Food Chemistry 115 (2009) 958–964

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Effects of light, temperature and water activity on the kinetics of lipoxidation in almond-based products

Sanaa Tazi [a], Floriane Plantevin [a], Christian Di Falco [b], Antoine Puigserver [a], El Hassan Ajandouz [a,*]

[a] BiosCiences-ISM², UMR 6263, CNRS-Université Paul Cézanne-Aix Marseille III, Case 342, Faculté des Sciences et Techniques de Saint-Jérôme, 13397 Marseille, France
[b] Confiserie du Roy René. La Pioline, Aix-en-Provence, France

ARTICLE INFO

Article history:
Received 21 July 2008
Received in revised form 20 November 2008
Accepted 9 January 2009

Keywords:
Lipoxidation kinetics
Light
Water activity
Temperature
Activation energy
Q_{10} factor

ABSTRACT

Lipoxidation in almond-derived products was investigated using the chemiluminescence (CL) and thiobarbituric acid-reactive substances (TBARS) methods to detect the first and later reaction products, respectively. The effects of light during storage at 5 °C, 22 °C and 40 °C were studied, as well as the effects of combined heat/water activity treatments in the 60–120 °C and 0.38–0.72 range. During storage, light was found to enhance the CL and TBARS values, and specific responses were observed in almond paste and the final Calisson product. During the heating of almond paste, as the initial water activity (a_w) increased, the CL rate constants increased during heating to 60 °C and 80 °C, but interestingly, these values decreased during further heating to 120 °C, whereas the maximum TBARS rate constants occurred at a_w 0.57 at all the heating temperatures tested. The activation energies, based on the CL and TBARS values, decreased specifically when the a_w increased from 0.38 to 0.72, giving overall values ranging from110 kJ mol^{-1} to 60 kJ mol^{-1}. Likewise, in the same water activity range, the temperature-dependent rate constant enhancing factor (Q_{10}) decreased from 3.3 to 1.6.

1. Introduction

Since the pioneer studies carried out in the field of phytochemistry by Théodore de Saussure at the beginning of the 19th Century (De Saussure, 1804), many attempts have been made to elucidate the mechanisms underlying the chemical reactions occurring in plants and other living organisms. The reactions involved in the chemical network recruit the proteins, lipids, carbohydrates and other low mass ratio organic and mineral fractions of a medium, such as a given foodstuff. Most of the partners involved also react with each other in response to environmental changes (in the temperature, pH, water activity, light, oxygen and metals). The main reactions studied so far *in vitro* have been the oxidation of lipids and proteins, which can be either enzyme-catalysed or not, as well as the non-enzymatic browning reactions of the Maillard type and caramelisation processes. The microbiological and chemical stabilities of foodstuffs, as well as their nutritional value, depend on how well these reactions are controlled while foods are being processed.

Lipoxidation reactions occur in lipid-rich dietary products in which the lipid fraction undergoes chemical changes during the processing, which are responsible for a wide range of chemical and biological properties, such as the attractive aromas conferred by compounds formed under short high-temperature treatments (frying, grilling, roasting) and the rancidity and discoloration caused by long exposure to low temperatures. Toxic substances can also be generated, which can be associated with health risks to consumers which are still far from being properly understood.

The large body of data available on lipoxidation processes has mainly stemmed from basic research programmes, whereas far fewer applied studies have been published. Model systems have been widely studied, as well as a few food systems, and the influence of some environmental factors has been studied. Dairy products are the most frequently studied foods, along with meat and some plant-based foods, in line with economic considerations. If one looks at the main factors studied so far, based on the content of cross key word indices, it can be seen that very little attention so far has been paid to the influence of water activity, although this is an essential factor, contributing to both enzyme-catalysed and non-enzyme-catalysed chemical processes in foods. Variable interest has been taken in other contributing factors (such as pH, light, oxygen, ionisation, concentrations of Ox/Red substances), and very few papers are available in which the combined effects of more than one of these factors have been described.

Among the analytical methods used in previous studies along these lines, the TBARS method has been widely used, along with the classical method based on peroxide levels. Other methods used in this context include those based on oxygen consumption and *Uv–Vis* absorbance, and those in which intermediate or final products are monitored spectroscopically after performing chromatographic separation. Methods based on luminescence detection

* Corresponding author. Tel.: +33 4 91 28 81 36; fax: +33 4 91 28 84 40.
E-mail address: el-hassan.ajandouz@univ-cezanne.fr (E.H. Ajandouz).

0308-8146/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2009.01.017

have been found to provide a sensitive means of screening lipoxidation processes, in both *in vitro* and *in vivo* situations (Sharov, Kasamanov, & Vladimirov, 1989; Yasuda & Narita, 1997).

The present study focuses on the lipoxidation processes occurring in almond-based products. Almond is a high added-value foodstuff, the annual world production of which amounts to approximately 1.5 million tons. The nut contains about 50% lipids, 20% proteins and 15% carbohydrates, while water (which accounts for about 9%) and the minor mass ratio organic and mineral fraction account for the remainder. The carbohydrate fraction consists mainly of non-starch polysaccharides, whereas the lipid fraction includes about 70% oleic acid, 20% linoleic acid and 8% saturated fatty acids, mostly in the form of palmitic acid (Abdallah, Ahumada, & Gradziel, 1998; Askin, Balta, Tekintas, Kazankaya, & Balta, 2007; Romojaro, Riquelme, Gimenez, & Liorante, 1988). This food system is a medium which favours the occurrence of lipoxidation processes, which may detract from its nutritional value, which is of special importance since increasing evidence has suggested that almond consumption has beneficial effects on human health (Jenkins et al., 2002; Spiller & Miller, 2003).

Several studies have focused on the quality and stability of almonds, whether shelled, peeled, roasted or not (García-Pascual, Mateos, Carbonell, & Salazar, 2003; Harris, Westcott, & Henick, 1972; Rizzolo, Senesi, & Colombo, 1994; Zacheo, Cappello, Gallo, Santino, & Cappello, 2000; Zacheo, Cappello, Perrone, & Gnoni, 1998). Very little attention has been paid so far, however, to almond pastes and other downstream products marketed for human consumption.

