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# Strecker Degradation of Phenylalanine Initiated by 2,4-Decadienal or Methyl 13-Oxooctadeca-9,11-dienoate in Model Systems

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The reaction of 2,4-decadienal and methyl 13-oxooctadeca-9,11-dienoate with phenylalanine was studied to determine if alkadienals and ketodienes are able to produce the Strecker-type degradation of amino acids to the corresponding Strecker aldehydes. When reactions were carried out at 180 °C, both carbonyl compounds degraded phenylalanine to phenylacetaldehyde, among other compounds. The yield of the phenylacetaldehyde produced depended on the reaction pH and increased linearly with both the amount of the lipid and the reaction time. The yield of this conversion was ∼8% when starting from decadienal and ∼6% when starting from methyl 13-oxooctadeca-9,11-dienoate, and the reaction rate was lower for the ketone than for the aldehyde. Simultaneous to these reactions, the lipid was converted into pyrrole, pyridine, or aldehyde derivatives as a result of several competitive reactions. In particular, 9−14% of the decadienal was converted into hexanal under the assayed conditions. All these reactions are suggested to be produced as a consequence of the oxidation of the alkadienal or the ketodiene to the corresponding epoxyalkenal or unsaturated epoxyketone, which were identified in the reaction mixtures by GC−MS. All these results suggest that alkadienals and ketodienes, which are quantitatively important secondary lipid oxidation products, can degrade amino acids to their corresponding Strecker aldehydes. Therefore, under appropriate conditions, these products are not final products of the lipid oxidation and can participate in carbonyl−amine reactions analogously to other lipid oxidation products with two oxygenated functions.

**KEYWORDS: Alkadienals; carbonyl−amine reactions; epoxyalkenals; flavors; ketodienes; lipid oxidation; long-chain pyridine-containing fatty esters; Maillard reaction; phenylacetaldehyde; Strecker aldehydes**

## INTRODUCTION

Analogous to carbohydrates (*1*, *2*), recent studies have shown that different lipid oxidation products are able to degrade amines and amino acids by a Strecker-type mechanism to the corresponding Strecker aldehydes and α-keto acids (*3*−*7*). This degradation is produced at 37 °C by lipid oxidation products with two oxygenated functions (one of them being a carbonyl group and the other either an epoxy or a hydroxyl group), and the presence of these two oxygenated functions seems to be needed for the reaction. However, oxidized lipids with only one oxygenated function, such as alkadienals and ketodienes, are produced to a much higher extent than the analogous oxygenated compounds during lipid oxidation (*8*), and they may suffer further oxidation under certain processing conditions (*9*, *10*). Therefore, alkadienals and ketodienes might also be contributing to the Strecker-type degradation of amines and amino acids observed for epoxyalkenals, hydroxyalkenals, and oxidized fatty acids having a 4,5-epoxy-1-oxo-2-pentene group in its structure.

The objective of this study was to investigate if amino acids may be degraded by alkadienals and ketodienes, and to characterize the reaction products of these reactions. Model reactions were carried out using 2,4-decadienal (or methyl 13-oxooctadeca-9,11-dienoate) and phenylalanine. Because Strecker-type degradation of amino acids by lipid oxidation products is always accompanied by other reactions that developed browning, fluorescence, and the pyrrolization of the amino group of the amino acid (*11*, *12*), all these changes were also studied in the different decadienal (or ketodiene)/phenylalanine reaction mixtures analyzed, in addition to the study of the reaction products formed.

## EXPERIMENTAL SECTION

**Materials.** Benzaldehyde, 2,4-decadienal (93%), L-phenylalanine, phenylacetaldehyde, hexanal, 2-pentylfuran, 2-ethylpyridine, and 2-pentylpyridine were obtained from Aldrich Chemical Co. (Milwaukee, WI). Linoleic acid and soybean lipoxygenase were purchased from Fluka Chemie AG (Buchs, Switzerland). All other chemicals were purchased from reliable commercial sources.

