Contents lists available at ScienceDirect

Food Chemistry

Lipid-derived aldehyde degradation under thermal conditions

Rosario Zamora, José L. Navarro, Isabel Aguilar, Francisco J. Hidalgo *

Instituto de la Grasa, Consejo Superior de Investigaciones Científicas, Avenida Padre García Tejero 4, 41012 Seville, Spain

ABSTRACT

Nucleophilic degradation produced by reactive carbonyls plays a major role in food quality and safety. Nevertheless, these reactions are complex because reactive carbonyls are usually involved in various competitive reactions. This study describes the thermal degradation of 2-alkenals (2-pentenal and 2-octenal) and 2,4-alkadienals (2,4-heptadienal and 2,4-decadienal) in an attempt to both clarify the stability of aldehydes and determine new compounds that might also play a role in nucleophile/aldehyde reactions. The obtained results showed that alkenals and alkadienals decomposed rapidly in the presence of buffer and air to produce formaldehyde, acetaldehyde, and the aldehydes corresponding to the breakage of the carbon—carbon double bonds: propanal, hexanal, 2-pentenal, 2-octenal, glyoxal, and fumaraldehyde. The activation energy of double bond breakage was relatively low (∼25 kJ/mol) and the yield of alkanals (10–18%) was higher than that of 2-alkenals (∼1%). All these results indicate that these reactions should be considered in order to fully understand the range of nucleophile/aldehyde adducts produced.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Reactive carbonyls are known to play a major role in some of the changes suffered by foods upon processing. These changes may have both positive and negative consequences for foods because of the formation of different compounds, including Strecker aldehydes (Maire, Rega, Cuvelier, Soto, & Giampaoli, 2013; Rendon, Salva, & Bragagnolo, 2014), vinylogous derivatives of amino acids, such as acrylamide (Arvanitoyannis & Dionisopoulou, 2014; Zamora, Delgado, & Hidalgo, 2011), biogenic amines (Granvogl & Schieberle, 2006; Hidalgo, Navarro, Delgado, & Zamora, 2013), and aromatic heterocyclic amines (Zamora, Alcon, & Hidalgo, 2012; Zochling & Murkovic, 2002), among others.

Reactive carbonyls are produced in foods as a consequence of oxidative and thermal processes of all major food components including carbohydrates, lipids, and amino acids or proteins (Choe & Min, 2006; Fuentes, Estevez, Ventanas, & Ventanas, 2014; Zamora, Alcon, & Hidalgo, 2013; Zamora & Hidalgo, 2005). Among these, lipids have long been known to be a major source of reactive carbonyls in foods (Brewer, 2009; Ganesan, Brothersen, & McMahon, 2014).

Lipid-derived reactive carbonyls are produced in the course of lipid oxidation, and they are a large number of short- and long-chain aldehydes and ketones with various degrees of unsaturation (Gardner, 1989). Among them, 2-alkenals and 2,4-alkadienals are produced to a significant extent (Guillen & Uriarte, 2012), and they

have been shown to be involved in many chemical reactions that take place in foods upon processing, such as the conversion of asparagine to acrylamide (Hidalgo, Delgado, & Zamora, 2009) or the formation of the heterocyclic aromatic amine PhIP (Zamora, Alcon, & Hidalgo, 2014), for example. These reactions require a high temperature at which unsaturated aldehydes might degrade and degradation products might also play a role in such reactions. However, thermal degradation of lipid-derived unsaturated aldehydes is not well known, although some studies have shown that these compounds degrade upon heating (Matthews, Scanlan, & Libbey, 1971).

In an attempt to clarify the stability of 2-alkenals and 2,4-alkadienals upon thermal processing, this study identifies and quantifies the thermal degradation products of 2-alkenals and 2,4-alkadienals. As models of 2-alkenals and 2,4-alkadienals, 2-pentenal and 2,4-heptadienal, respectively, were selected as oxidation products of ω3 fatty acid chains, and 2-octenal and 2,4-decadienal, respectively, were selected as oxidation products of ω6 fatty acid chains.

2. Materials and methods

2.1. Materials

2-Alkenals (2-pentenal and 2-octenal) and 2,4-alkadienals (2,4-heptadienal and 2,4-decadienal) were purchased from Aldrich (Milwakee, WI, USA) and had the highest available grade. All other chemicals were purchased from Aldrich (Milwakee, WI, USA), Sigma (St. Louis, MO, USA), Fluka (Buchs, Switzerland), or Merck (Darmstadt, Germany), and were of analytical grade.

* Corresponding author. Tel.: +34 954 611 550; fax: +34 954 616 790.
  E-mail address: fhidalgo@ig.csic.es (F.J. Hidalgo).

2.2. Thermal treatment of lipid-derived aldehydes

Two different procedures were followed depending on whether the formed compounds were going to be either identified or quantified. The identification of thermal degradation products of the studied aldehydes was carried out by GC–MS after derivatization with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride, according to a previously described procedure (Zamora, Navarro, Gallardo, & Hidalgo, 2006), which was modified. Quantification of the compounds produced was carried out by LC–MS/MS after derivatization with dansylhydrazine according to a previously described procedure (Zamora et al., 2014), which was also modified.

For samples destined for use in identification purposes, the aldehyde (4 μmol) was either heated alone or in the presence of 200 μl of 50 mM buffer (either sodium phosphate or sodium borate), pH 8, for 1 h at 200 °C in a closed test tube under either nitrogen or air. At the end of the heating process, samples were cooled (5 min at room temperature and 10 min at −20 °C) and derivatized with 400 μl of a freshly prepared solution of O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (10 mg/ml in methanol). The resulting solution was stirred and incubated for 1 h at 37 °C. Finally, reactions were studied by GC–MS.