The present study therefore focused on the kinetics of the lipoxidation process in the following situations: during the storage of almond paste and the finished Calisson product under light and dark conditions, at refrigeration, ambient and extremely hot storage conditions, and during the heating of almond paste, which has different initial water activities. The recently developed integrative analytical method of lipoxidation (Tazi et al., 2009), based on the detection of the first stage peroxides (CL) and advanced stage carbonyls (TBARS), was used for this purpose. The production of the substances detected by these two methods was monitored and the kinetic parameters (rate constants, activation energy and Q_{10} factor) were calculated. As the TBARS method can also be used to detect the carbonyls generated by non-enzymatic browning reactions, the present study gives an overall picture of the chemical events occurring during the manufacture of Calissons. The applicability of the present data to other related foodstuffs is also discussed.

2. Material and methods

2.1. Almond-based samples

Almond pastes (consisting of an equal mixture of peeled almond, sugar syrup and crystallized melon, a_w 0.56) and finished Calisson products (a_w 0.65) manufactured from the paste, which undergo heating and surface glazing, were provided by the Confiserie du Roy René (Aix-en-Provence, France).

2.2. Storage in the dark and light

The effects of light during storage were monitored for two months, under refrigeration (5 °C), ambient (22 °C) and severe (40 °C) conditions.

The almond paste (about 50 g of paste each time) was placed on glass plates and flattened (to a thickness of 1 cm), and the paste matrix was pre-cut to facilitate the sampling. The plates were then covered with transparent film and stored in the dark or under artificial lighting (with a 60 W electric lamp placed about 50 cm from the paste) at 5 °C (in a cold room), ambient laboratory temperature (about 22 °C) and 40 °C (in an incubator). Similar treatment was applied to finish Calissons, except for the cutting and flattening. The paste and Calisson samples were also stored in the processing area at the factory (mean temperature 24 °C), in the dark or under artificial lighting (ambient fluorescent lighting). Samples of almond paste and Calisson were collected at regular intervals and the CL and TBARS values were determined ($n = 4$).

2.3. Combined temperature/water activity treatment of the almond paste

2.3.1. The kinetic approach

The heating temperatures tested were 60 °C, 80 °C, 100 °C and 120 °C, combined with initial water activities of 0.38, 0.57 and 0.72. With each combination, CL and TBARS were monitored at suitable intervals. The rate constants were calculated on the basis of the slopes at the origin and expressed as relative light units (RLUs) per minute in the case of CL and absorbance units (AUs) per minute in that of TBARS. The values obtained were then used to calculate the activation energy values, according to the Arrhenius relationship $k = c - Ea/RT$, where k is the rate constant of the reaction(s), c is a constant representing the collision frequency, Ea is the activation energy (kJ mol^{-1}), R is the gas constant (8.31 j mol^{-1} K^{-1}) and T is the temperature (°K). The rate constants k_{CL} and k_{TBARS} account here for lipoxidation and for various reactions, including lipoxidation, respectively. Lastly, the value of the Q_{10} factor (the n-fold increase in the rate constant per 10 units of temperature) was calculated, based on the relationship $Log\ Q_{10} = 2.19.Ea/T(T + 10)$. This yielded the acceleration factors of the lipoxidation velocities (CL and TBARS) in the temperature range tested and in larger ranges, based on likely predictions.

2.3.2. Heating procedures

Almond paste, prepared as described above, was placed in desiccators with saturated potassium chloride or lithium chloride solutions, which give a_w values of 0.82 and 0.12, respectively, at equilibrium (Ruiz-Beviá, Fernández-Sempere, Gómez-Siurana, & Torregrosa-Fuerte, 1999). The desiccators were placed under the ambient light and temperature conditions pertaining at the laboratory. Paste samples were also stored in desiccators not containing salts under the same conditions. Thereafter, for up to three weeks, samples ($n = 4$) were withdrawn at regular intervals, their water activity was measured using an FA-st/1 AwMeter (GBX scientific instruments – France) and they were then heated. The a_w values of the pastes stored with salts changed slowly during the three weeks of storage, reaching up to 0.72 with potassium chloride and down to 0.38 with lithium chloride, whereas the a_w of the samples not exposed to salts remained completely unchanged (0.57). After the initial water activity had been measured, the samples were heated to 60 °C for 180, 360 and 540 min, to 80 °C for 60, 120 and 180 min, to 100 °C for 40, 80 and 120 min, and to 120 °C for 20, 40 and 60 min in a dry oven. At each of the times selected, parts of the heated paste were rapidly withdrawn from the dry oven, blended with DMSO-gum Arabic (for CL measurements) or trichloroacetic acid (for TBARS measurements), and stored at −20 °C prior to analysis. The zero point of the kinetic measurements, adopted for each a_w value, was that of the unheated samples.

2.4. Extraction and analysis

The procedures and handling conditions used have been described in detail elsewhere (Tazi et al., 2008). Briefly, for the CL analysis, samples blended in Eppendorf tubes with a dimethylsulphoxide-gum Arabic mixture were centrifuged. Samples were

aliquoted from the homogeneous phase and were used to perform luminescence measurements. For the TBARS analysis, samples blended in trichloroacetic acid solution, as above, were centrifuged. Samples were then withdrawn from the supernatant and successively mixed with thiobarbituric acid (TBA), heated, and cooled, and their absorbance measured at 532 nm.

CL values (RLU per gramme of peeled almond) were divided by 10^5 to adapt the scale and make them easily comparable with TBARS values (AU per gramme of peeled almond). The mean CL and TBARS values are given in the kinetic Figures with the standard deviations, whereas the correlation coefficients (r^2) of the CL and TBARS rate constants and those of the Arrhenius relationship are given in the text.