Methyl 13-oxooctadeca-9,11-dienoate was prepared as described previously (*13*). Briefly, linoleic acid was oxidized by soybean

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lipoxygenase to produce mainly the 13-hydroperoxide of linoleic acid. Reduction of the hydroperoxide with sodium borohydride followed by oxidation yielded the corresponding ketodiene. The obtained compound was chromatographically pure. The syntheses of 4.5-epoxy-2-decenal and methyl 9,10-epoxy-13-oxo-11-octadecenoate were also described previously (*7*, *13*).

**Decadienal (or Ketodiene)/Amino Acid Reaction Mixtures.** Mixtures of 0−0.05 mmol of 2,4-decadienal (or methyl 13-oxooctadeca-9,11-dienoate) and 0.05 mmol of phenylalanine in 1 mL of buffer were introduced in Schott Duran test tubes (16 × 1.5 cm), which were closed and heated at 180 °C. The buffer employed in the assay was previously bubbled for 15 min with oxygen. The atmosphere of the test tube was air. The buffers employed for controlling the reaction pH were 0.3 M sodium citrate buffer, pH 2.15−6; 0.3 M sodium phosphate buffer, pH 6.0−8.0 and 11.0−12.0; or 0.3 M sodium borate buffer, pH 8.0−10.0. At the end of the heating period, samples were cooled, diluted with 2 mL of acetonitrile and 40 $\mu$L of internal standard solution [50 $\mu$L of 2-ethylpyridine in 10 mL of methanol], and analyzed for color, fluorescence, and pyrrole content, as well as by GC−MS.

**Analytical Measurements.** The color of the samples was determined spectrophotometrically in the cooled diluted reaction mixtures employing a Shimadzu UV-2401 PC UV−vis spectrophotometer. Yellowness index (YI) was determined according to Francis and Clydesdale (*14*):

$$YI = 142.86b^*/L^*$$

Fluorescence spectra were recorded on a Perkin-Elmer LS-5 fluorescence spectrometer using diluted samples [50 $\mu$L of the cooled diluted reaction mixture diluted with 3 mL of acetonitrile−water (2:1)]. The fluorescence intensity was determined at 430 nm when excitation was carried out at 350 nm. The instrument was standardized with quinine sulfate (0.1 $\mu$M in 0.1 N $H_2SO_4$) to give a fluorescence intensity of 100 at 450 nm, when excitation was carried out at 350 nm (*15*).

Pyrrole content was determined spectrophotometrically after derivatization with *p*-dimethylaminobenzaldehyde, following the procedure of Hidalgo et al. (*16*), with 200 $\mu$L of reaction mixtures which were diluted with 800 $\mu$L of 150 mM sodium phosphate, pH 7.0, containing 3% sodium dodecyl sulfate, and treated with 160 $\mu$L of the Ehrlich reagent [a solution containing 200 mg of *p*-(dimethylamino)benzaldehyde, 2 mL of ethanol, and 8 mL of 1.25 N HCl]. The resulting solutions were incubated at 45 °C for 15 min, and the absorbance of the maximum at approximately 570 nm measured at room temperature.

**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 m × 0.25 mm i.d.; coating thickness, 0.25 $\mu$m) was used. Working conditions were as follows: carrier gas helium (1 mL/min at constant flow); injector, 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; and ionization EI, 70 eV.

**Determination of Phenylacetaldehyde and Hexanal Contents.** Quantification of phenylacetaldehyde and hexanal was carried out by preparing standard curves of both aldehydes in the 3.04 mL of solution prepared for GC−MS injection (see above). For each curve, eight different concentration levels of the aldehyde were used. Phenylacetaldehyde and hexanal contents were directly proportional to the aldehyde/internal standard area ratio ($r > 0.992$, $p < 0.0001$). The coefficients of variation were lower than 10%.

## RESULTS

**Effect of pH in the Reactions Produced in Decadienal/Phenylalanine Reaction Mixtures.** Differently from the reaction between oxygenated aldehydes (epoxyalkenals and hydroxyalkenals) and phenylalanine, the reaction between decadienal and phenylalanine occurred very slowly at 37 °C (data not shown). However, when the reaction was carried out at 180 °C, the development of browning and fluorescence, and the pyrrolization of the amino acid (the transformation of its amino group into a pyrrole ring), were rapidly observed. **Figure 1** shows the results obtained after heating for 1 h at 180 °C an equimolecular mixture of decadienal (**1**) and phenylalanine (**3**) as a function of pH.

