions of both the initial all-*trans*-β-cryptoxanthin and all-*trans*-β-carotene to yield, respectively, degradation compounds and mono-*cis* isomers.

KEYWORDS: Carotenoids; color; kinetics; thermal degradation; cashew apple juice model; *Anacardium occidentale*.

INTRODUCTION

Anacardium occidentale L. is a tropical tree native to the northern and northeastern regions of Brazil. Its pseudofruit, known as cashew apple, is very popular and highly consumed as ready-to-drink juice, concentrate, and nectar, among other thermally processed products.

As it is widely known, thermal treatments usually applied to extend the shelf life of fruit products affect their quality, leading to consumer dissatisfaction. Pigment transformations are one of the major causes for such problems, because these compounds are usually responsible for the fruit color. Depending on the severity of the thermal treatment, the degradation of carotenoids, for instance, causes color changes in several fruit juices (*1*, *2*). In cashew apple juice, due to the abundant presence of carotenoid pigments, notably β-cryptoxanthin and β-carotene (*3*), controlling such degradations is particularly important, as color is one of the most important attributes of the beverage.

The rate of pigment degradation depends on several conditions, such as medium composition, pH, temperature, UV exposure, and dissolved oxygen content (*2*, *4*−*7*); therefore, the kinetics of pigment degradation is rather complex in food systems. Nonetheless, when pigment degradation resulting from thermal processing needs to be minimized, kinetics studies capable of determining parameters such as reaction order and constant rates are required, being equally important to establish the impact of the compounds' degradation on the food color.

Thus, the goals of this study were to determine the degradation kinetics of the cashew apple main carotenoids in a juice model heated at 60 and 90 °C, and to relate this degradation kinetic with mathematically predictive models associating CIELAB color parameters with heating time. For cashew apple products, this information is fundamental to predicting quality loss resulting from thermal processes; nonetheless, it is rare to find it in related literature.

MATERIALS AND METHODS

Samples and Standards. Red cashew apple fruits (*A. occidentale* L.) from the Petrolina region (State of Pernambuco, Northeastern region, Brazil) were acquired in a supermarket of the city of Campinas (State of São Paulo, Brazil), during their harvest season (October 2006) and kept frozen at −18 °C until carotenoid extraction. The peel and the cashew nut of 40 fruits were manually removed, and the resulting pulp was homogenized. On average, the individual fruit weights ranged from 50 to 66 g, the soluble solids from 12.0 to 14.5 °Brix, and the pH values from 3.5 to 4.5.

The carotenoid standards all-*trans*-lutein, all-*trans*-zeaxanthin, all-*trans*-β-cryptoxanthin, all-*trans*-β-carotene, and all-*trans*-α-carotene, with purity degrees between 95 and 99% determined by HPLC-PDA, were provided by DSM Nutritional Products (Basel, Switzerland).

Methanol (MeOH), methyl *tert*-butyl ether (MTBE), and ethyl acetate (EtOAc) for HPLC were obtained from Merck (Darmstadt, Germany) or from Mallinckrodt Baker (Philipsburg, NJ). The other reagents were all of analytical grade from Labsynth (Diadema, Brazil). The distilled water was

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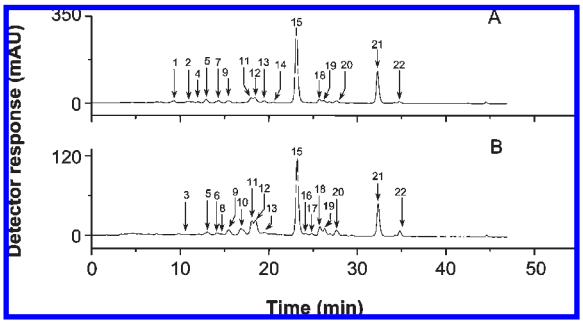