3. Results and discussion

3.1. Effects of light during storage

Fig. 1 shows the kinetics of CL and TBARS production in almond paste during storage in the dark and under artificial light at the three temperatures selected, while Fig. 2 shows those obtained on Calissons under the same experimental conditions. The kinetic behaviour of CL and TBARS in the almond paste and Calissons stored at the factory turned out to be similar to those obtained at 22 °C, which are shown in both Figs. 1 and 2.

In the almond pastes, the CL values increased faster under light than in the dark during storage, regardless of the temperature, although they decreased after 30-day storage periods at 5 °C or 22 °C. The CL values obtained at 22 °C under light were not much higher than those recorded at 5 °C (less than 1.5-fold), whereas a marked increase was observed at 40 °C (up to 15-fold). In the dark, similar values were obtained at 5 °C and 22 °C during the first two weeks of storage, but those obtained at 5 °C subsequently increased while those obtained at 22 °C, in contrast, decreased. The water activity, which was higher in the cold room than in the rest of the laboratory, was probably responsible for this difference. Thereafter, between ambient and severe storage conditions, the CL values increased markedly, as under artificial lighting. A rather slow increase was observed in the TBARS values for about two weeks of storage, which was followed by a TBARS peak, which continued up to the end of the storage period. The highest TBARS values reached at 5 °C and 22 °C were similar, and were about 1.5-fold lower than those measured at 40 °C.

To account for these findings, it seems likely that the formation of CL occurs before that of TBARS, especially at 5 °C and 22 °C and that the TBARS values may have decreased faster than the CL values at the end of the storage period. The latter pattern might be at least partly due to volatile carbonyls which escaped detection or to carbonyls which underwent polymerization and therefore no longer reacted with TBA, whereas the slower decrease in CL might be due to the presence of still available precursors originating from heavier lipid peroxides and radicals. These precursors might consist mainly of oleic and linoleic acids (which account for 90% of the total fatty acids), whereas linolenic acid accounts for less than 1%. In fact, the contribution of these fatty acids should not be assessed only on a mass basis, since their reactivity is known to increase greatly with the degree of unsaturation up to more than a 1000-fold (German, 1999; Kanner & Rosenthal, 1992). Although linoleic acid is not very abundant in almonds, it is expected to be the first fatty acid oxidized, and the products generated may trigger the lipoxidation of more highly saturated linoleic and oleic acids.

In Calissons (Fig. 2), a more pronounced chronological sequence of production of CL and TBARS was observed, with an early peak in CL occurring under artificial lighting, which was not found to occur in the dark. This finding is in agreement with the general pattern of

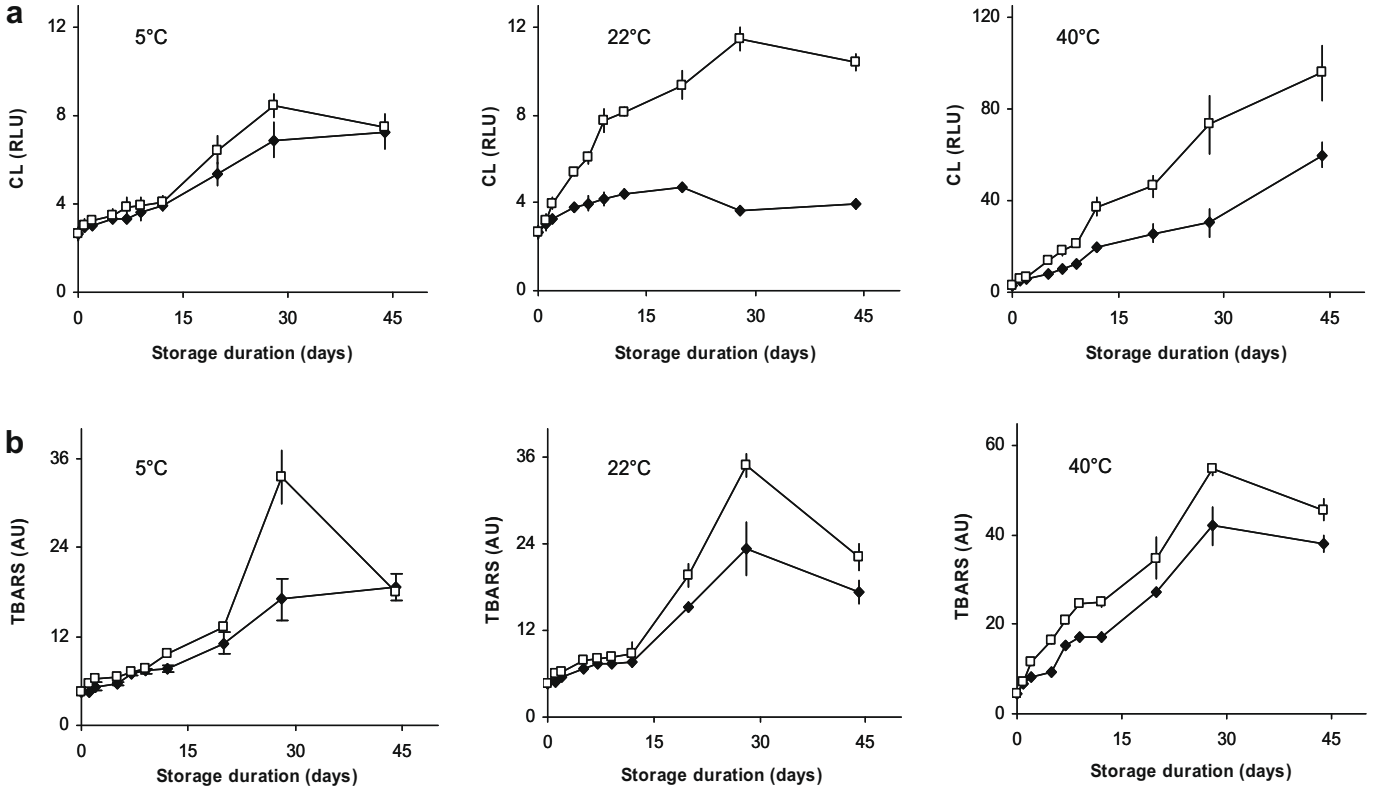

Fig. 1. Effects of light (□) versus dark (♦) on the development of CL (a) and TBARS (b) in almond paste during storage at 5 °C, 22 °C and 40 °C.

