Modelling ascorbic acid thermal degradation and browning in orange juice under aerobic conditions

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Summary The thermal degradation of ascorbic acid (AA) in orange juice was analysed over in a 20–45 °C temperature range. Dehydroascorbic acid (DA), pH and browning were also monitored. Small amounts of AA degradation could be described by first order kinetics, but when only low amounts of AA were retained sigmoidal kinetics were clearly appropriate. The Weibull model was used to describe this pattern ($R^2_{adj} > 0.995$). The rate constant increased with temperature according to an Arrhenius-type relationship. The activation energy was 38.6 kJ/mol and at the average temperature of the range tested, 32.5 °C, the rate constant was 64.4×10^{-3} h^{-1}. The shape constant decreased linearly with temperature, from 2.17 to 1.13. Before the time when the maximum degradation rate occurred, pH, DA concentration and browning remained fairly constant, and then increased. It was found that this behaviour, as well as the dependence of the shape constant on temperature, might be explained by (i) the reconversion of DA into AA, following first order kinetics in relation to DA and second order kinetics in relation to AA, and by (ii) different sensitivities of the reaction rate constants to temperature. Browning was also well described by the Weibull model with a temperature independent shape constant.

Keywords Aeration, dehydroascorbic acid, first-order kinetics, vitamin C, Weibull model.

Introduction

Ascorbic acid is an important indicator of orange juice quality. Its concentration decreases during storage, depending on storage conditions, such as temperature, oxygen content and light. The mechanisms involved in the degradation of ascorbic acid in orange juice are not yet fully understood, but the existence of two consecutive or parallel pathways, aerobic and anaerobic, is widely accepted. Several authors (Khan & Martell, 1967a; Khan & Martell, 1967b; Lee *et al.*, 1977; Singh *et al.*, 1976; Hughes, 1985; Sakai *et al.*, 1987) have presented possible pathway schemes for ascorbic acid degradation. Many of these studies have been conducted in model systems at a pH less than 2 or at high concentrations of organic acids, and therefore may not duplicate the exact degradation pattern that occurs in a particular food product that contains ascorbic acid (Tannenbaum *et al.*, 1985). In the case of orange juice, pH values range typically from 3.5 to 3.9 (Nagy & Smoot, 1977), although the pH of juice extracted from oranges can be as low as 3.2 (Anonymous, 1998). In addition, some of the models reported in the literature were developed based on data gathered for relatively small (AA) conversions and/or under varying oxygen concentration, as the depleted oxygen was not replaced during storage.

The complexity of the degradation mechanisms (Tannenbaum *et al.*, 1985; Liao & Seib, 1988)

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hinders the development of mechanistic models and pseudo kinetic models such as zero- (Laing *et al.*, 1978; Kaanane *et al.*, 1988), first- (Lee & Labuza, 1975; Lee *et al.*, 1977; Nagy, 1980; Robertson & Samaniego, 1986) or second-order kinetics (Singh *et al.*, 1976; Eison-Perchonok & Downes, 1982; Hsieh & Harris, 1993) are often applied, yielding a good fit to the experimental data. Sakai *et al.* (1987) applied a kinetic model consisting of two consecutive reactions (the first of zero-order and the second of first-order) to describe the ascorbic acid oxidation in an aqueous solution, with different initial ascorbic acid concentrations in which dissolved oxygen was held at a constant level. These authors showed that this reactive mechanism might be perceived as either apparent first or zero-order kinetics, depending on the initial concentration of ascorbic acid and on the ratio of the rate constants of the sequential reactions.

Non-enzymatic browning is one of the main reasons for the loss of commercial value in citrus products, as it is the first visible quality defect to be detected at ambient temperature storage. In citrus juices, non-enzymatic browning is owing to the reactions of sugars, amino acids and ascorbic acid. Many researchers have studied browning formation in anaerobic environments and its kinetics was usually modelled as zero- (Saguy *et al.*, 1978; Stamp & Labuza, 1983; Cohen *et al.*, 1994) or first-order kinetics (Toribio & Lozano, 1986; Johnson *et al.*, 1995). Petriella *et al.* (1985) suggested a mixed order kinetic model (between zero- and first-order) in a study of colour changes due to non-enzymatic browning in model food systems. Later, Nagy *et al.* (1990), in a study of non-enzymatic browning in grapefruit juice, reported behaviours that change with temperature from linear (30 °C) to higher polynomial functions (50 °C). In that work, the researchers indicated that assuming the reaction as zero- or first-order was rather simplistic, which is in accordance with the knowledge that browning in citrus juice involves a complex group of reactants that produce an assortment of brown pigments of highly unstable characteristics (Rouseff *et al.*, 1989).