For samples required for quantification purposes, a solution of the aldehyde (0–10 μmol) in tetrahydrofuran (80 μl) was treated with 420 μl of 0.2 M buffer (pH 2.15–11) and, then, heated for the indicated time and temperature in a closed test tube under air. At the end of the heating process, samples were cooled (5 min at room temperature and 10 min at −20 °C). Fifty microlitres of these cooled samples were diluted with 350 μl of methanol, and treated with 50 μl of the internal standard (a solution of 88 μmol of formaldehyde-d_2 in 2 ml of methanol), 150 μl of trifluoromethanesulfonic acid solution (3% in methanol), and 200 μl of dansylhydrazine solution (4 mg/ml in methanol). The resulting solution was incubated for 15 min at 100 °C, then maintained for 1 h at 25 °C, and finally diluted with 200 μl of eluent A (a 30:70 mixture of 0.2% formic acid in acetonitrile and 4 mM ammonium acetate), and analysed by LC–MS/MS.

2.3. GC–MS analyses

GC–MS analyses were conducted with a Hewlett–Packard 6890 GC Plus coupled with an Agilent 5973 MSD (Mass Selective Detector-Quadrupole type). A fused silica HP5-MS capillary column (30 × 0.25 mm i.d.; coating thickness 0.25 μm) was used. Working conditions were as follows: carrier gas, helium (1 ml/min at constant flow); injector temperature, 250 °C; oven temperature, from 70 (1 min) to 240 °C at 5 °C/min and, then, to 325 °C at 10 °C/min; transfer line to MSD, 280 °C; ionisation EI, 70 eV. Reaction products were identified by comparison of mass spectra and retention times to those of authentic standards.

2.4. LC–MS/MS analyses

The employed equipment was composed of an Agilent liquid chromatography system (1200 Series) consisting of a binary pump (G1312A), degasser (G1379B), and autosampler (G1329A), connected to a triple quadrupole API 2000 mass spectrometer (Applied Biosystems, Foster City, CA) using an electrospray ionisation interface in positive ionisation mode (ESI⁺). Compounds were separated on a Zorbax Eclipse XDB-C18 (150 × 4.6 mm, 5 μm) column from Agilent. As eluent A, a 30:70 mixture of 0.2% formic acid in acetonitrile and 4 mM ammonium acetate was used. As eluent B, a 0.2% formic acid solution in acetonitrile was employed. The mobile phase was delivered at 0.5 ml/min using the following gradient: for 0–13 min, the content of mobile phase B was 7%; for 13–20 min, the content of mobile phase B was increased linearly from 7% to 60%; for 20–30 min, the content of mobile phase B was 60%; for 30–32 min, the content of mobile phase B was increased linearly from 60% to 90%; for 32–42 min, the content of mobile phase B was 90%; and for 42–45 min, the content of mobile phase B was decreased linearly from 90% to 7%. Mass spectrometric acquisition was performed using multiple reaction monitoring (MRM). The nebulizer gas (synthetic air), the curtain gas (nitrogen), and the heater gas (synthetic air) were set at 40, 25, and 50 (arbitrary units), respectively. The collision gas (nitrogen) was set at 3 (arbitrary units). The heater gas temperature was set at 500 °C and the electrospray capillary voltage to 5.5 kV. The fragment ions in MRM mode were produced by collision-activated dissociation of selected precursor ions in the collision cell of the triple quadrupole and the selected products analysed with the second analyzer of the instrument. Three transitions were acquired for the identification of each dansylhydrazone derivative. To establish the appropriate MRM conditions for the individual compounds, the mass spectrometric conditions were optimised using infusion with a syringe pump to select the most suitable ion transitions for the target analytes. Precursor and product ions used for quantification and confirmation purposes, and operating conditions are summarised in Table 1.

Quantification of the different aldehydes was carried out by preparing five standard curves of aldehyde mixtures in 500 μl of the mixture tetrahydrofuran/sodium phosphate buffer, pH 8, and following the whole procedure described above. For each curve, seven different concentration levels of each aldehyde (0–2 nmol) were used. Aldehyde contents were directly proportional to aldehyde/IS area ratios ($r > 0.99$, $p < 0.0001$). All data given are the mean of, at least, three independent experiments.

3. Results

3.1. Thermal degradation of 2-alkenals and 2,4-alkadienals

2-Alkenals and 2,4-alkadienals were more or less stable upon heating depending on the presence of both air and buffers. Fig. 1 shows the chromatograms obtained after 1 h heating at 200 °C for the four assayed aldehydes: 2-pentenal (chromatograms a–d), 2-octenal (chromatograms e–h), 2,4-heptadienal (chromatograms i–l), and 2,4-decadienal (chromatograms m–p). The first chromatogram of each series (chromatograms a, e, i, and m) corresponds to the aldehyde with no solvent added and heated under nitrogen. The second chromatogram of each series (chromatograms b, f, j, and n) corresponds to the aldehyde with no solvent added and heating under air. The third chromatogram of each series (chromatograms c, g, k, and o) corresponds to the solution of the aldehyde in a buffer that was heated under nitrogen. The fourth chromatogram of each series (chromatograms d, h, l, and p) corresponds to the solution of the aldehyde in a buffer that was heated under air. As the results obtained using either sodium phosphate buffer, pH 8, or sodium borate buffer, pH 8, were identical, only the chromatograms obtained using sodium phosphate buffer are shown (chromatograms c, d, g, h, k, l, o, and p).

2-Alkenals and 2,4-alkadienals mostly remained unchanged in the absence of both buffer and air. Thus, 2-pentenal (**4**) with no solvent added was relatively stable after heating under nitrogen (chromatogram a). Something similar occurred for 2-octenal (**7**, chromatogram e), 2,4-heptadienal (**6**, chromatogram i), and 2,4-decadienal (**9**, chromatogram m).

The most significant change produced when the aldehyde with no solvent added was heated in the presence of air was the appearance of formaldehyde (**1**, chromatograms b, f, j, and n, for the heating of 2-pentenal, 2-octenal, 2,4-heptadienal, and 2,4-decadienal,

Table 1
Optimization of MRM transitions for detection of aldehydes.

