

1 **Lipid-derived aldehyde degradation under thermal conditions**

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9 ABSTRACT

10 Nucleophile degradations produced by reactive carbonyls play a major role in food
11 quality and safety. Nevertheless, these reactions are complex because reactive carbonyls
12 are usually involved in different competitive reactions. This study describes the thermal
13 degradation of 2-alkenals (2-pentenal and 2-octenal) and 2,4-alkadienals (2,4-
14 heptadienal and 2,4-decadienal) in an attempt of both clarifying the stability of
15 aldehydes and determining new compounds that might also play a role in
16 nucleophile/aldehyde reactions. Alkenals and alkadienals decomposed rapidly in the
17 presence of buffer and air to produce formaldehyde, acetaldehyde, and the aldehydes
18 corresponding to the breakage of the carbon-carbon double bonds: propanal, hexanal, 2-
19 pentenal, 2-octenal, glyoxal, and fumaraldehyde. The activation energy of double bond
20 breakage was relatively low (~25 kJ/mol) and the yield of alkanals (10-18%) was higher
21 than that of 2-alkenals (~1%). The obtained results indicate that these reactions should
22 be considered in order to fully understand the range of nucleophile/aldehyde adducts
23 produced.

24 *Keywords:* Alkanals; 2,4-Alkadienals; 2-Alkenals; Aldehyde degradation; Food flavors;
25 Lipid oxidation

26

27 **1. Introduction**

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

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

43 Lipid-derived reactive carbonyls are produced in the course of lipid oxidation, and
44 they are a large number of short- and long-chain aldehydes and ketones with various
45 degrees of unsaturation (Gardner, 1989). Among them, 2-alkenals and 2,4-alkadienals
46 are produced to a significant extent (Guillen and Uriarte, 2012), and they have been
47 shown to be involved in many chemical reactions that take place in foods upon
48 processing such as the conversion of asparagine to acrylamide (Hidalgo, Delgado, &
49 Zamora, 2009) or the formation of the heterocyclic aromatic amine PhIP (Zamora,
50 Alcon, & Hidalgo, 2014), for example. These reactions require a high temperature at
51 which unsaturated aldehydes might degrade and degradation products might also play a

52 role in those reactions. However, thermal degradation of lipid-derived unsaturated
53 aldehydes is not well known, although some studies have shown that these compounds
54 are degraded upon heating (Matthews, Scanlan, & Libbey, 1971).

55 In an attempt to clarify the stability of 2-alkenals and 2,4-alkadienals upon thermal
56 processing, this study identifies and quantifies the thermal degradation products of 2-
57 alkenals and 2,4-alkadienals. As models of 2-alkenals and 2,4-alkadienals, 2-pentenal
58 and 2,4-heptadienal, respectively, were selected as oxidation products of ω 3 fatty acid
59 chains, and 2-octenal and 2,4-decadienal, respectively, were selected as oxidation
60 products of ω 6 fatty acid chains.

61 **2. Materials and methods**

62 *2.1. Materials*

63 2-Alkenals (2-pentenal and 2-octenal) and 2,4-alkadienals (2,4-heptadienal and 2,4-
64 decadienal) were purchased from Aldrich (Milwaukee, WI, USA) and had the highest
65 available grade. All other chemicals were purchased from Aldrich (Milwaukee, WI,
66 USA), Sigma (St. Louis, MO, USA), Fluka (Buchs, Switzerland), or Merck (Darmstadt,
67 Germany), and were analytical grade.

68 *2.2. Thermal treatment of lipid-derived aldehydes*

69 Two different procedures were followed depending on whether the formed
70 compounds were going to be either identified or quantified. The identification of
71 thermal degradation products of the studied aldehydes was carried out by GC-MS after
72 derivatization with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride,
73 according to a previously described procedure (Zamora, Navarro, Gallardo, & Hidalgo,
74 2006), which was modified. Quantification of produced compounds was carried out by

75 LC-MS/MS after derivatization with dansylhydrazine according to a previously
76 described procedure (Zamora, Alcon, & Hidalgo, 2014), which was also modified.