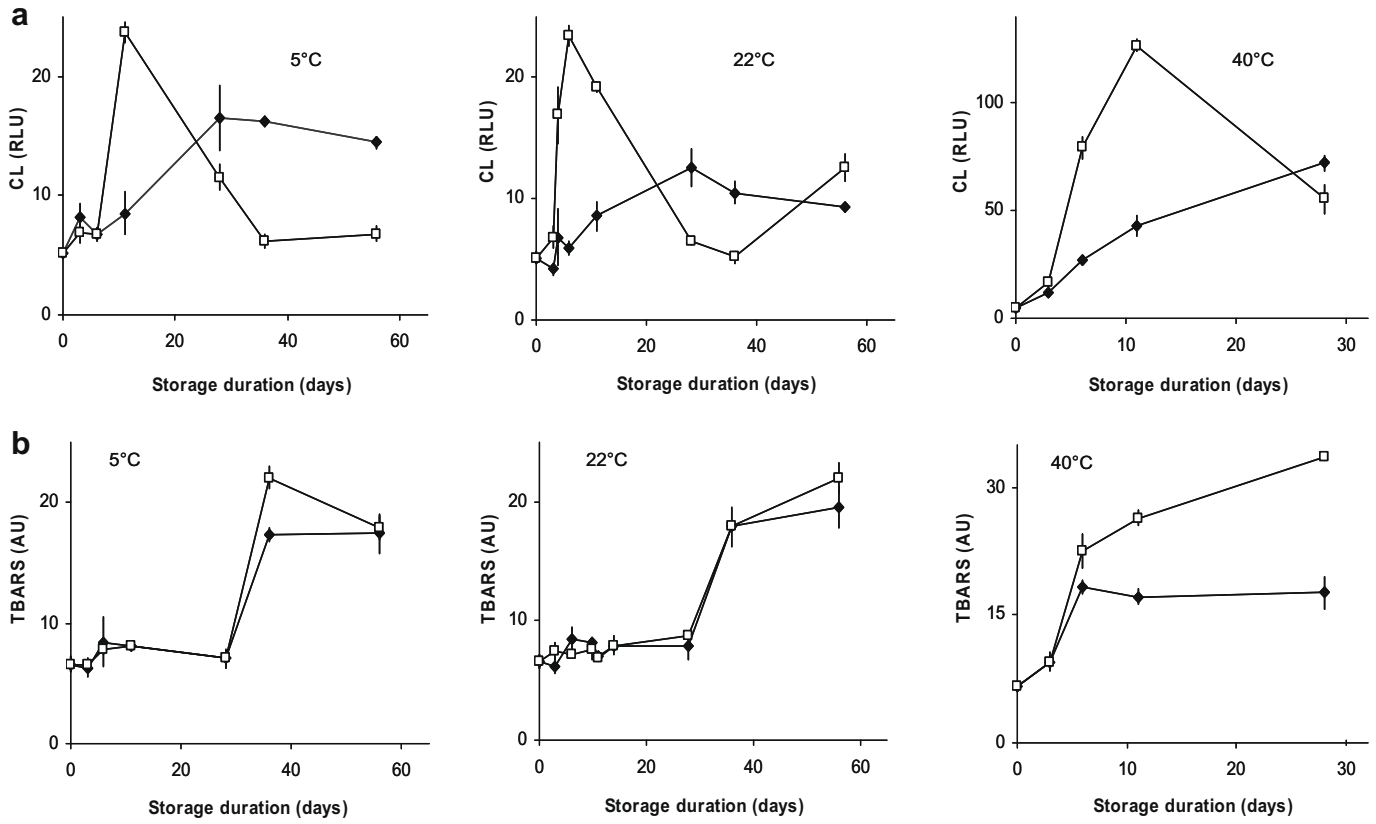

Fig. 2. Effects of light (□) versus dark (♦) on the development of CL (a) and TBARS (b) in Calisson during storage at 5 °C, 22 °C and 40 °C.

lipoxidation: peroxides are generated and converted into carbonyls during the more advanced stages of the reactions. The transient increase in the CL values observed probably reflected the fact that these precursors are less available in Calissons than in almond paste.

The effects of combined light/temperature treatments observed here are similar to those found to occur in dairy products (Mortensen, Bertelsen, Mortensen, & Stapelfeldt, 2004): light was always an enhancing factor. No marked differences were observed between refrigeration and ambient conditions, but the lipoxidation markers increased dramatically from ambient to extreme storage conditions (at temperatures above 40 °C). Light in particular was found to enhance the rates of hexanal production and, interestingly, also those of 3-methylbutanal, a Strecker aldehyde specific to Maillard reactions (Anderson & Lignert, 1998). The latter reactions, along with caramelisation reactions, can be expected to develop significantly in almond paste and Calissons at temperatures below 40 °C, due to the availability of reactants and the concomitant occurrence of the lipoxidation process.

The present data show the enhancing effects of light exposure on lipoxidation during the processing and storage of lipid-rich foodstuffs and the need which therefore arises to assess the risk of deterioration more closely. The findings also point to the need for accurate analytical methods to detect and if possible, quantify oxidation products and other reaction products, using an integrative approach whenever possible.