Aldehyde	Monitored transition	DP	FP	EP	CEP	CE	CXP
Formaldehyde-d$_2$	280.0 → 156.1	26	360	8	18	47	6
	280.0 → 115.2	26	360	8	18	67	4
	280.0 → 171.1	26	360	8	18	31	6
Formaldehyde	278.1 → 170.1	26	370	10	18	35	6
	278.1 → 128.1	26	370	10	18	71	4
	278.1 → 115.2	26	370	10	18	77	4
Propanal	306.2 → 156.0	26	370	10.5	14	53	6
	306.2 → 115.1	26	370	10.5	14	71	4
	306.2 → 171.1	26	370	10.5	14	31	6
2-Pentenal	332.2 → 156.1	26	370	10	14	55	6
	332.2 → 171.1	26	370	10	14	37	6
	332.2 → 115.1	26	370	10	14	79	4
2-Methyl-2-pentenal	346.2 → 156.1	21	370	6.5	26	57	6
	346.2 → 171.1	21	370	6.5	26	39	8
	346.2 → 115.1	21	370	6.5	26	79	6
2,4-Heptadienal	358.1 → 170.1	21	370	8	16	29	6
	358.1 → 171.1	21	370	8	16	35	6
	358.1 → 115.2	21	370	8	16	79	4
Hexanal	348.1 → 156.1	26	370	10.5	16	61	6
	348.1 → 115.1	26	370	10.5	16	83	4
	348.1 → 171.2	26	370	10.5	16	41	6
2-Octenal	374.1 → 156.1	26	350	11.5	14	61	6
	374.1 → 171.1	26	350	11.5	14	39	6
	374.1 → 115.1	26	350	11.5	14	83	4
2,4-Decadienal	400.1 → 170.0	21	370	10.5	16	33	6
	400.1 → 171.1	21	370	10.5	16	37	6
	400.1 → 95.1	21	370	10.5	16	37	6

respectively, under air). In addition, the formation of minute amounts of glyoxal (**8**) and fumaraldehyde (**10**) were also observed in chromatograms j and n. Furthermore, the formation of trace amounts of 2-pentenal (**4**) and propanal (**3**) in chromatogram j, and of 2-octenal (**7**) and hexanal (**5**) in chromatogram n were also observed.

Aldehydes suffered a higher decomposition in the presence of buffer. However, dialdehydes **8** and **10** were not observed under these reaction conditions, and formaldehyde (**1**) was detected to a lower extent than when the buffer was absent. On the other hand, shorter aldehydes were produced to a higher extent and a similar decomposition was observed in the presence and in the absence of air. Thus, 2-pentenal (**4**) disappeared completely after 1 h at 200 °C (chromatograms c and d for nitrogen and air, respectively) and the formation of propanal (**3**) and acetaldehyde (**2**) was observed. Something similar occurred for 2-octenal (**7**). It almost disappeared and the formation of hexanal (**5**) and acetaldehyde (**2**) was observed (chromatograms g and h for nitrogen and air, respectively). Results for 2,4-heptadienal (**6**) show slightly more stability and the initial aldehyde could still be detected after 1 h heating at 200 °C (chromatograms k and l for nitrogen and air, respectively). In addition, 2,4-heptadienal decomposition produced propanal (**3**), acetaldehyde (**2**) and small amounts of 2-pentenal (**4**). Finally, decomposition of 2,4-decadienal (**9**) (chromatograms o and p for nitrogen and air, respectively) mostly produced hexanal (**5**) and acetaldehyde (**2**).

With the exception of formaldehyde and acetaldehyde, the formed aldehydes corresponded to the breakage of the different double bonds present in the initial aldehyde as indicated in Fig. 1. Thus, 2-alkenals (**4** or **7**) produced the corresponding alkanals **3** or **5**. In addition, 2,4-alkadienals (**6** or **9**) produced both 2-alkenals (**4** or **7**, respectively) and alkanals (**3** or **5**, respectively). These reactions were accompanied by the formation of both glyoxal (**8**) and fumaraldehyde (**10**), although these last compounds seemed to be easily decomposed when buffer was present. The next sections will describe the formation of shorter aldehydes by thermal breakage of carbon—carbon double bonds in 2-alkenals and 2,4-alkadienals.

3.2. Thermal degradation of 2-pentenal

As discussed previously, the breakage of 2-pentenal produced propanal, in addition to formaldehyde and acetaldehyde. This reaction should be accompanied by the formation of glyoxal, although this compound was not detected when the reaction was carried out in the presence of buffer. 2-Pentenal decomposition in buffer solution and the formation of the corresponding propanal is shown in Fig. 2. As can be observed, propanal was formed to an extent that depended on the concentration of 2-pentenal and the reaction conditions. Fig. 2A shows that propanal formation took place over a wide pH-range with a maximum around pH 8. The amount of propanal produced increased linearly ($r = 0.993$, $p < 0.0001$) as a function of 2-pentenal concentration (Fig. 2B). The slope of the obtained line (0.125) indicates the reaction yield (12.5%), which was constant over the assayed concentration range (0–80 μmol of 2-pentenal).

2-Pentenal concentration decreased exponentially as a function of heating time and temperature (Fig. 2C), and 2-pentenal disappearance was more rapidly produced at a higher temperature. Thus, less than 10% of initial pentanal was observed after 25 min at 200 °C and after 45 min at 160 °C. When 2-pentenal was heated at 120 °C, 17% of the initial aldehyde was still present after 60 min.

This disappearance of 2-pentenal was parallel to the formation of propanal (Fig. 2D). Propanal concentration only increased linearly ($r > 0.994$, $p < 0.0067$) for most temperatures at the beginning of the heating, in accordance to the exponential degradation observed for 2-pentenal. In fact, there was an inverse correlation ($r > 0.935$, $p < 0.002$) between the concentrations of 2-pentenal and propanal as a function of heating time at the three assayed temperatures.