77 For samples with identification purposes, the aldehyde (4 μmol) was either heated
78 alone or in the presence of 200 μL of 50 mM buffer (either sodium phosphate or sodium
79 borate), pH 8, for 1 h at 200 $^{\circ}\text{C}$ in closed test tubes under either nitrogen or air. At the
80 end of the heating process, samples were cooled (5 min at room temperature and 10 min
81 at -20°C) and derivatized with 400 μL of a freshly prepared solution of *O*-(2,3,4,5,6-
82 pentafluorobenzyl)hydroxylamine hydrochloride (10 mg/mL in methanol). The
83 resulting solution was stirred and incubated for 1 h at 37 $^{\circ}\text{C}$. After that, reactions were
84 studied by GC-MS.

85 For samples with quantification purposes, a solution of the aldehyde (0–10 μmol) in
86 tetrahydrofuran (80 μL) was treated with 420 μL of 0.2 M buffer (pH 2.15–11) and,
87 then, heated for the indicated time and temperature in closed test tubes under air. At the
88 end of the heating process, samples were cooled (5 min at room temperature and 10 min
89 at -20°C). Fifty microliters of these cooled samples were diluted with 350 μL of
90 methanol, and treated with 50 μL of the internal standard (a solution of 88 μmol of
91 formaldehyde- d_2 in 2 mL of methanol), 150 μL of trifluoromethanesulfonic acid
92 solution (3% in methanol), and 200 μL of dansylhydrazine solution (4 mg/mL in
93 methanol). The resulting solution was incubated for 15 min at 100 $^{\circ}\text{C}$, then maintained
94 for 1 h at 25 $^{\circ}\text{C}$, and, finally diluted with 200 μL of eluent A (a 30:70 mixture of 0.2%
95 formic acid in acetonitrile and 4 mM ammonium acetate), and analyzed by LC-MS/MS.

96 2.3. GC-MS analyses

97 GC-MS analyses were conducted with a Hewlett-Packard 6890 GC Plus coupled
98 with an Agilent 5973 MSD (Mass Selective Detector-Quadrupole type). A fused silica

99 HP5-MS capillary column (30 × 0.25 mm i.d.; coating thickness 0.25 μm) was used.
100 Working conditions were as follows: carrier gas, helium (1 mL/min at constant flow);
101 injector temperature, 250 °C; oven temperature, from 70 (1 min) to 240 °C at 5 °C/min
102 and, then, to 325 °C at 10 °C/min; transfer line to MSD, 280 °C; ionization EI, 70 eV.
103 Reaction products were identified by comparison of mass spectra and retention times of
104 those of authentic standards.

105 2.4. LC-MS/MS analyses

106 The employed equipment was composed by an Agilent liquid chromatography
107 system (1200 Series) consisting of binary pump (G1312A), degasser (G1379B), and
108 autosampler (G1329A), connected to a triple quadrupole API 2000 mass spectrometer
109 (Applied Biosystems, Foster City, CA) using an electrospray ionization interface in
110 positive ionization mode (ESI⁺). Compounds were separated on a Zorbax Eclipse XDB-
111 C18 (150 mm x 4.6 mm, 5 μm) column from Agilent. As eluent A, a 30:70 mixture of
112 0.2% formic acid in acetonitrile and 4 mM ammonium acetate was used. As eluent B, a
113 0.2% formic acid solution in acetonitrile was employed. The mobile phase was
114 delivered at 0.5 mL/min using the following gradient: for 0–13 min, the content of
115 mobile phase B was 7%; for 13–20 min, the content of mobile phase B was increased
116 linearly from 7 to 60%; for 20–30 min, the content of mobile phase B was 60%; for 30–
117 32 min, the content of mobile phase B was increased linearly from 60 to 90%; for 32–42
118 min, the content of mobile phase B was 90%; and for 42–45 min, the content of mobile
119 phase B was decreased linearly from 90 to 7%. Mass spectrometric acquisition was
120 performed by using multiple reaction monitoring (MRM). The nebulizer gas (synthetic
121 air), the curtain gas (nitrogen), and the heater gas (synthetic air) were set at 40, 25, and
122 50 (arbitrary units), respectively. The collision gas (nitrogen) was set at 3 (arbitrary
123 units). The heater gas temperature was set at 500 °C and the electrospray capillary