The main objective of this work was to test the hypothesis that the kinetics of aerobic ascorbic acid degradation and browning in orange juice with constant oxygen concentration could be modelled in a more appropriate way than had been published previously.

Materials and methods

Experimental design

Single-strength orange juice (Minute Maid™ premium) from the same batch was bought at a local (Porto, Portugal) supermarket. Using juice from a single batch minimized variations due to the processing conditions and to the fruit variability (agronomic factors). The juice was strained and 750 mL poured into a 1-L Erlenmeyer flask (Schott Duran, Mainz, Germany), protected from light and immersed in a thermostatic bath (Julabo SW-21C, Julabo Labotechik GMBH, Seelbach, Germany). After the juice temperature had reached the bath temperature, the time was set to zero, a sample (10-mL) was removed for analysis and aeration was switched on. The juice was aerated continuously for up to 36 h and samples (10 mL) were removed at regular intervals and analysed for L-ascorbic acid, dehydroascorbic acid, browning and pH. At sampling times, the O_2 dissolved in the juice contained in the Erlenmeyer flask and the brix degree were also measured. Experiments were conducted at 20, 25, 30, 35, 40 and 45 °C (±0.5 °C) and replicated. The oxygen content varied between 4.70 and 5.67 ppm for different experiments, and variations during a given experiment were in general less than 10%. pH values varied from 3.69 to 3.77, the increase during a given experiment being less than 2.5%. The brix degree was constant throughout the experiments, with a value of 11°.

Analytical determinations

Dissolved oxygen content was measured with an Oxi 340 oxygen electrode, equipped with a CellOx 325 probe and an oxicall-SL air calibration beaker (WTW Wissenschaftlich Technische, Weinheim, Germany). Brix degree and pH were measured, respectively, with an Atago hand refractometer (Atago Co. Ltd, Tokyo, Japan) and a Crison micropH meter 2001 (Crison Instruments SA, Spain). Browning was measured as light absorbance at 420 nm (Meydav *et al.*, 1977) using a spectrometer (Unicam 8630 UV/VIS, Cambridge, UK).

L-ascorbic and dehydroascorbic acids were analysed simultaneously by HPLC using the method described by Zapata & Dufour (1992) and a Beckman System Gold HPLC (Beckman Instruments, Inc., San Remo, CA, USA) equipped with a Beckman Model 168 Diode Array detector. A 1-mL sample and 1 mL of freshly prepared internal standard solution (0.3 g/L isoascorbic acid Sigma, I-0502) were diluted in ultra-pure water : methanol (95:5 v/v) in a 10-mL volumetric flask. The solution was centrifuged at 10 000 rpm for 5 min at 4 °C. A 1-mL volume of OPDA (1,2-phenylenediamine dihydrochloride, 0.5 g L^{-1}) was added to 3 mL of the centrifuged solution in order to transform the dehydroascorbic acid into its derivatised form, DFQ (fluorophore 3-(1,2-dihydroxyethyl)furo[3,4-b]quinoxaline-1-one). The solution was filtered through a C-18 Sep-pak cartridge (Waters, Millipore Corporation, Mildford, USA), and then through 0.45 micron Nucleopore filters (Syrfil 25 mm, Waters, Millipore Corporation, Mildford, USA). The first millilitre of the solution was discarded and the remaining solution was kept for 37 min in the dark at ambient temperature, and finally 10 µL of the solution was injected into the HPLC. The mobile phase was water : methanol (95:5 v/v) with 6.82 g L^{-1} dipotassium phosphate (Sigma P-3786) and 1.86 g L^{-1} Cetrimide (Sigma T-4762) at a flow rate of 1.8 mL min^{-1}. A Spherisorb ODS 18 (250 × 4.6 mm) column was used. The detector (166 Beckman UV-VIS detector) wavelength was set at 348 nm and after the elution of DFQ it was shifted to 261 nm for AA detection.