Figure 1. Chromatogram (processed at 450 nm), obtained by HPLC-PDA, of carotenoids from cashew apple juice model: (**A**) unheated; (**B**) heated at 90 °C for 4 h. See text for chromatographic conditions. Peak identification was according to increasing retention time: (1) *cis*-neoxanthin; (2) neochrome; (3) auroxanthin; (4) *cis*-violaxanthin; (5) antheraxanthin; (6) mutatoxanthin; (7) all-*trans*-lutein; (8) *cis*-lutein; (9) all-*trans*-zeaxanthin; (10) 5,6-epoxy-β-cryptoxanthin; (11) 13- or 13′-*cis*-β-cryptoxanthin; (12) 13′- or 13-*cis*-β-cryptoxanthin; (13) zeinoxanthin; (14) all-*trans*-α-cryptoxanthin,; (15) all-*trans*-β-cryptoxanthin; (16) 15-*cis*-β-carotene; (17) 5,8-epoxy-β-carotene; (18) 13-*cis*-β-carotene; (19) 9- or 9′-*cis*-β-cryptoxanthin; (20) all-*trans*-α-carotene; (21) all-*trans*-β-carotene; (22) 9-*cis*-β-carotene.

purified by a Milli-Q Plus system (Millipore, Billerica, MA). Prior to HPLC analysis, the carotenoid extracts and solvents were filtered through 0.22 and 0.45 μm Millipore membranes, respectively.

Cashew Apple Juice Model Systems. The carotenoids were extracted with acetone, transferred to petroleum ether (bp 30−70 °C)/diethyl ether, and saponified overnight at room temperature with 10% methanolic KOH, followed by alkali removal. Due to the high oil content in the cashew apple pulp, it was necessary to physically remove the oil as follows: prior to the transfer to ether, the carotenoid extract was kept in the freezer at −18 °C for 2 h, followed by filtration using cold glassware and washing with cold acetone (*8*). The dried cashew apple carotenoid extract was flushed with pure N_2 (99.0%) and kept at −35 °C for 24 h.

The cashew apple extract, containing approximately 200 μg of carotenoid, was first dissolved in 5 mL of ethanol, which was further added to 25 mL of Milli-Q water previously acidified at pH 3.8 with 0.5 M of citric acid (*9*).

The cashew apple juice model was distributed in sealed glass tubes and heated at 60 and 90 °C in a water bath at different heating times: 0, 30, 60, 90, 120, 150, 180, 210, 240, 300, 360, 420, 480, and 540 min at 60 °C and 0, 5, 10, 15, 30, 45, 60 120, 180, and 240 min at 90 °C. In all of the experiments, the water bath temperature was monitored using a thermocouple. After each heating time, the tubes were removed from the water bath, immediately cooled under running tap water, and analyzed. Two independent experiments were carried out for each temperature. All samples, including the nonheated cashew apple juice model, were submitted to HPLC and color analysis as described below.

The temperature of 90 °C was chosen because it is the temperature usually associated with juice pasteurization. Similarly, the temperature of 60 °C is associated with the blanching of fruits and vegetables.

HPLC Analysis. The carotenoids were exhaustively extracted from the juice model system with ethyl acetate, by vortexing during 1 min (Phoenix, model AP 56, Araraquara, Brazil); following that, the extract was transferred to a separation funnel, washed with water until neutral pH, and dried under a N_2 stream. Prior to HPLC-PDA analysis, the carotenoid extract was completely solubilized in MeOH/MTBE (70:30) and filtered through a Millipore membrane (0.22 μm).

The carotenoids were analyzed in a Shimadzu HPLC (Kyoto, Japan) equipped with quaternary pumps (model LC-20AD), online degasser, and Rheodyne injection valve with a 20 μL loop (Rheodyne LCC, Rohnert Park, CA). The equipment also included, connected in series, a PDA detector (Shimadzu, model SPD-M20A). For all samples, carotenoid separation was carried out on a C_{30} YMC column (3 μm, 250 × 4.6 mm id.) (Waters, Wilmington, MA) using as mobile phase a linear gradient of MeOH/MTBE from 95:5 to 70:30 in 30 min and to 50:50 in 20 min at 0.9 mL/min.