Reaction rates for propanal formation were higher at higher temperatures. These reaction rates were calculated from the initial times in which the concentration of propanal increased linearly as a function of heating time (Fig. 2D) by using the equation:

$$[\text{propanal}] = kt$$

where k is the rate constant and t is the time. These rate constants were used in an Arrhenius plot for the calculation of the activation
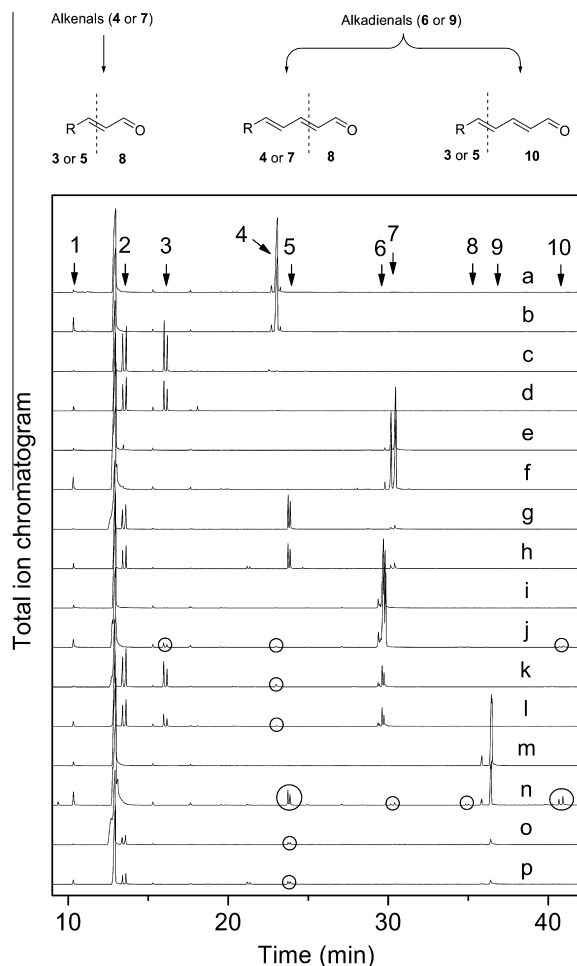
Fig. 1. Total ion chromatograms obtained for: (a) 2-pentenal heated under nitrogen; (b) 2-pentenal heated under air; (c) a solution of 2-pentenal in sodium phosphate buffer heated under nitrogen; (d) a solution of 2-pentenal in sodium phosphate buffer heated under nitrogen; (e) 2-octenal heated under nitrogen; (f) 2-octenal heated under air; (g) a solution of 2-octenal in sodium phosphate buffer heated under nitrogen; (h) a solution of 2-octenal in sodium phosphate buffer heated under air; (i) 2,4-heptadienal heated under nitrogen; (j) 2,4-heptadienal heated under air; (k) a solution of 2,4-heptadienal in sodium phosphate buffer heated under nitrogen; (l) a solution of 2,4-heptadienal in sodium phosphate buffer heated under air; (m) 2,4-decadienal heated under nitrogen; (n) 2,4-decadienal heated under air; (o) a solution of 2,4-decadienal in sodium phosphate buffer heated under nitrogen; (p) a solution of 2,4-decadienal in sodium phosphate buffer heated under air. All samples were heated for 1 h at 200 °C and, then, derivatized with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride. Compounds identified were: formaldehyde (**1**), acetaldehyde (**2**), propanal (**3**), 2-pentenal (**4**), hexanal (**5**), 2,4-heptadienal (**6**), 2-octenal (**7**), glyoxal (**8**), 2,4-decadienal (**9**), and fumaraldehyde (**10**).

energy (E_a) of propanal formation by heating 2-pentenal. The determined E_a was 25.2 kJ/mol.

3.3. Thermal degradation of 2-octenal

2-Octenal exhibited a behaviour analogous to that of 2-pentenal, and hexanal formation also depended on 2-octenal concentration and reaction conditions (Fig. 3). Hexanal was mainly produced at basic pH, with a maximum around pH 10 (Fig. 3A). The amount of hexanal formed increased linearly ($r = 0.999$, $p < 0.0001$) as a function of 2-octenal concentration (Fig. 3B). The slope of the obtained line (0.180) indicated the reaction yield (18.0%), which was constant over the assayed range (0–80 μmol of 2-octenal). This yield was slightly higher than that found for the formation of propanal from 2-pentenal.

Analogously to 2-pentenal, 2-octenal also disappeared exponentially as a function of reaction time and this disappearance was produced more rapidly at a higher temperature (Fig. 3C). Less than 10% of the initial 2-octenal was found after 10 min heating at 200 °C, 50 min heating at 160 °C, and about 60 min when heating at 120 °C.

Hexanal concentration increased linearly ($r > 0.971$, $p < 0.00097$) as a function of reaction time, and reaction rates were higher at higher temperatures (Fig. 3D). Reaction rates were calculated from the slopes of the adjusted lines as described previously. The determined E_a was 25.3 kJ/mol, which was very similar to the E_a obtained for propanal formation from 2-pentenal (see above).

3.4. Thermal degradation of 2,4-heptadienal

When 2,4-heptadienal was heated in the presence of buffer, the formation of the two aldehydes corresponding to the breakage of either one or the other double bond was observed, although propanal was always formed to a higher extent than 2-pentenal (Fig. 4). In addition, and analogously to 2-pentenal and 2-octenal decomposition, aldehyde formation depended on the concentration of 2,4-heptadienal and the reaction conditions.

Propanal and 2-pentenal were produced over a wide pH range with a maximum at about pH 7–8. There was no clear difference between the optimum pH values for the formation of both propanal and 2-pentenal, although 2-pentenal seemed to be produced better at a pH slightly more acidic than propanal (Fig. 4A).

Propanal and 2-pentenal increased as a function of 2,4-heptadienal concentration (Fig. 4B). This increase was linear ($r = 0.995$, $p < 0.0001$) for 2-pentenal for the whole concentration range assayed (0–80 μmol of 2,4-heptadienal), and also for propanal ($r = 0.996$, $p < 0.0001$) but only in the 0–40 μmol range of 2,4-heptadienal. The slopes of the obtained lines (0.09774 and 0.00973) indicated reaction yields of 9.8% and 1.0% for propanal and 2-pentenal, respectively.

Analogously to the above discussed behaviour of 2-alkenals, 2,4-heptadienal concentration decreased exponentially as a function of reaction time and this decrease was higher at higher temperature (Fig. 4C). This decrease was parallel to the formation of both propanal (Fig. 4D) and 2-pentenal (Fig. 4E). The E_a required for the formation of both aldehydes was calculated by using the slopes of the obtained lines as described previously. The E_a for propanal and 2-pentenal formation were 25.2 and 22.5 kJ/mol, respectively.