Data analysis

The models tested were fitted by non-linear regression to the experimental data in order to estimate the models' parameters. Fits were made for each experiment at a given temperature in order to assess the quality of the fit of the models, and to analyze further the dependence of the model parameters on temperature: these will be referred to as 'individual fits'. However, in order to improve parameter estimation, once the model had been checked, the best procedure was to apply a single regression to the whole set of experimental data for given kinetics, by combining the kinetic equations with the equations that relate the model parameters to temperature: this will be referred to as 'global fits'.

Non-linear regression of integrated equations was performed with the Stata™ 5.0 software (Computing Resource Centre, TX, USA).

Non-linear regression of ordinary differential equations (ODE) was performed using the least squares subroutine of ODRPACK (Boggs *et al.*, 1992). The simulation of the ODE system was performed with a LSODE pack (A.C. Hindmarsh, Computing and Mathematics Research Division, 1–136 Lawrence Livermore National Laboratory, Livermore, CA, USA).

The Mathematica® 3.0 Nonlinear Fit package software (Wolfram Research, IL, USA) was used to evaluate the parameter curvature and maximum relative parameter effects. These determinations are useful for checking the reliability of the confidence intervals and confidence regions calculated for model parameters, because most statistical packages base these calculations on expressions that are valid only for linear regressions, even when the models are non-linear. If the maximum relative intrinsic curvature (max intrinsic) is much smaller than the confidence region relative curvature (95% conf. region), the solution locus is approximately linear over the confidence region, and the parameter effects curvature (max parameter effects) is below the critical value (95% conf. region), the estimates are said to have a 'nearly' linear behaviour and the confidence regions are reliable (Wolfram, 1996). Otherwise, they just provide asymptotic approximations.

Results and discussion

Ascorbic acid degradation

An analysis over the entire experimental time range showed clearly that the decrease of AA concentration with time followed a sigmoidal pattern (Fig. 1). This pattern may also be noticed in data reported in the literature (Sakai *et al.*, 1987; Kebede *et al.*, 1998). Indeed, for many types of growth/decay data, the growth/decay rate does not decline immediately as predicted by the first-order model, but increases to a maximum before steadily declining to zero. This may be described by a number of so-called sigmoidal models, such as the Logistic, Gompertz, Richards Morgan and

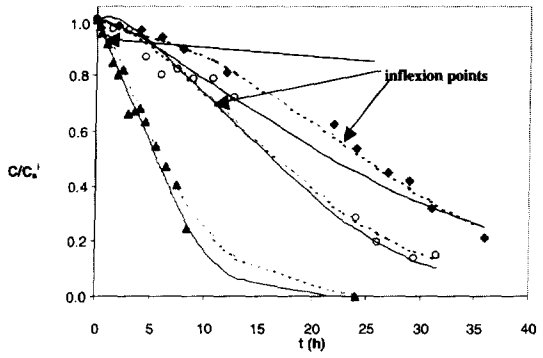


Figure 1 Weibull model fits to ascorbic acid data at ◆ 20, ○ 30 and ▲ 45 °C. The dashed line indicates the individual fit of the Weibull model and the solid line the individual fit of the differential model. C_a and C_a^i are the AA concentrations at time t and initially, respectively.

Weibull models (Seber & Wild, 1989). These models were fitted to the experimental data (results not shown), but while the fits to the individual experiments were very good for all the models tested, the kinetic parameters did not show a logical relation with temperature, varying extremely erratically, with the exception of the Weibull model.