3.2. Effects of combined heat/water activity

3.2.1. Kinetics and rate constants of CL and TBARS formation

Fig. 3 shows the kinetics of CL and TBARS formation in almond pastes at 60 °C and 120 °C under controlled initial water activity conditions. The kinetics recorded at 80 °C and 100 °C (data not shown) were similar to those shown in Fig. 3: after the short lag phases observed especially in the CL plots, a variably fast linear increase occurred, depending on a_w and the heating temperature. The velocity constants, k_{CL} and k_{TBARS} ($r^2 > 0.9$, see the kinetic approach described in Section 2.3.1), increased exponentially with the temperature, whatever the initial water activity. This pattern was in fact to be expected, as the Arrhenius relationship was found to fit the experimental data in many food systems, in terms of the lipoxidation (discussed below in Section 3.2.2) and non-enzymatic browning reactions (Ajandouz, Desseaux, Tazi, & Puigserver, 2008). As regards the effects of the water activity, Fig. 4 shows (i) that k_{CL} increased at 60 °C and 80 °C with a_w from 0.38 to 0.72, increased at 100 °C with a_w from 0.57 to 0.72, but decreased at 120 °C with a_w from 0.38 to 0.72 and (ii) that k_{TBARS} reached a maximum at a_w 0.57 at all the temperatures tested.

Previous studies on the effects of the water activity on lipoxidation, using specific methods of detection, have mostly supported the commonly accepted scheme described by Labuza (1971), according to which the rate constants decrease with increasing a_w values, up to about 0.3, when the tendency is reversed. However, some authors have reported that this is not the case in all situations; for example, Pimpo and Seri (1992), who studied fish-based systems stored at −25 °C, have shown that the rate constants of conjugated dienes and the TBARS values increased with a_w from 0.0 to 0.8. In whole milk powder, treated with various combinations of temperature and water activity, the pooled concentrations of lipid radicals increased or decreased with a_w at a given time, depending on the severity of the preheating treatments applied (Stapelfeldt, Nielsen, & Skibsted, 1997). These data, along with those presented here, suggest that the general pattern mentioned above needs to be revised, taking the storage conditions and/or the heating temperature into account.

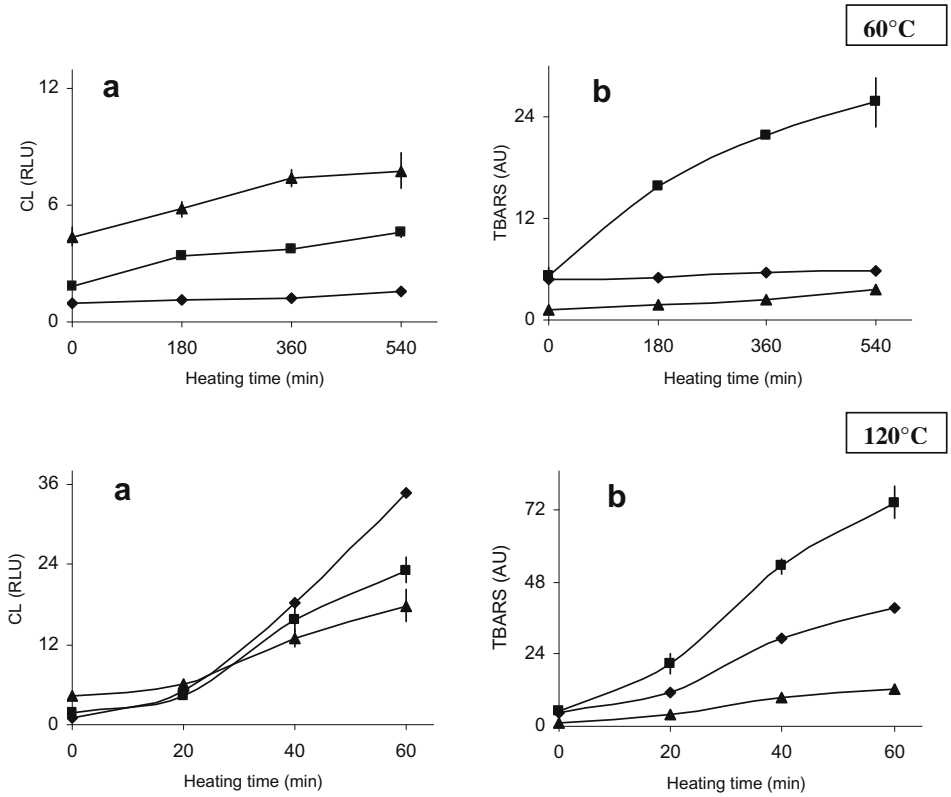

Fig. 3. Kinetics of CL (a) and TBARS (b) formation in almond paste at two temperatures and three water activity values: 0.72 (▲), 0.57 (■) and 0.38 (♦)

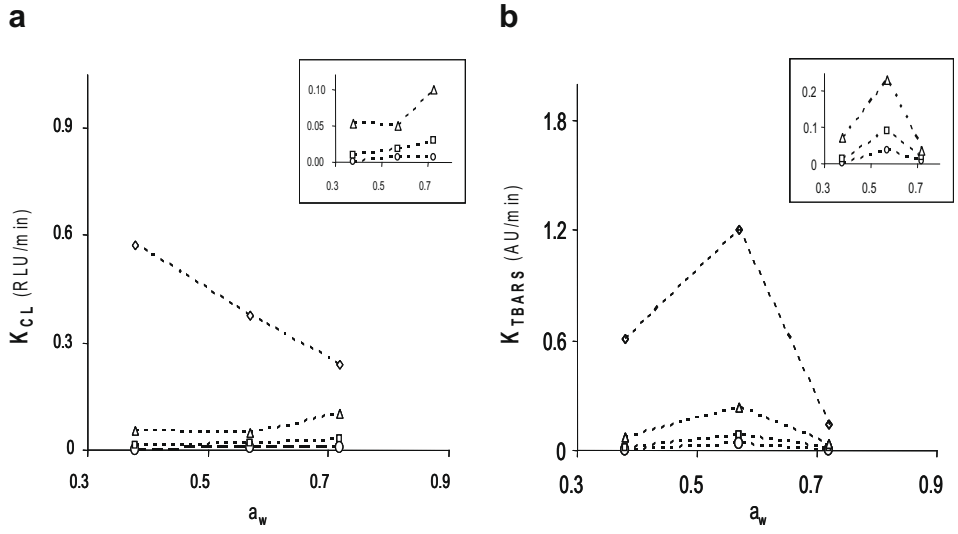

Fig. 4. Effects of a_w on k_{CL} (a) and k_{TBARS} (b) in almond paste at various heating temperatures: 60 °C (○), 80 °C (□), 100 °C (△) and 120 °C (◇). The inserts show the effects observed in the 60 °C-100 °C temperature range.