The carotenoids were identified by HPLC-PDA and tandem mass spectrometry, as previously described (*9*). The carotenoids were quantified by HPLC, using external calibration curves for all-*trans*-lutein, all-*trans*-zeaxanthin, all-*trans*-β-cryptoxanthin, all-*trans*-β-carotene, and all-*trans*-α-carotene with a minimum of five concentration levels. Neoxanthin, neochrome, antheraxanthin, mutatoxanthin, *cis*-violaxanthin, and auroxanthin were quantified using the curve of lutein; the β-cryptoxanthin epoxides, α-cryptoxanthin, and zeinoxanthin using the curve of all-*trans*-β-cryptoxanthin; β-carotene epoxides by the curve of all-*trans*-β-carotene; and the *cis* isomers of lutein, β-cryptoxanthin, and β-carotene using the curve of the corresponding all-*trans* isomers. Total carotenoid content was calculated considering all identified peak areas.

The absorption coefficient values used for the quantification of carotenoids were 2550 for all-*trans*-lutein in ethanol, 2350 for all-*trans*-zeaxanthin in petroleum ether, 2386 for all-*trans*-β-cryptoxanthin in petroleum ether, 2800 for all-*trans*-α-carotene in petroleum ether, and 2592 for all-*trans*-β-carotene in petroleum ether (*10*).

Color Analysis. Color changes due to heating of the cashew apple juice model were quantified through CIELAB parameters (L^*, a^*, and b^*) obtained by a spectrocolorimeter (Hunter, model Color Quest XE, Reston, VA), equipped with D65 as the light source and using an observation angle of 10°. Additionally, values of ΔE^* (total color difference), C^* (chrome), and h (hue) were calculated using eqs 1, 2, and 3, respectively. Triplicate measurements were carried out for each experiment.

$$\Delta E^* = \sqrt{(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2} \quad (1)$$

$$C^* = \sqrt{(a^*)^2+(b^*)^2} \quad (2)$$

$$h = \arctan\left(\frac{b^*}{a^*}\right) \quad (3)$$

Kinetic Analysis. The kinetic data were fitted by nonlineal regression based on the Levenberg−Marquardt (LM) algorithm using Microcal Origin 7.0 (OriginLab Corp., Northampton, MA).

RESULTS AND DISCUSSION

Heating Effect on Carotenoid Composition. Figure 1 shows the HPLC chromatogram profiles of the cashew apple juice model before and after 4 h of heat treatment at 90 °C. The identification of the peaks in the figure was based on the elution order on a C_{30} column, coelution with standards, and UV−visible and mass spectra patterns, as previously described (*9*). Before heating, at least 16 carotenoids (total carotenoids) were identified, **Figure 1A** (Supplemental **Table 1**). The major carotenoids were all-*trans*-β-cryptoxanthin (57.4%) and all-*trans*-β-carotene (22.0%) in proportions similar to those previously reported for cashew apple juice (*3*) and fresh fruits (*11*). The complementary ca. 20% was constituted by traces of other all-*trans* carotenoids (e.g., lutein, α-carotene, and zeaxanthin) and mono-*cis* isomers (mainly 9-, 9′-, 13-, or 13′-) of both β-cryptoxanthin and β-carotene.

After 4 h of heating at 90 °C, HPLC analysis indicated a pronounced degradation of both main all-*trans* carotenoids, accompanied by the increment of *cis* isomers (including 15-*cis*) and oxidation products, such as 5,6-epoxides and 5,8-furanoids (**Figure 1B**). However, analysis of the total carotenoid content (Supplemental **Table 2**) demonstrated that only a fraction of the degraded carotenoids can be associated with the formation of those isomerization and/or oxidation products. The disappearance of carotenoids can be attributed to the generation of both volatile and low molecular weight compounds not detected by HPLC-PDA. In fact, recent GC-MS study involving the heating of cashew apple carotenoids reported the generation of more than 10 volatile compounds, including low molecular

Table 1. Kinetic Parameters Obtained by Fitting HPLC and Color Data, Using Equation 4, for Degradation of Carotenoids and Color Changes during Thermal Treatment of a Cashew Apple Juice Model