Modelling AA degradation with the Weibull model

The Weibull model was developed initially to describe the failure of a given system subjected to stress conditions over time. This model is extremely flexible owing to the inclusion of a shape constant in addition to the rate constant, which allows for its application to a number of diverse situations, and it has proved to have an interesting potential for describing microbial, enzymatic and chemical degradation kinetics (Cunha *et al.*, 1998). When applied to AA degradation, it can be described by the following equation:

$$C_a = C_a^i \times e^{-\left(\frac{t}{\alpha}\right)^\beta} \qquad (1)$$

where C_a is the AA concentration at a time t, C_a^i is the initial AA concentration, α is a scale constant (its inverse corresponds to the reaction time constant) and β is the shape constant, which is a behaviour index (Seber & Wild, 1989). It is evident from equation 1 that α is the time when the concentration has decreased by one natural log cycle (approx. 67%), and that the Weibull model corresponds to the first-order model for the specific case of $\beta = 1$. Equation 1 has a sigmoidal shape for $\beta > 1$ and a monotonous decrease, steeper than exponential at low times, for $\beta < 1$ (Nelson, 1969). The reaction time constant is temperature-sensitive and this dependence can often be described by an Arrhenius-type relationship (Shepherd & Bhardwaj, 1988; Machado *et al.*, 1999). The β parameter, or shape constant, is related to the kinetic mechanisms and may be expected to be temperature-independent, at least within a limited range of temperature.

Figure 1 shows typical examples of the fit of the Weibull model to the experimental data ($R^2_{adj} > 0.995$). The rate constant increased with temperature (T) according to an Arrhenius-type relationship (Fig. 2a), whereas β appeared to decrease

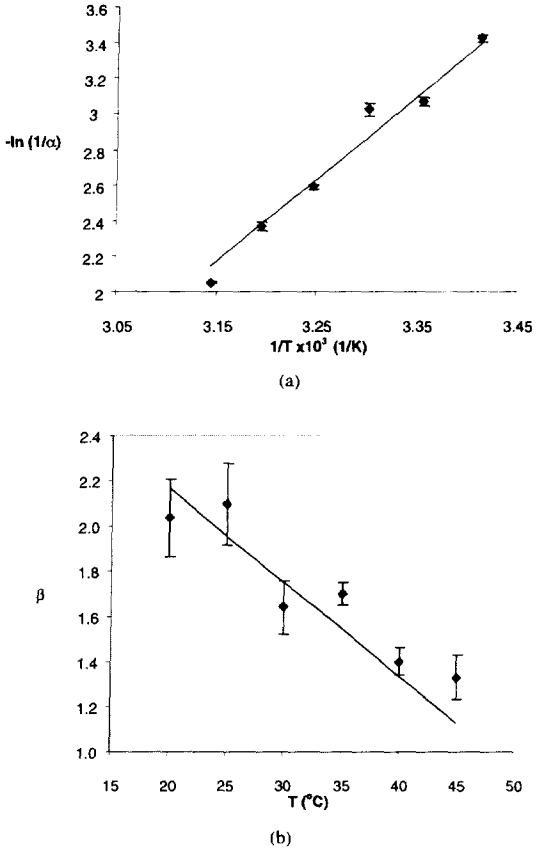


Figure 2 Dependence of the Weibull model parameters on temperature for ascorbic acid: (a) rate constant ($1/\alpha$); (b) shape constant (β). The ◆ symbols are the parameters obtained with each individual fit and the solid line indicates the global fit.

approximately linearly with temperature (see Fig. 2b), which indeed shows that the degradation patterns differ with temperature, ascorbic acid being more stable for short times at lower temperatures. Kanner *et al.* (1982) reported changes in the degradation pattern at temperatures between 25 and 37 °C, and Nagy & Smoot (1977) reported a critical temperature transition region between 22 and 26.7 °C. The relationships of $1/\alpha$ and β with temperature were incorporated in equation 1 to build up a global model:

$$C_a = C_a^i \times e^{-\left[\left(\left(\frac{1}{\alpha}\right)_{ref} \times e^{-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \times t\right)^{[\beta_{ref}-m\times(T-T_{ref})]}\right]} \quad (2)$$

where $(1/\alpha)_{ref}$ is the rate constant at a reference temperature T_{ref}, E_a is the activation energy regarding the dependence of the rate constant on temperature, β_{ref} is the shape constant at a reference temperature, m is the slope of the dependence of the shape constant on temperature and R is the universal gas constant. The Arrhenius equation was written in terms of a reference finite temperature rather than in terms of an infinite temperature in order to improve parameter estimation (Van Boeckel, 1996). The average temperature of the range tested, 32.5 °C, was chosen as the reference temperature.