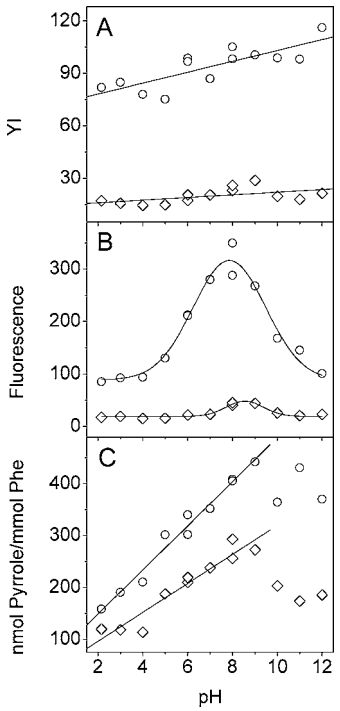


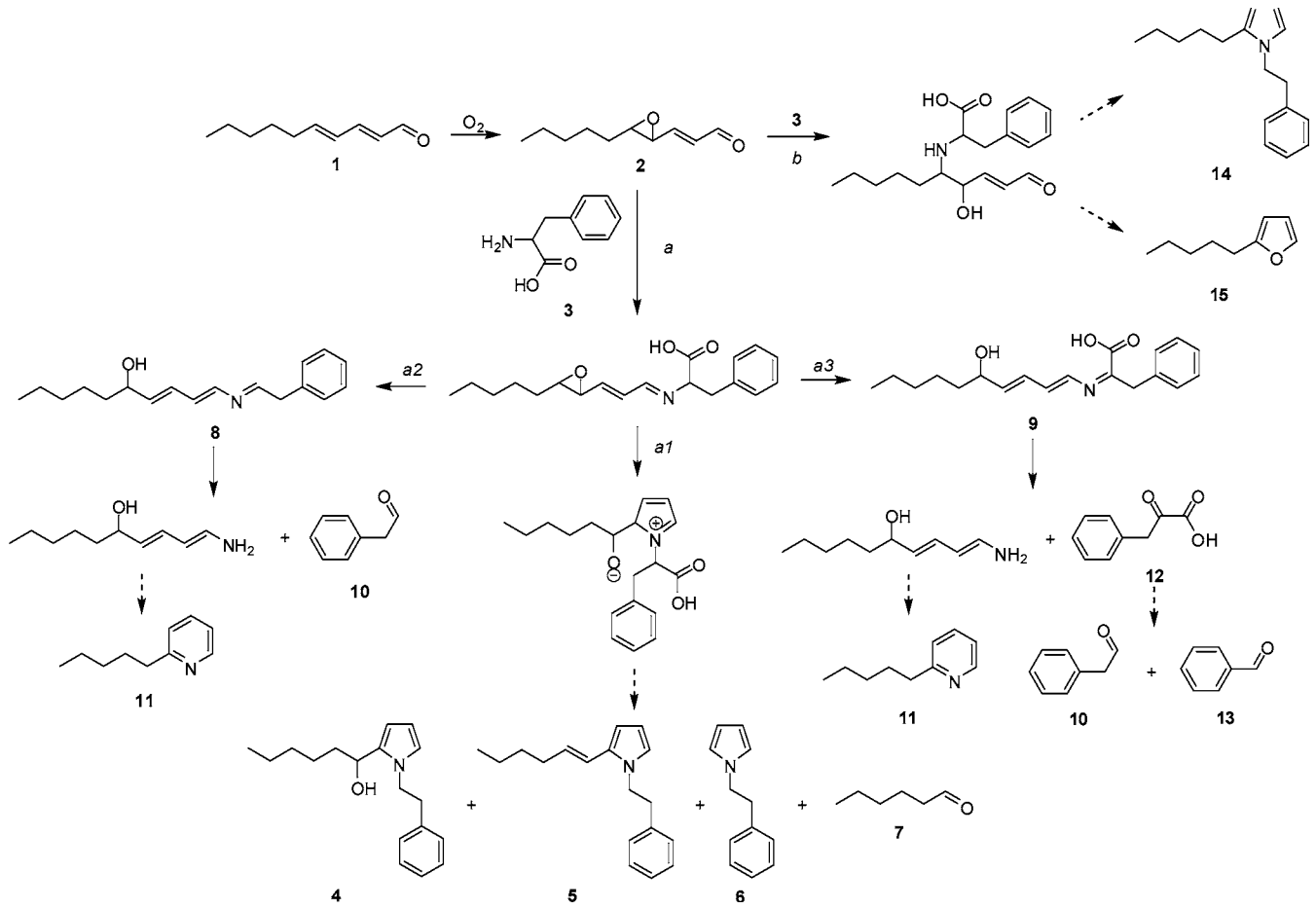

**Figure 1.** Effect of pH on (**A**) yellowness index (YI), (**B**) fluorescence development, and (**C**) pyrrolization of phenylalanine (Phe) in 2,4-decadienal/phenylalanine (○) and methyl 13-oxooctadeca-9,11-dienoate/phenylalanine (◇) reaction mixtures. Samples were heated at 180 °C for 1 h in acetonitrile/buffer (2:1). The employed buffers were 0.3 M sodium citrate buffer for pH 2.15–6, 0.3 M sodium phosphate buffer for pH 6–8 and 11–12, and 0.3 M sodium borate buffer for pH 8–10.

The heating of reaction mixtures always resulted on browning development, and this browning seemed to increase slightly and linearly ($r = 0.81$, $p = 0.00082$) as a function of pH (**Figure 1A**). In addition, samples also developed fluorescence (**Figure 1B**), and the intensity of the developed fluorescence as a function of pH could be described using a Gaussian fit ($r^2 = 0.969$) with a maximum at pH ∼ 8. Furthermore, the amino acid was also pyrrolizated (**Figure 1C**). This pyrrolization increased linearly ($r = 0.988$, $p < 0.0001$) as a function of reaction pH in the range 2.15−9. At pH 9, the maximum of pyrroles was achieved, and amino acid pyrrolization seemed to decrease slightly at higher pHs.

All these changes should have been a consequence of the different reactions produced in the decadienal/phenylalanine reaction mixtures studied. Thus, when reaction mixtures were studied by GC−MS, the presence of epoxydecenal (**2**) was detected in samples heated at acid pHs, therefore suggesting that decadienal was being oxidized during heating and the reaction between compound **2** and the amino acid should be occurring.