3.5. Thermal degradation of 2,4-decadienal

Analogously to the above described for 2,4-heptadienal, when 2,4-decadienal was heated, the formation of the two aldehydes corresponding to the breakage of the two double bonds was observed and hexanal was always formed to a higher extent than 2-octenal (Fig. 5). In addition, and analogously to the above described decompositions for the other aldehydes, the yields of hexanal and 2-octenal formation depended on the concentration of 2,4-decadienal and the reaction conditions.

Hexanal and 2-octenal were produced over a wide pH range with a maximum at about pH 8 and there was no clear difference between the optimum pH values for the formation of both aldehydes. Nevertheless, and in accordance with the above observations for 2,4-heptadienal decomposition, the 2-alkenal seemed to be produced in a greater yield at a pH value slightly more acidic than the alkanal (Fig. 5A).

Hexanal and 2-octenal increased as a function of 2,4-decadienal concentration (Fig. 5B). This increase was linear ($r > 0.998$, $p < 0.0001$) for both hexanal and 2-octenal for the whole concentration range assayed (0–80 μmol of 2,4-decadienal). The slopes
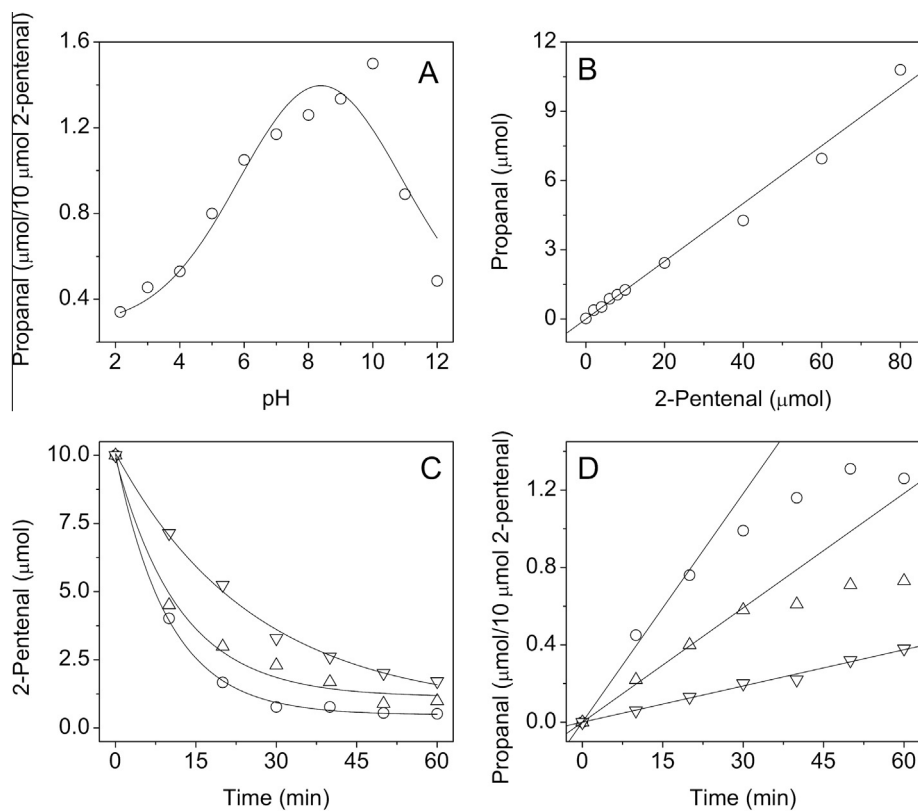
Fig. 2. Formation of propanal by thermal decomposition of 2-pentenal: (A) effect of pH in the formation of propanal; (B) effect of 2-pentenal concentration in the formation of propanal; (C) time-course of 2-pentenal disappearance; and (D) time-course of propanal formation. Reactions were heated at 200 (○), 160 (△), or 120 °C (▽) for 1 h in panels (A) and (B) and the indicated times in panels (C) and (D).
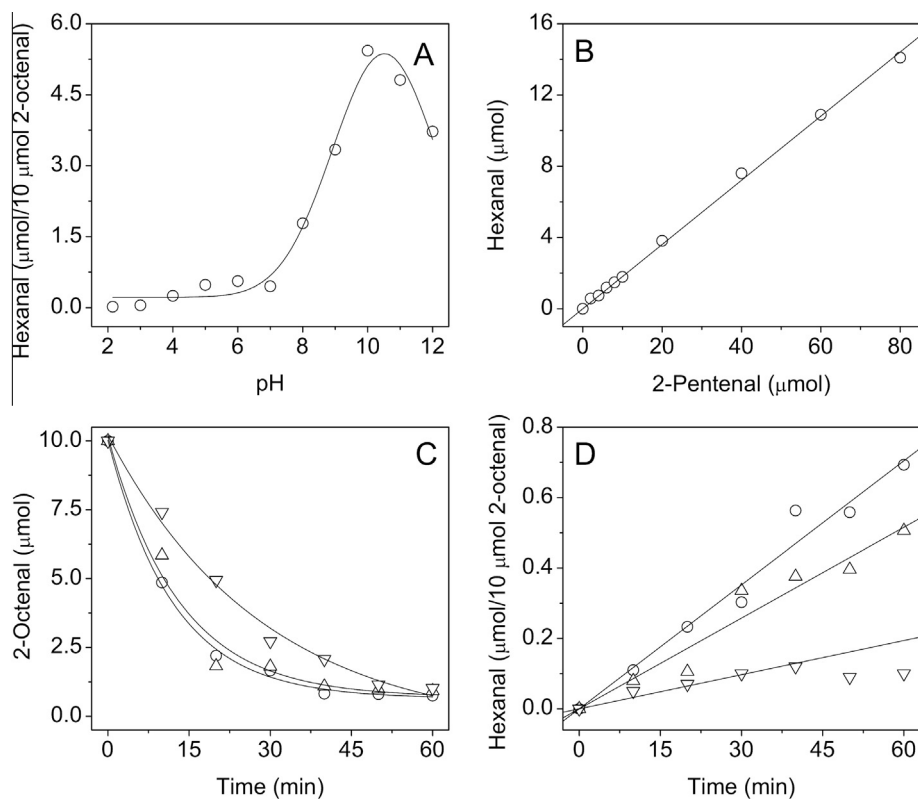