The situation is quite different when TBARS values are used as lipoxidation markers. Besides detecting the carbonyls generated in the advanced stages of lipoxidation, as discussed above in connection with the effects of light exposure, the TBARS method can also be used to detect the carbonyls generated by non-enzymatic browning reactions, among other chemical events. The peak in the TBARS rate constants observed at a_w 0.57 in almond paste (Fig. 4) is in agreement with the data obtained by Sun, Senecal, Chinachoti, and Faustman (2002), who investigated the effects of water activity on the lipoxidation process in freeze-dried beef, based on the TBARS values, at similar temperature levels. On the other hand, in model systems, the maximum rate constants of either the browning process and/or the disappearance of free amino groups, were found to occur at around a_w 0.6 (Labuza, Warren, & Warmbier, 1977; Warmbier, Schnickles, & Labuza, 1976). This shows the existence of a link between non-enzymatic browning reactions and the lipoxidation process *via* the carbonyl pool detected by the TBARS method, as well as showing the value of using

both the CL and TBARS approaches simultaneously to obtain an overall picture of what occurs in a treated medium containing the substrates involved in these reactions.

The maximum shelf life of Calissons is more than 9 months, reflecting the existence of efficient natural protective mechanisms against the damaging effects of lipid and protein oxidation, along with the use of efficient packaging and marketing practices at the manufacturing firm. Parent almond pastries (composition: 50% almond, 40% sugar and 10% whole egg and aromas) remain stable for up to 4.5 months (Baiano & Del Nobile, 2005). The differences between these two products are likely to be attributable to many factors, such as the lipid content, the use of dehydrated melon in Calissons, that of additives in pastries and the processing/packaging conditions.

3.2.2. Activation energy and Q_{10} values

The Arrhenius plots of the CL and TBARS data obtained with heated almond paste are shown in Fig. 5. The fact that the plots based on the CL values are less widely dispersed than are those based on the TBARS values, indicates that reactions other than lipoxidation may also be involved in the latter case. It can also be seen from Fig. 5 that the plots of the CL and TBARS data depend on the initial water activity of almond paste. The activation energy values ($r^2 > 0.956$) reached a maximum at a_w 0.38 in the case of both CL (114 kJ mol^{-1}) and TBARS (100 kJ mol^{-1}). The Ea_{CL} values then decreased to 65 kJ mol^{-1} at a_w 0.72; whereas the Ea_{TBARS} values decreased to 61 kJ mol^{-1} at a_w 0.57, but remained completely unchanged (62 kJ mol^{-1}) at a_w 0.72.

In previous studies on quite similar situations, the *Ea* of the formation of lipid radicals in whole milk powder was found to be 112 kJ mol^{-1} (Thomsen, Lauridsen, Skibsted, & Risbo, 2005). In rapeseed oil model systems, encapsulated or not in a carbohydrate/protein glassy matrix, the *Ea* values (recorded using the peroxide-value method with a lipoxidation initiator) were found to be 80 kJ mol^{-1} and 60 kJ mol^{-1} in the bulk oil and in the encapsulated systems, respectively (Orlien, Risbo, Rantanen, & Skibsted, 2006). Lastly, based on data by Chen, Tai, Chen, and Chen (2001), the *Ea* values of the disappearance of methyl-oleate and methyl-linoleate were found to be 30 kJ mol^{-1} and 34 kJ mol^{-1}, respectively. The peroxide values, also determined by Chen et al. (2001), did not fit the Arrhenius relationship, possibly due to the fragmentation associated with the lipoxidation process in the temperature range used (100–200 °C), which corresponds to severe heating conditions in comparison with those used in the other two studies mentioned above, where the temperatures used did not exceed 60 °C.

Whatever the case may be, the *Ea* values determined here in almond paste, based on the CL data, were similar to those previously determined in whole milk powder, based on the production of lipid radicals: both of the markers used reflect the first stages in the process of lipoxidation, occurring under fairly similar experimental conditions. In addition, in the studies mentioned above, the *Ea* of lipoxidation seems to be lower in the model systems studied than in foodstuffs, which suggests that greater competitive and/or inhibitory processes occur in foodstuffs.

The decrease in the *Ea* of the lipoxidation process observed here with the increase in the initial a_w, on the basis of both the CL and TBARS data, was possibly attributable to the fact that more water was available for the diffusion of reactants, favouring non-enzymatic reactions at any temperature, as well as the enzyme-catalysed reactions occurring at the lower temperatures studied. Almond lipoxygenase activity was previously found to increase with the water activity and correlated well with the pattern of TBARS behaviour observed under accelerated storage conditions (Zacheo et al., 1998); in addition, the enzyme was still largely active (80%) after 10 min of heating at 60 °C (Zacheo et al., 2000).

As shown in Table 1, the values of Q_{10}, based on both the CL and TBARS data obtained in the temperature range tested (see Section 2.3.1 for details), ranged between 3.3 and 1.6. Those based on the CL data were higher than those based on the TBARS data, which means that the heat accelerating effect is more pronounced during the early stages of lipoxidation than during the later ones. Both the CL- and TBARS-based Q_{10} values decreased with the temperature and the water activity, especially from 0.38 to 0.57 in the latter case.