The reaction between epoxyalkenals and amines and amino acids has been the objective of different studies, and several competitive reactions are always produced to different extents (*3*, *6*, *7*). Therefore, if decadienal (**1**) was being oxidized to epoxydecenal (**2**), the cascade of reactions collected in **Scheme 1** should be produced in the presence of phenylalanine (**3**). Thus, the main reaction pathway (pathway a) should produce, in a first step, the corresponding imine that, then, would evolve into a cyclic intermediate (pathway a1) or other imines (pathways

**Scheme 1.** Reaction of 2,4-Decadienal with Phenylalanine




a2 and a3). The cyclic intermediate produced by pathway a1 is the origin of different pyrrole derivatives as well as hexanal (**7**). In epoxydecenal/phenylalanine reaction mixtures, these pyrrole derivatives should be: 1-(1-phenethyl-1*H*-pyrrol-2-yl)-hexan-1-ol (**4**), 2-(hex-1-enyl)-1-phenethyl-1*H*-pyrrole (**5**), and 1-phenethyl-1*H*-pyrrole (**6**). Alternatively, the imine produced by pathway a has also been shown to evolve into intermediate imines **8** and **9**, which are intermediate in the Strecker-type degradation of the amino acid (*3*, *7*). Thus, the imine **8** is believed to be the origin of phenylacetaldehyde (**10**) and 2-pentylpyridine (**11**) (*3*). In addition, the imine **9** produces 2-pentylpyridine (**11**) and 2-phenylpyruvic acid (**12**), which is then thermically decomposed into benzaldehyde (**13**) and phenylacetaldehyde (**10**) (*7*). As a minor reaction pathway (pathway b), the amino acid may be added to the epoxyakenal and this reaction seems to be the origin of 2-pentyl-1-phenethyl-1*H*-pyrrole (**14**) and 2-pentylfuran (**15**) (*12*). All these compounds were unambiguously identified in the GC−MS chromatograms of decadienal/phenylalanine reaction mixtures on the basis of their retention indices and mass spectra. The retention indices of all these compounds are collected in **Table 1**. Mass spectra of noncommercial compounds were described previously (*4*, *12*, *13*).