124 voltage to 5.5 kV. The fragment ions in MRM mode were produced by collision-
125 activated dissociation of selected precursor ions in the collision cell of the triple
126 quadrupole and the selected products analyzed with the second analyzer of the
127 instrument. Three transitions were acquired for the identification of each
128 dansylhydrazone derivative. To establish the appropriate MRM conditions for the
129 individual compounds, the mass spectrometric conditions were optimized using infusion
130 with a syringe pump to select the most suitable ion transitions for the target analytes.
131 Precursor and product ions used for quantification and confirmation purposes, and
132 operating conditions are summarized in Table 1.

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

139 **3. Results**

140 *3.1. Thermal degradation of 2-alkenals and 2,4-alkadienals*

141 2-Alkenals and 2,4-alkadienals were more or less stable upon heating depending on
142 the presence of both air and buffers. Fig. 1 shows the chromatograms obtained after 1 h
143 heating at 200 °C for the four assayed aldehydes: 2-pentenal (chromatograms a–d), 2-
144 octenal (chromatograms e–h), 2,4-heptadienal (chromatograms i–l), and 2,4-decadienal
145 (chromatograms m–p). The first chromatogram of each series (chromatograms a, e, i,
146 and m) corresponded to the aldehyde with not solvent added and heated under nitrogen.
147 The second chromatogram of each series (chromatograms b, f, j, and n) corresponded to

148 the aldehyde with not solvent added and heated under air. The third chromatogram of
149 each series (chromatograms c, g, k, and o) corresponded to the solution of the aldehyde
150 in a buffer which was heated under nitrogen. The fourth chromatogram of each series
151 (chromatograms d, h, l, and p) corresponded to the solution of the aldehyde in a buffer
152 which was heated under air. Because the results obtained using either sodium phosphate
153 buffer, pH 8, or sodium borate buffer, pH 8, were identical, only the chromatograms
154 obtained using sodium phosphate buffer are shown (chromatograms c, d, g, h, k, l, o,
155 and p).

156 2-Alkenals and 2,4-alkadienals mostly remained unchanged in the absence of both
157 buffer and air. Thus, 2-pentenal (**4**) with not solvent added was relatively stable after
158 heating under nitrogen (chromatogram a). Something similar occurred for 2-octenal (**7**,
159 chromatogram e), 2,4-heptadienal (**6**, chromatogram i), and 2,4-decadienal (**9**,
160 chromatogram m).

161 The most significant change produced when the aldehyde with not solvent added was
162 heated in the presence of air was the appearance of formaldehyde (**1**, chromatograms b,
163 f, j, and n, for the heating of 2-pentenal, 2-octenal, 2,4-heptadienal, and 2,4-decadienal,
164 respectively, under air). In addition, the formation of minute amounts of glyoxal (**8**) and
165 fumaraldehyde (**10**) were also observed in chromatograms j and n. Furthermore, the
166 formation of trace amounts of 2-pentenal (**4**) and propanal (**3**) in chromatogram j, and of
167 2-octenal (**7**) and hexanal (**5**) in chromatogram n were also observed.

168 Aldehydes suffered a higher decomposition in the presence of buffer. However,
169 dialdehydes **8** and **10** were not observed under these reaction conditions, and
170 formaldehyde (**1**) was detected to a lower extent than when the buffer was absent. On
171 the other hand, shorter aldehydes were produced to a higher extent and a similar
172 decomposition was observed in the presence and in the absence of air. Thus, 2-pentenal