Equation 2 was fitted to the whole set of data and Table 1 shows the parameter estimates. This global fit had a high R^2_{adj} (0.995) and the collinearity between the model parameters was below 0.51, except between b_{ref} and m (coefficient of correlation 0.97). However, values below 0.99 are considered acceptable (Bates & Watts, 1988; Van Boeckel, 1996).

The location of an inflexion point on a degradation curve relates to the time, $t_{w_{max}}$, w_{max} when the degradation rate is maximum, w_{max}. It corresponds to the time when the first derivative of w_{max}, with respect to time t, is zero, and can be calculated from:

$$t_{w_{max}} = \alpha\left[\frac{(\beta-1)}{\beta}\right]^{\frac{1}{\beta}} \quad (3)$$

$$w_{max} = -C_a^i \frac{\beta}{\alpha}\exp\left(-\frac{\beta-1}{\beta}\right)\left(\frac{\beta-1}{\beta}\right)^{\left(\frac{\beta-1}{\beta}\right)} \quad (4)$$

These times decreased exponentially with temperature, as shown in Table 2, and correspond fairly well to those when the values of dehydroascorbic acid, browning and pH start to increase. Before these times, the juice pH, dehydroascorbic acid concentration and browning index remained fairly constant, respectively, 3.7, 113 mg/L and 0.24 (absorbance at 420 nm). An example is shown in Fig. 3, for dehydro-

Table 1 Estimates of the model parameters for the ascorbic acid, Weibull and first-order models, obtained by global fitting, as well as the respective curvature fit parameters

Weibull model	$(1/a)_{32.5°C} \times 10^3$ (h^{-1})	E_a (kJ/mol)	β_{ref}	m ($°C^{-1}$)
	64.4 ± 1.2	38.6 ± 1.6	1.65 ± 0.35	0.0415 ± 0.0071
Curvature fit	Max intrinsic	Max parameter effects		95% conf. Region
	0.17	0.23		0.63
First-order model	$k_{32.5°C} \times 10^3$ (h^{-1})		E_a (kJ/mol)	
	37.8 ± 1.8		71.0 ± 3.8	
Curvature fit	Max intrinsic	Max parameter effects		95% conf. region
	0.023	0.13		0.52

Table 2 Maximum growth/decay rate and the time at which it occurs, calculated based on the parameters of the Weibull model (estimated by global fitting) for ascorbic acid and browning index

	Ascorbic acid		Browning index	
Temperature (°C)	$t_{w_{max}}$ (H)	w_{max}(mg L^{-1} h^{-1})	$t_{w_{max}}$ (H)	$w_{max} \times 10^3$ (h^{-1})
20	22.3	9.4	51.4	1.6
25	15.8	13.0	32.6	2.3
30	10.9	16.5	21.1	4.4
35	7.0	19.2	13.8	6.1
40	3.8	21.3	9.1	10.7
45	1.2	28.2	6.1	16.5

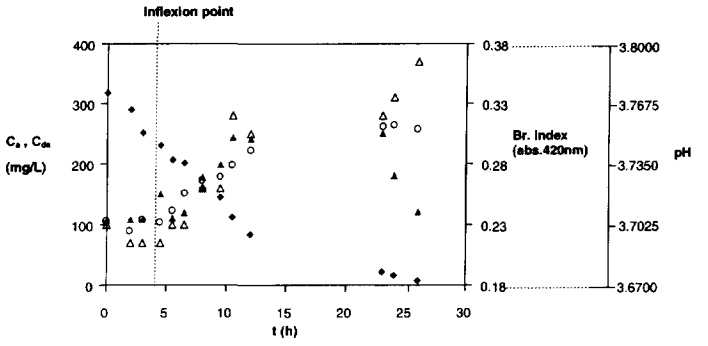


Figure 3 Variation with time of ascorbic acid, C_a ◆, dehydroascorbic acid, C_{da} (▲), browning, *Br* ○ and pH △ at 40 °C.

ascorbic acid, browning index and pH values at 40 °C.