temp (°C)	parameter[a]	total carotenoids	β-cryptoxanthin	β-carotene	total 9-*cis*-isomers	total epoxides	*a**	*b**	*L**	Δ*E**	*C**	*h*
60	Y_0	107.2 ± 1.0	61.3 ± 0.2	23.5 ± 0.5	1.8 ± 0.1	0.0	6.8 ± 0.1	28.4 ± 0.1	31.5 ± 1.0	0.0	29.2 ± 0.1	76.5 ± 2.0
	Y_∞	68.3 ± 29.4	21.7 ± 6.6	11.7 ± 4.3	9.4 ± 1.5	7.6 ± 4.5	1.2 ± 0.5	18.6 ± 0.2	22.2 ± 1.7	16.5 ± 1.9	18.4 ± 2.0	82.1 ± 3.4
	A_1	37.3 ± 4.7	28.2 ± 1.2	11.7 ± 0.9	−2.1 ± 0.2	−3.2 ± 0.7	0.8 ± 0.1	1.3 ± 0.3	2.8 ± 0.3	−3.1 ± 0.2	1.4 ± 0.3	−1.5 ± 0.9
	γ_1	0.6 ± 0.1	0.7 ± 0.1	0.5 ± 0.2	1.0 ± 0.2	1.2 ± 0.6	0.5 ± 0.1	0.6 ± 0.2	0.8 ± 0.1	0.7 ± 0.1	0.6 ± 0.2	0.3 ± 0.2
	A_2	2.5 ± 9.5	12.6 ± 7.4	0.9 ± 4.2	−5.6 ± 1.7	−4.8 ± 5.0	4.8 ± 0.5	8.6 ± 2.4	6.5 ± 1.9	−13 ± 2.1	9.8 ± 2.4	−4.1 ± 4.3
	γ_2	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.02	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.02
90	Y_0	107.0 ± 1.5	61.4 ± 0.5	23.5 ± 0.3	0.0	0.0	7.7 ± 0.1	29.8 ± 0.3	32.0 ± 0.5	0.0	30.8 ± 0.2	76.0 ± 0.5
	Y_∞	30.3 ± 4.1	9.1 ± 3.3	5.1 ± 1.5	5.3 ± 0.1	10.8 ± 0.5	4.9 ± 0.1	26.0 ± 0.3	27.6 ± 1.3	6.1 ± 0.6	26.5 ± 0.3	79.1 ± 0.4
	A_1	15.4 ± 2.2	14.1 ± 2.2	5.5 ± 0.9	−2.3 ± 0.1	−1.0 ± 0.3	0.6 ± 0.1	2.1 ± 0.2	3.7 ± 0.9	−4.0 ± 0.4	2.1 ± 0.2	−0.2 ± 0.2
	γ_1	6.0 ± 1.0	6.7 ± 2.0	7.6 ± 2.9	1.8 ± 1.5	8.9 ± 3.3	6.9 ± 1.7	7.7 ± 1.8	3.5 ± 1.5	4.3 ± 1.0	8.3 ± 1.8	8.6 ± 4.0
	A_2	63.6 ± 5.3	38.9 ± 4.7	13.3 ± 2.1	−1.3 ± 1.1	−9.8 ± 0.7	2.2 ± 1.0	1.6 ± 0.5	1.0 ± 2.0	−2.1 ± 0.1	2.1 ± 0.47	−3.5 ± 0.5
	γ_2	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.2	0.2 ± 0.1	0.2 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.2

[a] All values are average and standard deviation of two independent experiments. γ_1 and γ_2 in h^{-1}; Y_0, Y_∞, A_1, and A_2 in $\mu g\ mL^{-1}$ for carotenoid concentration. Total 9-*cis*-isomers and total epoxides were products of all-*trans*-β-carotene and all-*trans*-β-cryptoxanthin.

Table 2. Rate Constant Values Calculated According to the Proposed Mechanism Shown in **Scheme 1** for the Thermal Degradation of Carotenoids in a Cashew Apple Juice Model

	rate constant (h^{-1})				
temp (°C)	$\langle\gamma_1\rangle$	$\langle\gamma_2\rangle$	k_1	k_2	k_3
60	0.68 ± 0.11	0.02 ± 0.01	0.003 ± 0.001	0.021 ± 0.004	0.555 ± 0.040
90	6.4 ± 2.2	0.22 ± 0.04	0.11 ± 0.020	0.22 ± 0.05	6.67 ± 0.80

weight aromatic volatiles such as *p*-xylene, *p*-cymene, *p*-cresol, and naphthalene, as well as nonaromatic volatiles such as *n*-dodecane and 1-tetradecene (data not published).