These kinetic data were used to predict the Q_{10} values likely to occur in lower temperature ranges in order to obtain a wider picture of the accelerating effects of heat on the chemical events detected by CL and TBARS (Table 2). In the temperature range used here (60–120 °C), the k_{CL} values increased up to 500 times and the k_{TBARS} values up to 200 times, whereas those predicted to occur (see details in the legend of the Table) between 20 °C and 120 °C correspond to increases of approximately 10^5-fold and 2.10^4-fold,

Table 1
CL and TBARS-based values of Q_{10} in almond paste in the 60 °C–120 °C temperature interval, depending on the initial water activity value.

T (°C)	0.38		0.57		0.72	
	CL	TBARS	CL	TBARS	CL	TBARS
60–70	3.3	2.8	2.2	1.9	2	1.9
80–90	2.9	2.5	2.1	1.8	1.8	1.8
100–110	2.6	2.3	1.9	1.7	1.7	1.7
120–130	2.4	2.1	1.8	1.6	1.6	1.6

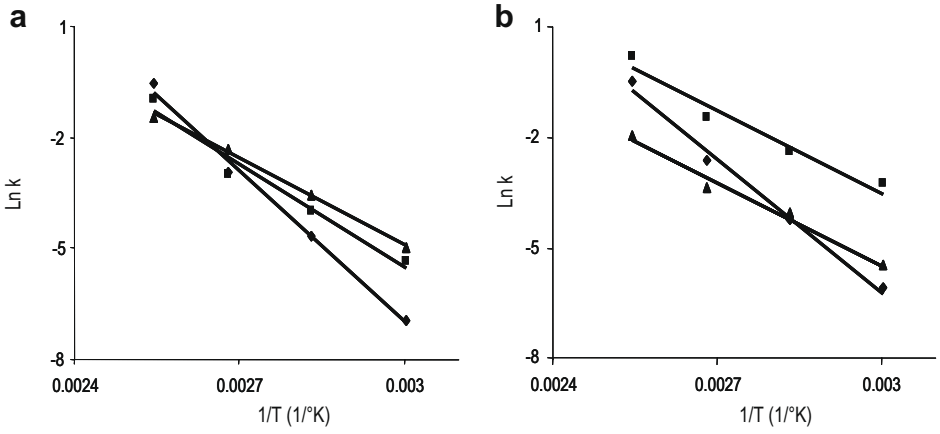

Fig. 5. Arrhenius plots of the CL (a) and TBARS (b) data around the usual water activity of almond paste. Symbols are as in Fig. 3.

Table 2
Predicted* values of the heat factors accelerating lipoxidation in almond paste at various initial water activity conditions.

T (°C)	0.38		0.57		0.72	
	CL	TBARS	CL	TBARS	CL	TBARS
60–120	531	211	68	30	36	30
20–120	93028	17584	2232	500	724	522

* The acceleration factors in the 60–120 °C temperature range are based on the present kinetic data, whereas those in the 20–120 °C range are based on predictions, using the plots of Q_{10} versus temperature (medians: 65 °C, 75 °C, 85 °C…). At a_w 0.38, 0.57 and 0.72, the regression equations obtained were $y = -0.0156x + 4.27$ ($r^2 = 0.986$), $y = -0.0074x + 2.70$ ($r^2 = 0.989$) and $y = -0.0057x + 2.34$ ($r^2 = 0.990$) for CL, and $y = -0.0114x + 3.48$ ($r^2 = 0.988$), $y = -0.0052x + 2.23$ ($r^2 = 0.991$) and $y = -0.0053x + 2.25$ ($r^2 = 0.991$) for TBARS, respectively.

respectively; the lower the a_w, the greater was the predicted acceleration factor of the lipoxidation velocity. The factor Q_{10} gives more practical insights into how lipoxidation, or any other reaction, progresses with the temperature and other contributing factors. It should provide a helpful means of managing well-controlled food processing programmes.

4. Conclusion

The results obtained in the present study suggest the following questions:

- Has the influence of the water activity on the lipoxidation processes occurring during food storage and processing been sufficiently and thoroughly investigated?
- Do we have sufficiently well-designed kinetic studies on the combined effects of the various contributing factors involved?
- Do there exist appropriate integrative research programmes giving an overall picture of the chemical events occurring during food processing?
- What are the links between lipoxidation and its products, if any, and *in vivo* situations?

Increasing attention is now being paid to the interactions between the various reactions which occur during food processing, including the interactions between Maillard reactions and lipoxidation processes (Whitfield & Mottram, 1996; Zamora & Hidalgo, 2005). However, there still exists a need for well-designed integrative research programmes targetting several points in the chemical network involved. The products generated by the chemical network are all candidates, liable to be absorbed by human and animal consumers at various levels in the gastrointestinal system or to serve as substrates for the microbiota residing in the distal parts of the gut.

Acknowledgements

This study was supported by the Confiserie du Roy René (Aix-en-Provence, France). The authors are grateful to Dr. Valérie Deyris for technical assistance and discussions.

References

Abdallah, A., Ahumada, M. H., & Gradziel, T. M. (1998). Oil content and fatty acid composition of almond kernels from different genotypes and California production regions. *Journal of the American Society for Horticultural Science, 123*, 1029–1033.

Ajandouz, E. H., Desseaux, V., Tazi, S., & Puigserver, A. (2008). Effects of temperature and pH on the kinetics of caramelisation, protein cross-linking and Maillard reactions in aqueous model system. *Food Chemistry, 107*, 1244–1252.

Anderson, K., & Lignert, H. (1998). Influence of oxygen concentration and light on the oxidative stability of cream powder. *Lebensm.-Wiss. u.-Technology, 31*, 169–176.

Askin, M. A., Balta, M. F., Tekintas, F. E., Kazankaya, A., & Balta, F. (2007). Fatty acid composition affected by kernel weight in almond [*Prunus dulcis* (Mill) D.A. Webb.] genetic resources. *Journal of Food Composition and Analysis, 20*, 7–12.

Baiano, A., & Del Nobile, M. A. (2005). Shelf life extension of almond paste pastries. *Journal of Food Engineering, 66*, 487–495.