173 (4) disappeared completely after 1 h at 200 °C (chromatograms c and d for nitrogen and
174 air, respectively) and the formation of propanal (3) and acetaldehyde (2) was observed.
175 Something similar occurred for 2-octenal (7). It almost disappeared and the formation of
176 hexanal (5) and acetaldehyde (2) was observed (chromatograms g and h for nitrogen
177 and air, respectively). 2,4-Heptadienal (6) resulted slightly more stable and the initial
178 aldehyde could still be detected after 1 h heating at 200 °C (chromatograms k and l for
179 nitrogen and air, respectively). In addition, 2,4-heptadienal decomposition produced
180 propanal (3), acetaldehyde (2) and small amounts of 2-pentenal (4). Finally,
181 decomposition of 2,4-decadienal (9) (chromatograms o and p for nitrogen and air,
182 respectively) mostly produced hexanal (5) and acetaldehyde (2).

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

192 3.2. *Thermal degradation of 2-pentenal*

193 As discussed previously, the breakage of 2-pentenal produced propanal, in addition
194 to formaldehyde and acetaldehyde. This reaction should be accompanied by the
195 formation of glyoxal, although this compound was not detected when the reaction was
196 carried out in the presence of buffer. 2-Pentenal decomposition in buffer solution and
197 the formation of the corresponding propanal is shown in Fig. 2. As can be observed,

198 propanal was formed to an extent that depended on the concentration of 2-pentenal and
199 the reaction conditions. Fig. 2A shows that propanal formation took place over a wide
200 pH-range with a maximum around pH 8. The amount of produced propanal increased
201 linearly ($r = 0.993$, $p < 0.0001$) as a function of 2-pentenal concentration (Fig. 2B). The
202 slope of the obtained line (0.125) indicated the reaction yield (12.5%), which was
203 constant over the assayed concentration range (0-80 μmol of 2-pentenal).

204 2-Pentenal concentration decreased exponentially as a function of heating time and
205 temperature (Fig. 2C), and 2-pentenal disappearance was more rapidly produced at a
206 higher temperature. Thus, less than 10% of initial pentanal was observed after 25 min at
207 200° C and after 45 min at 160 °C. When 2-pentenal was heated at 120 °C, 17% of the
208 initial aldehyde was still present after 60 min.

209 This disappearance of 2-pentenal was parallel to the formation of propanal (Fig. 2D).
210 Propanal concentration only increased linearly ($r > 0.994$, $p < 0.0067$) for most
211 temperatures at the beginning of the heating, in accordance to the exponential
212 degradation observed for 2-pentenal. In fact, there was an inverse correlation ($r > 0.935$,
213 $p < 0.002$) between the concentrations of 2-pentenal and propanal as a function of
214 heating time at the three assayed temperatures.

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

$$218 \quad [\text{propanal}] = kt$$

219 where k is the rate constant and t is the time. These rate constants were used in an
220 Arrhenius plot for the calculation of the activation energy (E_a) of propanal formation by
221 heating 2-pentenal. The determined E_a was 25.2 kJ/mol.

222 3.3. Thermal degradation of 2-octenal

223 2-Octenal exhibited a behavior analogous to that of 2-pentenal, and hexanal
224 formation also depended on 2-octenal concentration and reaction conditions (Fig. 3).
225 Hexanal was mainly produced at basic pH, with a maximum around pH 10 (Fig. 3A).
226 The amount of hexanal formed increased linearly ($r = 0.999$, $p < 0.0001$) as a function
227 of 2-octenal concentration (Fig. 3B). The slope of the obtained line (0.180) indicated the
228 reaction yield (18.0%) which was constant over the assayed range (0-80 μmol of 2-
229 octenal). This yield was slightly higher than that found for the formation of propanal
230 from 2-pentenal.

231 Analogously to 2-pentenal, 2-octenal also disappeared exponentially as a function of
232 reaction time and this disappearance was produced more rapidly at a higher temperature
233 (Fig. 3C). Less than 10% of the initial 2-octenal was found after 10 min heating at 200
234 $^{\circ}\text{C}$, 50 min heating at 160 $^{\circ}\text{C}$, and about 60 min when heating at 120 $^{\circ}\text{C}$.