Moreover, in the juice model, heat treatment at both 60 and 90 °C promoted not only the increase of the *cis* isomers already present in the sample but also the formation of two new *cis* isomers (*cis*-lutein and 15-*cis*-β-carotene) and four epoxide derivatives (auroxanthin, mutatoxanthin, 5,6-epoxy-β-cryptoxanthin, and 5,8-epoxy-β-carotene) (*9*). Additionally, at 90 °C the formation of luteoxanthin and one short-chain product, 12′-apo-β-carotenal (*9*), was observed. The rearrangement of 5,6-epoxides to their corresponding 5,8-furanoids and formation of *cis* are very common reactions that occur during the thermal processing of juices (*2*, *12*).

The initial overall isomeric *trans*/*cis* ratio of both β-cryptoxanthin and β-carotene was found to be ca. 92:8, changing to stable values of 70:30 and 75:25 after 3 and 8 h of heating at 90 and 60 °C, respectively. These results indicate that a steady-state equilibrium of β-cryptoxanthin and β-carotene isomers was reached in the cashew apple juice model after those conditions. In addition, the stable isomeric ratio of 65:35 reported for β-carotene standard diluted in toluene was achieved after 1 h of heating at 98 °C (*13*). These results reveal that for the all-*trans* ⇔ *cis* isomerization process, similar global equilibrium constant $K_{e,iso}$ and activation energy $E_{a,iso}$ are operating for both main carotenoids in aqueous solvent. By applying the isomeric percentage change between the initial ($t = 0$) and final ($t = \infty$) times, estimations of $K_{e,iso} \approx 0.50$ at 90 °C and $K_{e,iso} \approx 0.17$ at 60 °C were obtained.

Heating Effect on Color Parameters. The thermal treatment of the juice model reduced the redness (*a**) and yellowness (*b**) of the system at both 60 and 90 °C, with simultaneous darkening of the solution, as demonstrated by the reduction of the *L** parameter. In the first 60 min of heating, the decrease of the *b** parameter (yellowness) occurred at a higher rate than for the *a** values (redness). This phenomenon can be attributed to the fact that β-carotene and β-cryptoxanthin, the most abundant pigments present in the juice model, are yellowish carotenoids (*14*); as a consequence, their degradation produced higher impact in the *b** as compared to the *a** values. The calculated chrome (*C**, eq 2) and hue (*h*, eq 3) parameters also changed during heating due to the degradation of carotenoids (Supplemental **Table 2**).

The total color change Δ*E** increased to ca. 5 after 4 h of heating at 90 °C, and similar changes were observed after 9 h of heating at 60 °C. According to Lee and Coates (*15*), a value of $\Delta E^* \approx 2$ represents a noticeable color difference and, for many products $\Delta E^* > 3$ is unacceptable by the consumers. In fact, $\Delta E^* = 2$ was already verified after the first 15 min of cashew apple juice model heating at 90 °C. This deep variation of total color can be mostly associated with the transformation of the main all-*trans* carotenoids in *cis* isomers, oxidation compounds, volatiles, and other nondetectable low molecular weight compounds. Thus, the total color change (Δ*E**) observed in **Figure 2** for the heated cashew apple juice model is expected to negatively affect the consumer's color perception of the sample.

Kinetics of Thermal Degradation. Figure 2 also shows that both carotenoid level and color parameter changes followed a biphasic behavior that was best fitted by the biexponential eq 4. The same kinetics was also observed at 60 °C.

$$y_t = A_1 \exp(-\gamma_1 t) + A_2 \exp(-\gamma_2 t) + y_\infty \quad (4)$$

In eq 4, y_t and y_∞ are carotenoid concentration or color parameter values at real time and infinite time, respectively. A_1 and A_2 are the pre-exponential factors, whereas γ_1 and γ_2 are the observed rate constants for the fast and slow decays, respectively.

Table 1 shows the calculated kinetic parameters obtained by fitting the data with eq 4. It reveals that similar γ_1 and γ_2 values were obtained for both the chemical (carotenoids) and the physical (color) parameters at the same heating temperature. **Table 1** also indicates that the extrapolation of the total carotenoid concentration at infinite time $[Car]_\infty$ was larger than the sum of those for all-*trans*-β-carotene and all-*trans*-β-cryptoxanthin. This occurred because the evaluation of total carotenoids included the formation of *cis* isomers and epoxides, which were the main products detected by HPLC analysis.