It is curious to note that for small conversions (experimental times ≤ 8 h, corresponding to conversions < 60% at 45 °C, < 30% at 35 °C and < 14% at 20 °C), the ascorbic acid degradation curves could be described well by first-order kinetics, with the rate constant following an Arrhenius dependency on temperature ($R^2_{adj} > 0.999$, correlation coef. < 0.845), as reported by several authors (Fig. 4):

$$C_a = C_a^i \times e^{-k_{ref} \times e^{-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \times t} \qquad (5)$$

where k_{ref} is the rate constant at a reference temperature T_{ref}. The average temperature of the range tested, 32.5 °C, was also chosen as the reference temperature. The parameter estimates are presented in Table 1. The activation energy of the first-order model was almost twice that of the Weibull model owing to the change of degradation patterns with temperature, which in the later model is accounted for by the β constant. Both for the first-order and for the Weibull model, the analysis of the fit curvature (Table 1) shows that the confidence intervals calculated for the different parameters are reliable.

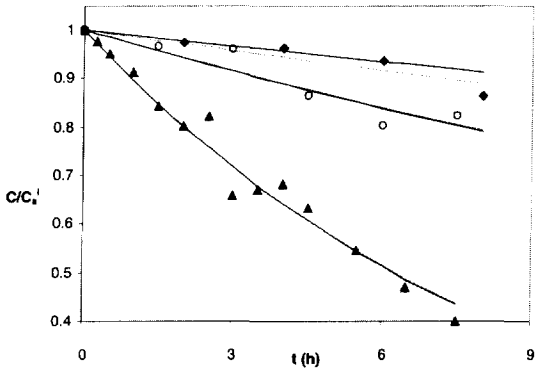


Figure 4 First-order model fits to ascorbic acid data for times less than 8 hours at ◆ 20, ○ 30 and ▲ 45 °C. The dashed line indicates the individual fit and the solid line the global fit.

Modelling AA degradation with the mechanistic model

The inflexion points observed in the AA degradation curves suggest that the degradation kinetics might be reversible. Indeed, under aerobic conditions ascorbic acid is degraded to dehydroascorbic acid, which in turn can be reconverted to ascorbic acid by mild reduction as well as hydrolysed into 2,3-diketogluconic acid, which will lead to the formation of browning pigments (Tannenbaum *et al.*, 1985). As at the inflexion times dehydroascorbic acid, browning and pH increase, one may infer that at this time the rate of reconversion of dehydroascorbic acid to ascorbic acid lowers considerably. This might be explained by a dependence of the reconversion of dehydroascorbic acid into ascorbic acid on the concentration of the latter component. In this case, the differential equations relating the changes of ascorbic acid and dehydroascorbic acid (C_{da}) with time could be written as:

$$\frac{dC_a}{dt} = -k_1 C_a + k_2 C_a C_{da} \qquad (6)$$

$$\frac{dC_{da}}{dt} = k_1 C_a - k_2 C_a C_{da} - k_3 C_{da} \qquad (7)$$

where k_1, k_2 and k_3 are the rate constants of, respectively, the degradation of ascorbic acid, the reconversion of dehydroascorbic acid and the degradation of dehydroascorbic acid.

It was, however, found that these equations were not able to describe the sudden increase of dehydroascorbic acid concentration, and thus they were slightly modified by making the reconversion of dehydroascorbic acid a second-order reaction in relation to ascorbic acid concentration. Equation 6 and 7 thus become:

$$\frac{dC_a}{dt} = -k_1 C_a + k_2 C_a^2 C_{da} \quad (8)$$

$$\frac{dC_{da}}{dt} = k_1 C_a - k_2 C_a^2 C_{da} - k_3 C_{da} \quad (9)$$

These equations were then fitted to the experimental data of ascorbic acid degradation. The fits were very good and the rate constants also increased with temperature according to an Arrhenius-type equation:

$$\frac{dC_a}{dt} = -k_{1ref} \times e^{-\frac{E_{a1}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \times C_a + k_{2ref} \times e^{-\frac{E_{a2}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \times C_a^2 \times C_{da} \quad (10)$$

$$\frac{dC_{da}}{dt} = -k_{1ref} \times e^{-\frac{E_{a1}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \times C_a - k_{2ref} \times e^{-\frac{E_{a2}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \times C_a^2 \times C_{da} - k_{3ref} \times e^{-\frac{E_{a3}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \times C_{da} \quad (11)$$

where k_{1ref}, k_{2ref} and k_{3ref} are the rate constants at T_{ref} of, respectively, the degradation of ascorbic acid, the reconversion of dehydroascorbic acid and the degradation of dehydroascorbic acid and E_{a1}, E_{a2} and E_{a3} are the corresponding activation energy values.