An additional confirmation of the oxidation of decadienal as the preliminary step to the cascade of reactions collected in **Scheme 1** was obtained by heating decadienal/phenylalanine reaction mixtures under an inert atmosphere. These reactions developed much lower browning and fluorescence than those heated under air, and both pyrroles and phenylacetaldehyde were only formed in very small amounts (data not shown).

**Table 1.** Retention Indices of Compounds Identified in This Study[a]

| compd no. | compd name | retention index |
|---|---|---|
| **1** | 2,4-decadienal | 1282/1306 |
| **2** | 4,5-epoxy-2-decenal | 1364 |
| **4** | 1-(1-phenethyl-1*H*-pyrrol-2-yl)hexan-1-ol[b] | 2136 |
| **5** | 2-(hex-1-enyl)-1-phenethyl-1*H*-pyrrole[b] | 2012/2035 |
| **6** | 1-phenethyl-1*H*-pyrrole[b] | 1428 |
| **7** | hexanal | 801 |
| **10** | phenylacetaldehyde | 1053 |
| **11** | 2-pentylpyridine | 1192 |
| **13** | benzaldehyde | 960 |
| **14** | 2-pentyl-1-phenethyl-1*H*-pyrrole[b] | 1885 |
| **15** | 2-pentylfuran | 993 |
| **16** | methyl 13-oxooctadeca-9,11-dienoate | 2359/2421 |
| **17** | methyl 9,10-epoxy-13-oxooctadec-11-enoate[c] | 2461 |
| **18** | methyl 8-(6-pentylpyridin-2-yl)octanoate[d] | 2214 |

[a] Structures for these compounds are given in **Schemes 1** and **2**. [b] These compounds were described in ref 12. [c] This compound was described in ref *13*. [d] This compound was described in ref *4*.

As expected, the different reactions collected in **Scheme 1** were not produced to the same extent, and the major products of decadienal/phenylalanine reaction mixtures heated under air for 1 h at 180 °C resulted in hexanal (**7**) and phenylacetaldehyde (**10**), suggesting that pathway a was preferred. Hexanal is produced by autoxidation of decadienal (*17*) but also in the formation of pyrrole **6** (*2*). Thus, although hexanal was a major reaction product, monomeric pyrroles (**4**−**6**) were only detected in trace amounts. However, they were formed because they were detected by GC−MS. Nevertheless, they might not be stable

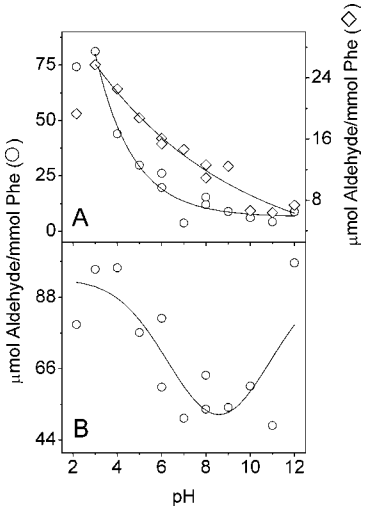



**Figure 2.** Effect of pH on (**A**) phenylacetaldehyde and (**B**) hexanal formation in 2,4-decadienal/phenylalanine (○) and methyl 13-oxooctadeca-9,11-dienoate/phenylalanine (◇) reaction mixtures. Samples were heated at 180 °C for 1 h in acetonitrile/buffer (2:1). The employed buffers were 0.3 M sodium citrate buffer for pH 2.15–6, 0.3 M sodium phosphate buffer for pH 6–8 and 11–12, and 0.3 M sodium borate buffer for pH 8–10.