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

240 3.4. Thermal degradation of 2,4-heptadienal

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

246 Propanal and 2-pentenal were produced over a wide pH range with a maximum at
247 about pH 7–8. There was not a clear difference between the optimum pH values for the
248 formation of both propanal and 2-pentenal, although 2-pentenal seemed to be produced
249 better at a pH slightly more acidic than propanal (Fig. 4A).

250 Propanal and 2-pentenal increased as a function of 2,4-heptadienal concentration
251 (Fig. 4B). This increase was linear ($r = 0.995$, $p < 0.0001$) for 2-pentenal for the whole
252 concentration range assayed (0–80 μmol of 2,4-heptadienal), and also for propanal ($r =$
253 0.996 , $p < 0.0001$) but only in the 0–40 μmol range of 2,4-heptadienal. The slopes of
254 the obtained lines (0.09774 and 0.00973) indicated reaction yields of 9.8% and 1.0% for
255 propanal and 2-pentenal, respectively.

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

263 *3.5. Thermal degradation of 2,4-decadienal*

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

270 Hexanal and 2-octenal were produced over a wide pH range with a maximum at
271 about pH 8 and there was not a clear difference between the optimum pH values for the
272 formation of both aldehydes. Nevertheless, and in accordance with the observed above
273 for 2,4-heptadienal decomposition, the 2-alkenal seemed to be produced better at a pH
274 value slightly more acidic than the alkanal (Fig. 5A).

275 Hexanal and 2-octenal increased as a function of 2,4-decadienal concentration (Fig.
276 5B). This increase was lineal ($r > 0.998$, $p < 0.0001$) for both hexanal and 2-octenal for
277 the whole concentration range assayed (0–80 μmol of 2,4-decadienal). The slopes of the
278 obtained lines (0.1154 and 0.00821) indicated reaction yields of 11.5% and 0.8% for
279 hexanal and 2-octenal, respectively.

280 As observed for other aldehydes, 2,4-decadienal concentration decreased
281 exponentially as a function of reaction time and this decrease was higher at higher
282 temperature (Fig. 5C). This decrease was parallel to the formation of both hexanal (Fig.
283 5D) and 2-octenal (Fig. 5E). The E_a required for the formation of both aldehydes was
284 calculated by using the slopes of the obtained lines as described previously. The E_a for
285 hexanal and 2-octenal formation were 21.3 and 29.6 kJ/mol, respectively.

286 **4. Discussion**

287 Lipid oxidation is a complex cascade of reactions in which primary, secondary and
288 tertiary lipid oxidation products are produced (Bekhit, Hopkins, Fahri, & Ponnampalam,
289 2013; Ibargoitia, Sopelana, & Guillen, 2014; Maqsood, Benjakul, & Kamal-Eldin,
290 2012; Varlet, Prost, & Serot, 2007). Some of these compounds are stable, such as
291 alkanes. However, other lipid oxidation products are unstable and are usually involved
292 in further reactions, which might also imply other food components. Among them,
293 aldehydes can be either oxidized to the corresponding acids or reduced to alcohols by

294 both chemical and enzymatic processes. In addition, and as described in this study,
295 unsaturated aldehydes can also be degraded as a consequence of thermal heating.

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

309 The E_a for the breakage of the different carbon-carbon double bonds was always very
310 similar and was about 25 kJ/mol. However, alkanals were produced to a much higher
311 extent than 2-alkenals. Thus, 10–18% of the initial either 2-alkenal or 2,4-alkadienal
312 was converted into alkanal after 1 h heating at 200 °C and only about 1% of the initial
313 2,4-alkadienal was converted into 2-alkenal under the same reaction conditions. The
314 lower amount of 2-alkenals found during 2,4-alkadienal degradation in relation to that
315 of alkanals is likely a consequence of the degradation suffered by 2-alkenals, which also
316 produce alkanals. However, alkanals were also produced directly from 2,4-alkadienals
317 because fumaraldehyde was found in these reactions (Figs. 1j and 1n for 2,4-heptadienal
318 and 2,4-decadienal, respectively).

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

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Figure legends

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 air; 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**).

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.

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 |