Fig. 3. Formation of hexanal by thermal decomposition of 2-octenal: (A) effect of pH in the formation of hexanal; (B) effect of 2-octenal concentration in the formation of hexanal; (C) time-course of 2-octenal disappearance; and (D) time-course of hexanal formation. Reactions were heated at 200 (○), 160 (△), or 120 °C (▽) for 1 h in panels (A) and (B), and the indicated times in panels (C) and (D).
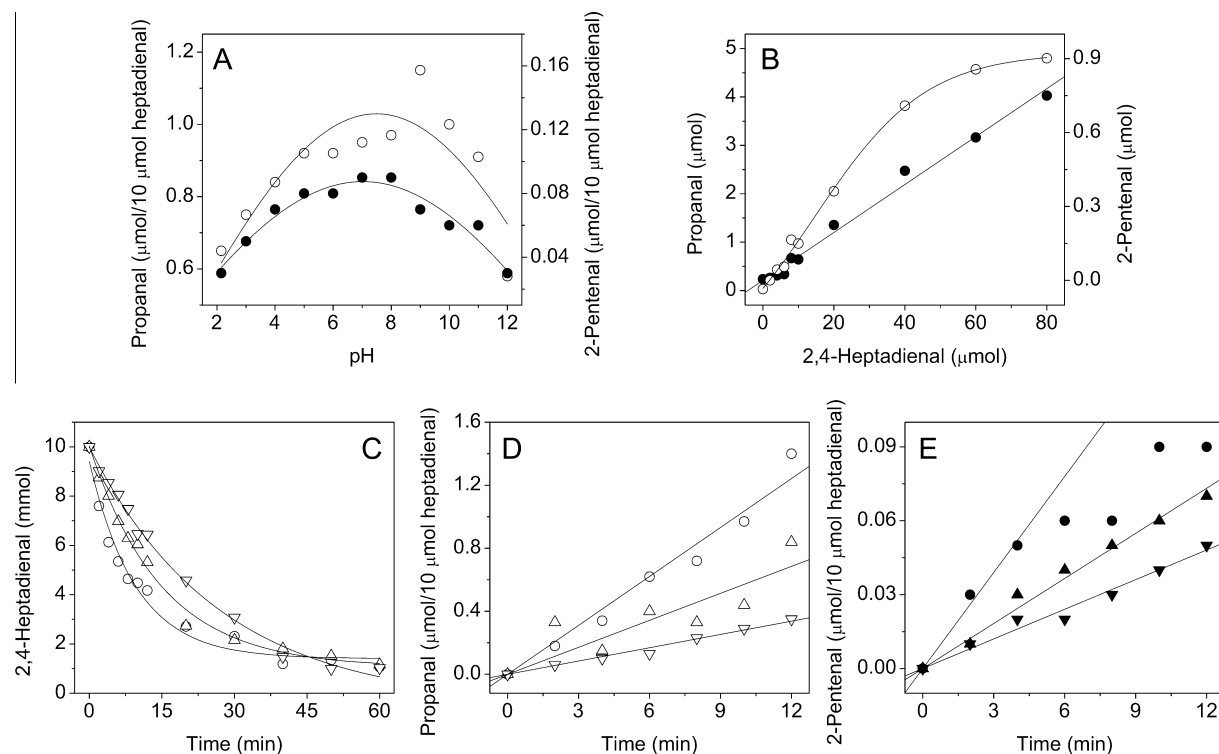
Fig. 4. Formation of propanal (open symbols) and 2-pentenal (closed symbols) by thermal decomposition of 2,4-heptadienal: (A) effect of pH in the formation of propanal (○) and 2-pentenal (●); (B) effect of 2,4-heptadienal concentration in the formation of propanal (○) and 2-pentenal (●); (C) time-course of 2,4-heptadienal disappearance; (D) time-course of propanal formation; and (E) time-course of 2-pentenal formation. Reactions were heated at 200 (○, ●), 160 (△, ▲), or 120 °C (▽, ▼) for 1 h in panels (A) and (B), and the indicated times in panels (C), (D), and (E).
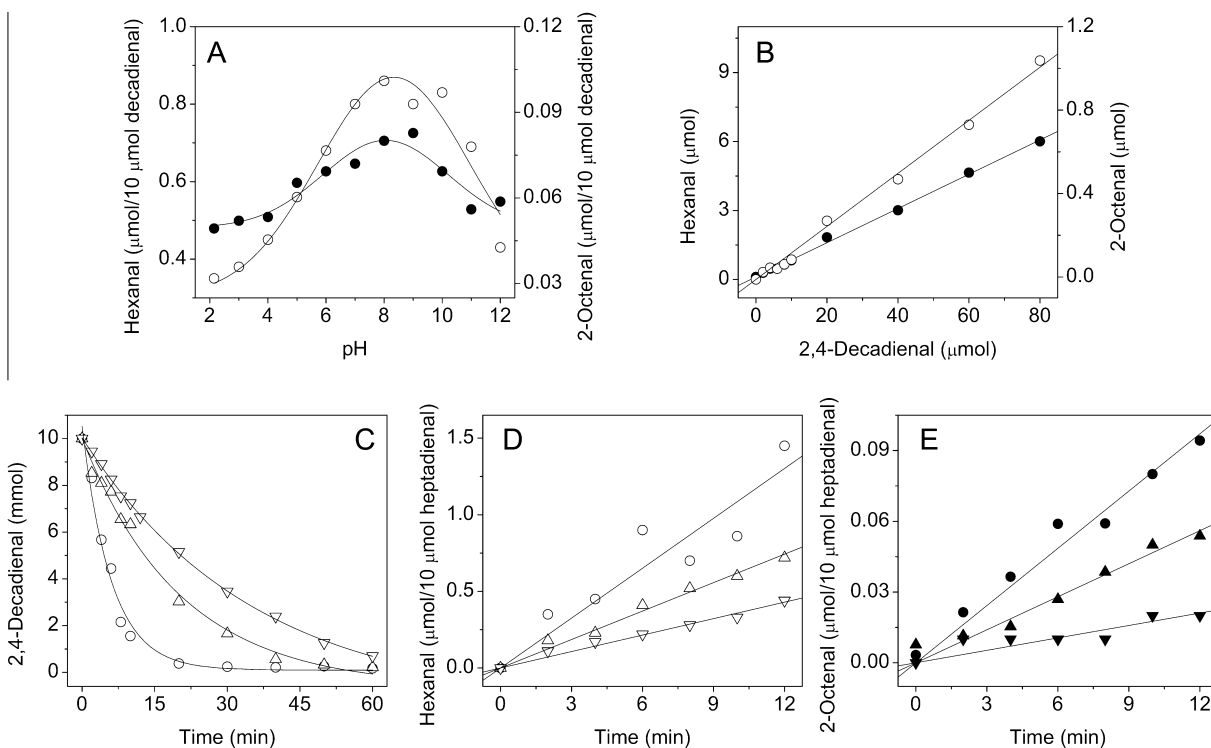