The estimates of the model parameters, obtained by global fitting of equations 10 and 11 to the whole set of data, are summarized in Table 3 and the fits are also shown in Fig. 1. The degradation kinetics of dehydroascorbic acid showed a much smaller sensitivity to temperature than the degradation kinetics of ascorbic acid and the reconversion of dehydroascorbic acid to ascorbic acid. The rate constant of this reaction was also much smaller.

Although this may be considered a mechanistic model, one should, however, take into consideration that there is no real evidence that the dehydroascorbic acid degradation follows second-order kinetics in relation to ascorbic acid concentration, and as such this model also relies on empiricism to a great extent. Furthermore, the parameter estimates of this model show a large confidence interval, in some cases of the order of magnitude of the estimates themselves, which is owing to the inability of the model to separate the influence of the different reactions on the concentration changes. The Weibull model, although lacking any theoretical basis, provides good fits and a much better statistical significance. The changes of the shape constant (β) with temperature might be explained by the different sensitivity of the three reactions to temperature.

Browning

The Weibull model, adapted to growth kinetics,

$$\frac{C - C^\infty}{C^i - C^\infty} = 1 - e^{-\left(\frac{t}{\alpha}\right)^\beta} \quad (12)$$

(where C^∞ is the equilibrium concentration) also yielded good fits to the browning index experimental data ($0.992 < R^2_{adj} < 0.999$). Figure 5 shows the fits for some of the temperatures tested. The rate constant ($1/\alpha$) increased with temperature according to an Arrhenius-type equation (Fig. 6a),

Table 3 Estimates of the model parameters of the differential equations, obtained by global fitting of experimental data

K_{1ref} (h^{-1})	k_{2ref} (h^{-1})	k_{3ref} (h^{-1})	E_{a1} (kJ/mol)	E_{a2} (kJ/mol)	E_{a3} (kJ/mol)
0.33 ± 0.07	7.5 ± 1.9	0.044 ± 0.005	94.0 ± 11.2	107.1 ± 12.7	26.7 ± 9.3

Table 4 Estimates of the model parameters for the browning data, Weibull model, obtained by global fitting, as well as the respective curvature fit parameters

Weibull model	$(1/a)_{32.5°C} \times 10^3$ (h^{-1})	E_a (kJ/mol)	β	C^∞ (mg/L)
	32.2 ± 3.2	65.8 ± 2.8	1.6 ± 0.1	0.328 ± 0.007
Curvature fit	Max intrinsic	Max parameter effects		95% conf. Region
	1.06	0.20		0.63

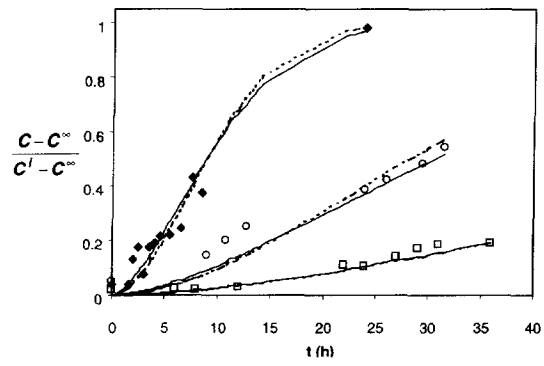
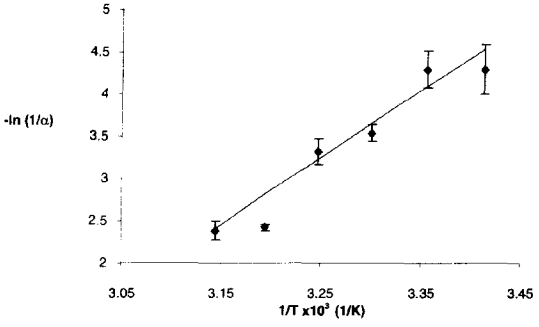
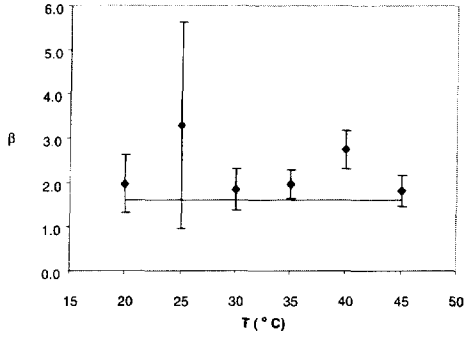