Chen, J. F., Tai, C.-Y., Chen, Y. C., & Chen, B. H. (2001). Effects of conjugated linoleic acid on the degradation and oxidation stability of model lipids during heating and illumination. *Food Chemistry, 72*, 199–206.

De Saussure, N.T. (1804). Recherches chimiques sur la végétation. V. Nyon Ed., Paris.

García-Pascual, P., Mateos, M., Carbonell, V., & Salazar, D. M. (2003). Influence of storage conditions on the quality of shelled and roasted almonds. *Biosystems Engineering, 84*, 201–209.

German, J. B. (1999). Food processing and lipid oxidation. *Advances in Experimental Medicine and Biology, 459*, 23–50.

Harris, N. E., Westcott, D. E., & Henick, A. S. (1972). Rancidity in almonds: Shelf life studies. *Journal of Food Science, 37*, 824–827.

Jenkins, D. J. A., Kendall, C. W. C., Marchie, A., Parker, T. L., Connelly, P. W., Qian, W., et al. (2002). Dose response of almonds on coronary heart disease risk factors – blood lipids, oxidized LDL, Lp(a), homocysteine and pulmonary nitric oxide: A randomized controlled cross-over trial. *Circulation, 106*, 1327–1332.

Kanner, J., & Rosenthal, I. (1992). An assessment of lipid oxidation in foods. *Pure and Applied Chemistry, 64*, 1959–1964.

Labuza, T. P. (1971). Kinetics of lipid oxidation in foods. *CRC Critical Reviews in Food Technology, 2*, 355–405.

Labuza, T. P., Warren, R. M., & Warmbier, H. C. (1977). The physical aspects with respect to water and non-enzymatic browning. *Advances in Experimental Medicine and Biology, 86B*, 379–418.

Mortensen, G., Bertelsen, G., Mortensen, B. K., & Stapelfeldt, H. (2004). Light-induced changes in packaged cheeses – a review. *International Dairy Journal, 14*, 85–102.

Orlien, V., Risbo, J., Rantanen, H., & Skibsted, L. H. (2006). Temperature-dependence of rate of oxidation of rapeseed oil encapsulated in a glassy food matrix. *Food Chemistry, 94*, 37–46.

Pimpo, M. T., & Seri, S. (1992). Study of lipid changes in freeze-dried fish during storage. I. The interaction of relative humidity and tissue lipids. *Bollettino-Societa Italiana Biologia Sperimentale, 68*, 735–739.

Rizzolo, A., Senesi, E., & Colombo, C. (1994). Studies on the storage of shelled and in-shell almonds. *Acta Horticulturae, 373*, 259–264.

Romojaro, F., Riquelme, F., Gimenez, J. L., & Liorante, S. (1988). Fat content and oil characteristic of some almond varieties. *Fruit Science Reports, 17*, 53–57.

Ruiz-Beviá, F., Fernández-Sempere, J., Gómez-Siurana, A., & Torregrosa-Fuerte, E. (1999). Determination of sorption and diffusion properties of peeled almond nuts. *Journal of Food Engineering, 41*, 209–214.

Sharov, V. S., Kasamanov, V. A., & Vladimirov, Y. A. (1989). Selective sensitisation of chemiluminescence resulted from lipid and oxygen radical reactions. *Free Radical Biology and Medicine, 7*, 237–242.

Spiller, G. A., & Miller, A. (2003). Effects of plant-based diets high in raw or roasted almonds or roasted almond butter on serum lipoproteins in humans. *Journal of the American College of Nutrition, 22*, 195–200.

Stapelfeldt, H., Nielsen, B. R., & Skibsted, L. H. (1997). Effect of heat treatment, water activity and storage temperature on the oxidative stability of whole milk powder erratum: 871. *International Dairy Journal, 7*, 331–339.

Sun, Q., Senecal, A., Chinachoti, P., & Faustman, C. (2002). Effect of water activity on lipid oxidation and protein solubility in freeze-dried beef during storage. *Journal of Food Science, 6*, 2512–2516.

Tazi, S., Puigserver, A., Ajandouz, E.H. (2009). A fast, safe and accurate chemiluminescence method for measuring peroxidation in almonds and almond-based products during processing and storage. FOODCHEM-D-08-00301.

Thomsen, M. K., Lauridsen, L., Skibsted, L. H., & Risbo, J. (2005). Temperature effect on lactose crystallisation, Maillard reactions, and lipid oxidation in whole milk powder. *Journal of Agricultural and Food Chemistry, 53*, 7082–7090.

Warmbier, H. C., Schnickles, R. A., & Labuza, T. P. (1976). Effect of glycerol on non-enzymatic browning in a solid intermediate moisture model food system. *Journal of Food Science, 41*, 528–531.

Whitfield, F.B, & Mottram, D.S. (1996). Maillard lipid interactions in low moisture systems. In P. Wilhelm, H. Chi-Tang, S.M. Arthur (Eds.), *Contribution of low- and non-volatile materials to the flavor of foods* (pp. 149–181).

Yasuda, M., & Narita, S. (1997). Simultaneous determination of phospholipids hydroperoxides and cholesteryl ester hydroperoxides in human plasma by high-performance liquid chromatography with chemiluminescence detection. *Journal of Chromatography B: Biomedical Sciences and Applications, 693*, 211–217.

Zacheo, G., Cappello, M. S., Gallo, A., Santino, A., & Cappello, A. R. (2000). Changes associated with harvest ageing in almond seeds. *Lebensm-Wiss.u.-Technology, 33*, 415–423.

Zacheo, G., Cappello, A. R., Perrone, L. M., & Gnoni, G. V. (1998). Analysis of factors influencing lipid oxidation of almond seeds during accelerated ageing. *Lebensm-Wiss.u.-Technology, 3*, 6–9.

Zamora, R., & Hidalgo, F. J. (2005). Coordinate contribution of lipid oxidation and Maillard reaction to the nonenzymatic food browning. *Critical Reviews in Food and Nutrition, 45*, 49–59.