The biexponential decay behavior verified for the initial all-*trans* carotenoids and products formed showed in all cases the same observed fast and slow lifetimes at each temperature, confirming the occurrence of a common overall degradation mechanism (**Scheme 1**), which involves parallel irreversible and reversible

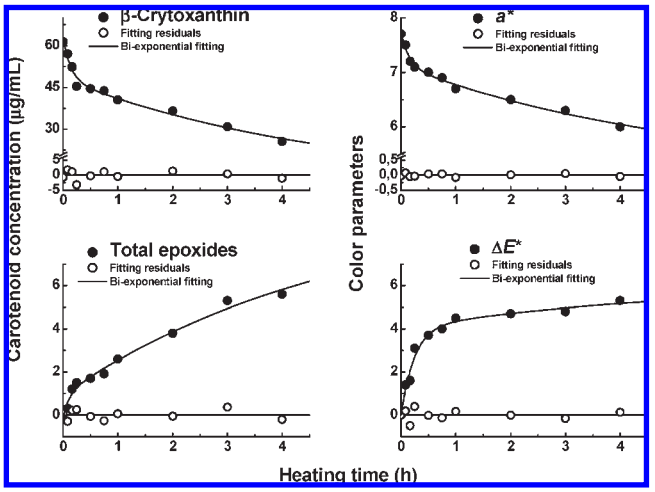


Figure 2. Biexponential fitting with eq 4 of the experimental data obtained for cashew apple juice model heating at 90 °C.

coupled degradation reactions. In this overall mechanism, three main types of chemical compounds are involved, that is, the initial main all-*trans*-β-cryptoxanthin and all-*trans*-β-carotene, the reversibly equilibrated mono-*cis* isomers (9-, 9′-, 13-, 13′-, 15-, 15′-), and degradation products, such as epoxides, apo-carotenals, and volatiles (*p*-xylene, *p*-cresol, and dodecane) produced by irreversible oxidation and/or breakdown reactions (*9*). Degradation of both mono-*cis* isomers and epoxides was not kinetically detected during the heating period. A similar mechanism for the thermal degradation of bixin in a water/ethanol (8:2) solution, studied by HPLC as a function of temperature (70−125 °C), was also reported (*5*).

The simplest mathematical solution of the differential equations that describe the mechanism proposed can be obtained by assuming that the initial concentration of *cis* isomers and epoxides is negligible as compared with the concentration of the precursors all-*trans* carotenoids, that is, $[C]_0 \neq 0$, and $[I]_0 = [P]_0 = 0$ (*16*). In the present case, both all-*trans*-β-cryptoxanthin and all-*trans*-β-carotene represent ca. 90% of the initial mixture, approximating the above assumption. Thus, according to **Scheme 1**, the integrated equation for the carotenoid degradation is given by eq 5.

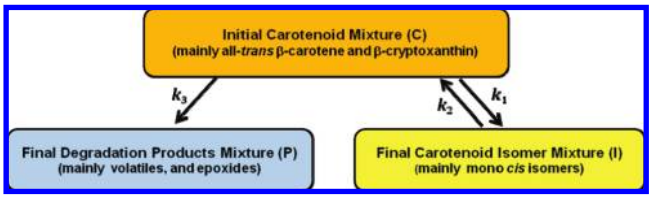
$$\frac{[C]_t}{[C]_0} = \left(\frac{k_2-\gamma_1}{\gamma_2-\gamma_1}\right) e^{-\gamma_1 t} + \left(\frac{k_2-\gamma_2}{\gamma_1-\gamma_2}\right) e^{-\gamma_2 t} \quad (5)$$

This equation contains also two exponential terms supporting the use of the operative fitting eq 4. In this framework, the meanings of γ_1 and γ_2 are as follows:

$$\gamma_1 = \frac{1}{2}(p+q); \quad \gamma_1 = \frac{1}{2}(p-q); \quad p = k_1+k_2+k_3;$$
$$q = \sqrt{p^2-4k_2k_3} \quad (6)$$

