Lipid-derived aldehyde degradation under thermal conditions

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ABSTRACT

Nucleophile degradations produced by reactive carbonyls play a major role in food quality and safety. Nevertheless, these reactions are complex because reactive carbonyls are usually involved in different 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 of both clarifying the stability of aldehydes and determining new compounds that might also play a role in nucleophile/aldehyde reactions. 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%). The obtained results indicate that these reactions should be considered in order to fully understand the range of nucleophile/aldehyde adducts produced.

Keywords: Alkanals; 2,4-Alkadienals; 2-Alkenals; Aldehyde degradation; Food flavors; Lipid oxidation
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, & Hidalgo, 2005; Zamora, Alcon, & Hidalgo, 2013). Among them, 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 and 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 those reactions. However, thermal degradation of lipid-derived unsaturated aldehydes is not well known, although some studies have shown that these compounds are degraded 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 \( \omega_3 \) fatty acid chains, and 2-octenal and 2,4-decadienal, respectively, were selected as oxidation products of \( \omega_6 \) 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 (Milwaukee, WI, USA) and had the highest available grade. All other chemicals were purchased from Aldrich (Milwaukee, WI, USA), Sigma (St. Louis, MO, USA), Fluka (Buchs, Switzerland), or Merck (Darmstadt, Germany), and were analytical grade.

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 produced compounds was carried out by
LC-MS/MS after derivatization with dansylhydrazine according to a previously described procedure (Zamora, Alcon, & Hidalgo, 2014), which was also modified. For samples with 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 closed test tubes 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 ºC) 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. After that, reactions were studied by GC-MS.

For samples with 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 closed test tubes under air. At the end of the heating process, samples were cooled (5 min at room temperature and 10 min at –20 ºC). Fifty microliters 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-d2 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 ºC, then maintained for 1 h at 25 ºC, 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 analyzed 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 ºC; oven temperature, from 70 (1 min) to 240 °C at 5 ºC/min and, then, to 325 °C at 10 ºC/min; transfer line to MSD, 280 ºC; ionization EI, 70 eV. Reaction products were identified by comparison of mass spectra and retention times of those of authentic standards.

2.4. LC-MS/MS analyses

The employed equipment was composed by an Agilent liquid chromatography system (1200 Series) consisting of 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 ionization interface in positive ionization mode (ESI⁺). Compounds were separated on a Zorbax Eclipse XDB-C18 (150 mm x 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 by 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 ºC 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 analyzed 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 optimized 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 summarized 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 aldehydes (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 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 ºC 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) corresponded to the aldehyde with not solvent added and heated under nitrogen.
The second chromatogram of each series (chromatograms b, f, j, and n) corresponded to
the aldehyde with not solvent added and heated under air. The third chromatogram of each series (chromatograms c, g, k, and o) corresponded to the solution of the aldehyde in a buffer which was heated under nitrogen. The fourth chromatogram of each series (chromatograms d, h, l, and p) corresponded to the solution of the aldehyde in a buffer which was heated under air. Because 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 not 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 not 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, 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 present 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 ºC (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). 2,4-Heptadienal (6) resulted slightly more stable and the initial aldehyde could still be detected after 1 h heating at 200 ºC (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 with the formation of both glyoxal (8) and fumaraldehyde (10), although these last compounds seemed to be easily decomposed when buffer was present. 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 produced propanal 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) indicated 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 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 behavior 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 not a 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 lineal \( (r = 0.995, p < 0.0001) \) 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 behavior 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 not a clear difference between the optimum pH values for the formation of both aldehydes. Nevertheless, and in accordance with the observed above for 2,4-heptadienal decomposition, the 2-alkenal seemed to be produced better 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 lineal ($r > 0.998, p < 0.0001$) for both hexanal and 2-octenal for the whole concentration range assayed (0–80 μmol of 2,4-decadienal). The slopes 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 oxidized 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 resulted 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 ºC 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 (Figs. 1j and 1n for 2,4-heptadienal 
and 2,4-decadial, respectively).
Lipid-derived aldehydes are important secondary lipid oxidation products because both their contribution to food aroma and 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; Hidalgo & Zamora, in press; Tang, Wang, Hu, Chen, Akao, Feng, & Hu, 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) analyzed 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.

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References


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 ºC 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 ºC (▽) 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

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Monitored transition</th>
<th>DP</th>
<th>FP</th>
<th>EP</th>
<th>CEP</th>
<th>CE</th>
<th>CXP</th>
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<tr>
<td>Formaldehyde-d$_2$</td>
<td>280.0$\rightarrow$156.1</td>
<td>26</td>
<td>360</td>
<td>8</td>
<td>18</td>
<td>47</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>280.0$\rightarrow$115.2</td>
<td>26</td>
<td>360</td>
<td>8</td>
<td>18</td>
<td>67</td>
<td>4</td>
</tr>
<tr>
<td></td>
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