Fig. 5. Formation of hexanal (open symbols) and 2-octenal (closed symbols) by thermal decomposition of 2,4-decadienal: (A) effect of pH in the formation of hexanal (○) and 2-octenal (●); (B) effect of 2,4-decadienal concentration in the formation of hexanal (○) and 2-octenal (●); (C) time-course of 2,4-decadienal disappearance; (D) time-course of hexanal formation; and (E) time-course of 2-octenal formation. Reactions were heated at 200 (○, ●), 160 (△, ▲), or 120 °C (▽, ▼) for 1 h in panels (A) and (B), and the indicated times in panels (C), (D), and (E).

of the obtained lines (0.1154 and 0.00821) indicated reaction yields of 11.5% and 0.8% for hexanal and 2-octenal, respectively.

As observed for other aldehydes, 2,4-decadienal concentration decreased exponentially as a function of reaction time and this decrease was higher at higher temperature (Fig. 5C). This decrease was parallel to the formation of both hexanal (Fig. 5D) and 2-octenal (Fig. 5E). The E_a required for the formation of both aldehydes was calculated by using the slopes of the obtained lines as described previously. The E_a for hexanal and 2-octenal formation were 21.3 and 29.6 kJ/mol, respectively.

4. Discussion

Lipid oxidation is a complex cascade of reactions in which primary, secondary and tertiary lipid oxidation products are produced (Bekhit, Hopkins, Fahri, & Ponnampalam, 2013; Ibargoitia, Sopelana, & Guillen, 2014; Maqsood, Benjakul, & Kamal-Eldin, 2012; Varlet, Prost, & Serot, 2007). Some of these compounds are stable, such as alkanes. However, other lipid oxidation products are unstable and are usually involved in further reactions, which might also imply other food components. Among them, aldehydes can be either oxidised to the corresponding acids or reduced to alcohols by both chemical and enzymatic processes. In addition, and as described in this study, unsaturated aldehydes can also be degraded as a consequence of thermal heating.

According to the above results, the stability of the aldehydes depended on the presence of buffer and oxygen. Aldehydes were shown to be relatively stable in the absence of buffer and oxygen, but when aqueous solutions were employed, a rapid decomposition was observed. This decomposition was similar for 2-alkenals and 2,4-alkadienals and always produced shorter aldehydes, among other compounds. The aldehydes produced were formaldehyde, acetaldehyde and the corresponding carbonyl compounds produced as a consequence of the breakage of the carbon—carbon double bonds present in the molecule. Thus, because 2-alkenals only have one carbon—carbon double bond, the products formed were alkanals and glyoxal. The reaction was more complex for 2,4-alkadienals because these compounds have two carbon—carbon double bonds. The breakage of the double bond between C2 and C3 produced 2-alkenals and glyoxal, and the breakage of the double bond between C4 and C5 produced alkanals and fumaraldehyde.

The E_a for the breakage of the different carbon—carbon double bonds was always very similar and was about 25 kJ/mol. However, alkanals were produced to a much higher extent than 2-alkenals. Thus, 10–18% of the initial either 2-alkenal or 2,4-alkadienal was converted into alkanal after 1 h heating at 200 °C and only about 1% of the initial 2,4-alkadienal was converted into 2-alkenal under the same reaction conditions. The lower amount of 2-alkenals found during 2,4-alkadienal degradation in relation to that of alkanals is likely a consequence of the degradation suffered by 2-alkenals, which also produce alkanals. However, alkanals were also produced directly from 2,4-alkadienals because fumaraldehyde was found in these reactions (Fig. 1j and n for 2,4-heptadienal and 2,4-decadienal, respectively).

Lipid-derived aldehydes are important secondary lipid oxidation products because of their contribution to food aroma, as well as their ability to induce changes in surrounding food components. Thus, once produced, they are further involved in reactions with the nucleophiles present in food products (Choe & Min, 2006; Hidalgo & Zamora, 2014, in press; Tang et al., 2011). In addition, the results obtained in the present study show that unsaturated lipid-derived aldehydes are degraded. Therefore, these degradations should also be considered to fully understand the range of nucleophile/aldehyde adducts formed as well as the changes produced in the volatile composition of foods during processing or storage, and the role of aldehyde degradation products in the produced food changes. Thus, for example, in a recent study Lee and Pangloli (2013) analysed the changes of volatile compounds produced during the storage of potato chips fried in mid-oleic sunflower oil. They found that the concentration of hexanal increased upon storage at the same time that the concentration of decadienal seemed to decrease slightly, which is in agreement with the results obtained in the present study. Moreover, polymers formed by reaction between amino acids and alkadienals have been traditionally believed to be produced between the amino acid and the aldehyde (see, for example, Adams, Kitryte, Venskutonis, & De Kimpe, 2009). However, the results obtained in the present study suggest a potential role in these reactions of the dicarbonyl compounds (glyoxal and fumaraldehyde) produced by alkadienal decomposition.