In the set of eq 6, k_1 and k_2 represent the overall first-order rate constants for the direct and reverse isomerization reactions, respectively, and k_3 is the overall first-order rate constant for the irreversible reaction to both volatile and nonvolatile degradation compounds. According to **Scheme 1**, $K_{e,iso} = k_1/k_2$, and the values of k_1, k_2, and k_3 can be calculated by solving eq 6, using the average values of the fast and slow observed rate constants, that is, $\langle\gamma_1\rangle$ and $\langle\gamma_2\rangle$ (**Table 2**). From this calculation it is clear that k_3 was 1 order of magnitude larger than k_1 and k_2, indicating that the formation of degradation compounds is much faster than the isomerization processes. A rough estimation of the activation

Scheme 1. Proposed Overall Mechanism for the Thermal Degradation of Carotenoids in a Cashew Apple Juice Model



energy $E_{a,i}$ of each individual steps can be done with the overall rate constants of each step at 60 and 90 °C, assuming a linear behavior of the classical Arrhenius equation between both temperatures. From this calculation it is clear that the irreversible formation of degradation compounds needs to overcome a lower barrier of $E_{a,3} = 82.8 \pm 8.4$ kJ/mol than that for direct formation of the mono-*cis* isomers with $E_{a,1} = 114.2 \pm 18.8$ kJ/mol favoring this degradation pathway of the all-*trans* carotenoids with the consequent strong total color (ΔE*) change. On the other hand, the reversible step of the isomerization process favors the formation of the all-*trans* carotenoids, because $E_{a,2} = 78.2 \pm 10.5$ kJ/mol. It is interesting to note that the activation energy values of the irreversible degradation reaction and the *cis*→ *trans* back isomerization reaction are almost the same, that is, $E_{a,3} \approx E_{a,2}$. However, the $k_3/k_2 \approx 30$ indicates that the formation of degradation compounds is a highly entropic process, probably due to breakdown of the large all-*trans* molecules into shorter chain derivatives. In addition, the present mechanism allows the calculation of the overall activation energy for the thermal degradation of the main all-*trans* carotenoids in the cashew apple juice model as $E_{a,1} - E_{a,2} + E_{a,3} = 118.6$ kJ/mol. This value is close to those reported for thermal degradation of all-*trans*-β-carotene (109.6 kJ/mol) in safflower seed oil (*17*) and for astaxanthin in dichloromethane (105.8 kJ/mol) (*18*). Although a similar E_a value was also reported by Dhuique-Mayer et al. (*2*) for the thermal degradation of β-carotene (110.0 kJ/mol) in orange juice, in their study β-cryptoxanthin was less affected by temperature (E_a = 156.0 kJ/mol), contrary to that found in the present study.

In conclusion, although carotenoid degradation kinetics and visual color changes in model and food systems submitted to heating processes are a complex phenomena, the simplest mechanism with two parallel reactions proposed in our study (**Scheme 1**) adequately explains the thermal degradation of cashew apple carotenoids in a juice model. Furthermore, the close relationship between carotenoid degradation and color change suggests that color monitoring (a physical property) could be a useful approach to control in real-time the quality of cashew apple juice during thermal processing. In particular, determination of ΔE* can be a good predictor of both all-*trans*-β-cryptoxanthin and all-*trans*-β-carotene losses during the thermal processing of cashew apple juice.

Preventing the loss of carotenoid contents during juice thermal treatment is also of interest to the juice industry, due to their nutritional value as provitamin A. However, online control of these compounds is inconvenient, due to the time-consuming nature of the chemical analysis. Thus, data shown in Supporting Information Table 2 provide useful information for the quality control of carotenoids and the related juice nutritional value during the thermal process of cashew apple juice. For instance, Supporting Information Table 2 shows that ΔE* = 1.9, which is visually perceived (*19*), promotes a 16% reduction of provitamin A value, whereas ΔE* = 3 implies a more relevant 36% loss of the provitamin A value. This type of information is already available for orange juice (*20*) but was, until now, not found for cashew apple juice.

Supporting Information Available: Color paramaters and carotenoid contents of cashew apple juice model. This material is available free of charge via the Internet at http://pubs.acs.org.

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