Figure 5 Weibull model fits to the browning index data at 20, ○ 30 and ◆ 45 °C. The dashed line indicates the individual fit and the solid line the global fit.



(a)



(b)

Figure 6 (a) Dependence of the Weibull model rate constant on temperature for the browning index temperature; (b) dependence of the shape constant on temperature. The ◆ symbols are the parameters obtained with each individual fit and the solid line indicates the global fit.

whereas the equilibrium concentration and the β parameter were temperature-independent (Fig. 6b):

$$\frac{C-C^{\infty}}{C^{i}-C^{\infty}} = 1 - e^{-\left(\left(\frac{1}{a}\right)_{ref} \times e^{-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \cdot t\right)^{\beta}} \quad (13)$$

The estimates of this model's parameters, obtained by the global fitting of equation 13 to the whole set of data, are summarized in Table 4. The fit had a very high R^2_{adj} (0.999) and the correlation between parameters was generally low (correlation coef. < 0.89). The activation energy value is in the range of others reported in the literature for the cases of zero e.g. Saguy *et al.*, (1978); Stamp & Labuza, (1983); and Cohen *et al.*, (1994) reported, respectively, values of 62.7, 92 and 89 kJ mol^{-1}) or first-order kinetics e.g. Toribio & Lozano, (1986) reported a value of 105 kJ mol). The maximum relative intrinsic curvature and the parameter-effects curvature were greater than the confidence region relative curvature (Table 4), showing that in this case the confidence intervals can only be considered as asymptotic approximations, which may be due to the fact that the model was applied in concentration ranges quite below equilibrium. The maximum browning rates also occurred at times that decreased exponentially with temperature, their values being approximately twice of those for ascorbic acid degradation (Table 2).

Conclusions

The Weibull model provided a good description of the kinetics of degradation of ascorbic acid and of the evolution of the browning index in the range of temperatures and conversions tested, and therefore is appropriate for predictive purposes. A first-order model could also be applied to the data satisfactorily, but only for lower conversions (experimental times up to 8 h), as for greater conversions degradation curves showed a sigmoidal pattern. The inflexion points of AA degradation curves coincided roughly with the time when the concentration of dehydroascorbic acid started to increase, together with the pH and the browning index. The temperature dependency of the rate constants was described well by the Arrhenius law. The shape constant of the Weibull model was temperature-independent for browning kinetics but decreased with temperature for ascorbic acid degradation. The later observation shows that the pattern of AA

degradation is temperature-dependent. This might be explained by (i) the reconvertion of DA into AA, following first-order kinetics in relation to DA and second-order kinetics in relation to AA, and by (ii) different sensitivities of the different reactions rate constants to temperature. Browning, on the other hand, appears to follow a single reactive pathway in the range of temperatures tested.

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Nomenclature

C	concentration at time t (mgL^{-1}) or absorbance (at 420 nm) at time t
C^i	concentration at time zero (mgL^{-1}) or absorbance (at 420 nm) at time zero
C^∞	absorbance (at 420 nm) at equilibrium
E_a	activation energy (kJ mol^{-1})
k	rate constant of first-order kinetics (h^{-1})
k_{ref}	rate constant of first-order kinetics at T_{ref} (h^{-1})
R	universal gas constant (8.314 kJ/(molK))
t	time (h)
$t_{w_{max}}$	time when the degradation/growth rate is maximum (h)
T	temperature (K or °C)
T_{ref}	reference temperature (K or °C)
w_{max}	maximum degradation/growth rate (h^{-1})
α	scale constant of the Weibull model (h) ($1/\alpha$ is the rate constant)
α_{ref}	scale constant of the Weibull model at T_{ref} (h)
β	shape constant of the Weibull model

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