Acknowledgements

References

Adams, A., Kitryte, V., Venskutonis, R., & De Kimpe, N. (2009). Formation and characterisation of melanoidin-like polycondensation products from amino acids and lipid oxidation products. *Food Chemistry, 115*, 904–911.

Arvanitoyannis, I. S., & Dionisopoulou, N. (2014). Acrylamide: Formation, occurrence in food products, detection methods, and legislation. *Critical Reviews in Food Science and Nutrition, 54*, 708–733.

Bekhit, A. E. A., Hopkins, D. L., Fahri, F. T., & Ponnampalam, E. N. (2013). Oxidative processes in muscle systems and fresh meat: Sources, markers, and remedies. *Comprehensive Reviews in Food Science and Food Technology, 12*, 565–597.

Brewer, M. S. (2009). Irradiation effects on meat flavor. *Meat Science, 81*, 1–14.

Choe, E., & Min, D. B. (2006). Chemistry and reactions of reactive oxygen species in foods. *Critical Reviews in Food Science and Nutrition, 46*, 1–22.

Fuentes, V., Estevez, M., Ventanas, J., & Ventanas, S. (2014). Impact of lipid content and composition on lipid oxidation and protein carbonylation in experimental fermented sausages. *Food Chemistry, 147*, 70–77.

Ganesan, B., Brothersen, C., & McMahon, D. J. (2014). Fortification of foods with omega-3 polyunsaturated fatty acids. *Critical Reviews in Food Science and Nutrition, 54*, 98–114.

Gardner, H. W. (1989). Oxygen radical chemistry of polyunsaturated fatty acids. *Free Radical Biology and Medicine, 7*, 65–86.

Granvogl, M., & Schieberle, P. (2006). Thermally generated 3-aminopropionamide as a transient intermediate in the formation of acrylamide. *Journal of Agricultural and Food Chemistry, 54*, 5933–5938.

Guillen, M. D., & Uriarte, P. S. (2012). Study by 1H NMR spectroscopy of the evolution of extra virgin olive oil composition submitted to frying temperature in an industrial fryer for a prolonged period time. *Food Chemistry, 2012*, 162–172.

Hidalgo, F. J., & Zamora, R. (in press). Amino acid degradations produced by lipid oxidation products. *Critical Reviews in Food Science and Nutrition,* in press. Doi: 10.1080/10408398.2012.761173.

Hidalgo, F. J., Delgado, R. M., & Zamora, R. (2009). Degradation of asparagine to acrylamide by carbonyl-amine reactions initiated by alkadienals. *Food Chemistry, 116*, 779–784.

Hidalgo, F. J., Navarro, J. L., Delgado, R. M., & Zamora, R. (2013). Histamine formation by lipid oxidation products. *Food Research International, 52*, 206–213.

Hidalgo, F. J., & Zamora, R. (2014). 2-Alkenal-scavenging ability of *m*-diphenols. *Food Chemistry, 160*, 118–126.

Ibargoitia, M. L., Sopelana, P., & Guillen, M. D. (2014). (1)H Nuclear Magnetic Resonance monitoring of the degradation of margarines of varied compositions when heated to high temperature. *Food Chemistry, 165*, 119–128.

Lee, J. H., & Pangloli, P. (2013). Volatile compounds and storage stability of potato chips fried in mid-oleic sunflower oil. *International Journal of Food Properties, 16*, 563–573.

Maire, M., Rega, B., Cuvelier, M. E., Soto, P., & Giampaoli, P. (2013). Lipid oxidation in baked products: Impact of formula and process on the generation of volatile compounds. *Food Chemistry, 141*, 3510–3518.

Maqsood, S., Benjakul, S., & Kamal-Eldin, A. (2012). Haemoglobin-mediated lipid oxidation in the fish muscle: A review. *Trends in Food Science & Technology, 2012*, 33–43.

Matthews, R. F., Scanlan, R. A., & Libbey, L. M. (1971). Autoxidation products of 2,4-decadienal. *Journal of the American Oil Chemists' Society, 48*, 745–747.

Rendon, M. Y., Salva, T. D. G., & Bragagnolo, N. (2014). Impact of chemical changes on the sensory characteristics of coffee beans during storage. *Food Chemistry, 147*, 279–286.

Tang, M. S., Wang, H. T., Hu, Y., Chen, W. S., Akao, M., Feng, Z. H., et al. (2011). Acrolein induced DNA damage, mutagenicity and effect on DNA repair. *Molecular Nutrition & Food Research, 55*, 1291–1300.

Varlet, V., Prost, C., & Serot, T. (2007). Volatile aldehydes in smoked fish: Analysis methods, occurrence and mechanisms of formation. *Food Chemistry, 105*, 1536–1556.

Zamora, R., Alcon, E., & Hidalgo, F. J. (2012). Effect of lipid oxidation products on the formation of 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP) in model systems. *Food Chemistry, 135*, 2569–2574.

Zamora, R., Alcon, E., & Hidalgo, F. J. (2013). Effect of amino acids on the formation of 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP) in creatinine/ phenylalanine and creatinine/phenylalanine/4-oxo-2-nonenal reaction mixtures. *Food Chemistry, 141*, 4240–4245.

Zamora, R., Alcon, E., & Hidalgo, F. J. (2014). Ammonia and formaldehyde participate in the formation of 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP) in addition to creati(ni)ne and phenylacetaldehyde. *Food Chemistry, 155*, 74–80.

Zamora, R., Delgado, R. M., & Hidalgo, F. J. (2011). Strecker aldehydes and α-keto acids, produced by carbonyl-amine reactions, contribute to the formation of acrylamide. *Food Chemistry, 128*, 465–470.

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

Zamora, R., Navarro, J. L., Gallardo, E., & Hidalgo, F. J. (2006). Chemical conversion of α-amino acids into α-keto acids by 4,5-epoxy-2-decenal. *Journal of Agricultural and Food Chemistry, 54*, 6101–6105.

Zochling, S., & Murkovic, M. (2002). Formation of the heterocyclic aromatic amine PhIP: Identification of precursors and intermediates. *Food Chemistry, 79*, 125–134.