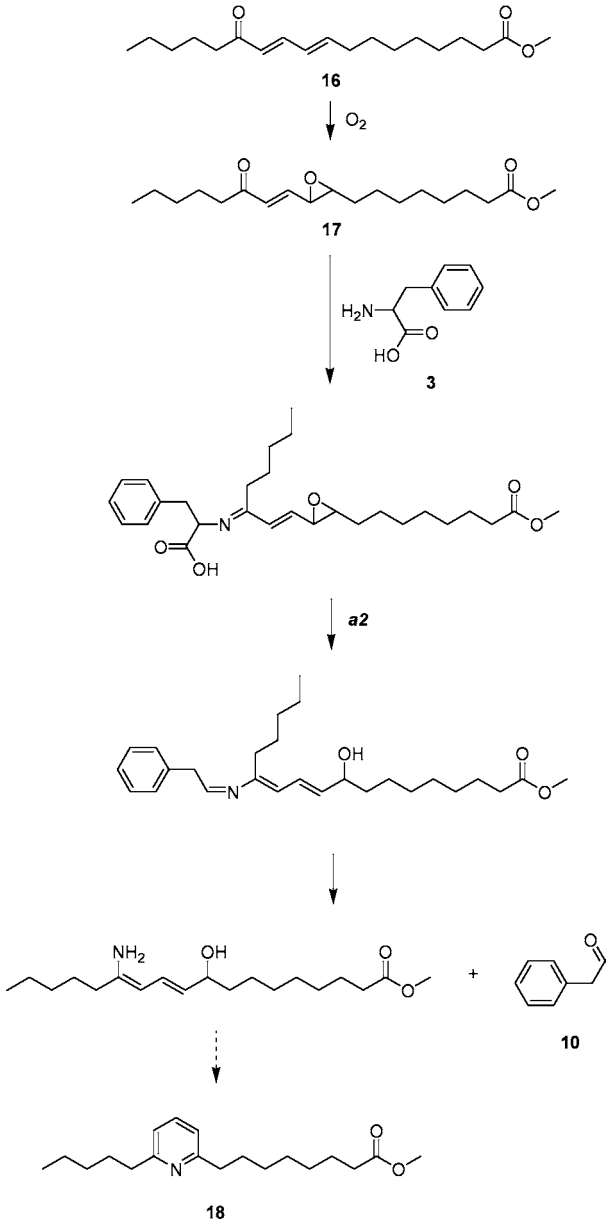
under the assayed conditions. In this context, polymerization of this type of pyrrole derivative has been described (*18*), and these polymers have been shown to contribute to browning and fluorescence development in these reactions. For this reason, although only trace amounts of pyrroles **4**−**6** were detected by GC−MS, decadienal/phenylalanine reaction mixtures developed browning and fluorescence, and the pyrrolization of the amino acid was found by applying a spectrophotometric procedure that is also valid for pyrrole polymers (*15*).

**Figure 2** collects the amounts of phenylacetaldehyde (**10**) and hexanal (**7**) produced as a function of reaction pH. Phenylacetaldehyde content (**Figure 2A**) decreased exponentially ($r^2 = 0.96$) in the range pH 3−12 when reaction pH increased, therefore confirming that the Strecker-type degradation of the amino acid was produced to a higher extent at acid pHs. On the contrary, although hexanal was produced to a high extent at the different pHs (**Figure 2B**), there was not a clear correlation between the amount of hexanal produced and the pH of the reaction.

**Effect of pH in the Reactions Produced in Methyl 13-Oxooctadeca-9,11-dienoate/Phenylalanine Reaction Mixtures.** When the aldehyde was replaced by the analogous ketodiene, the reactions also developed browning, fluorescence, and pyrrolization, but the keto ester seemed to be less reactive than the aldehyde and less browning, fluorescence and pyrrolization were observed (**Figure 1**). Nevertheless, the behavior of the ketodiene and the aldehyde were very similar. Thus, the browning changed very slightly as a function of pH; the intensity of the developed fluorescence as a function of pH could be described using a Gaussian fit ($r^2 = 0.95$) with a maximum at pH ∼ 8, and pyrrolization increased linearly ($r = 0.957$, $p < 0.0001$) as a function of reaction pH in the range pH 2.15−9.

Analogous to the above-described for decadienal/phenylalanine reactions, these changes were also a consequence of the different reactions produced in the ketodiene/phenylalanine reaction mixtures studied. Thus, when reaction mixtures were studied by GC−MS, the presence of the corresponding epoxyketoester was detected in samples heated at acid pHs, therefore suggesting that the lipid was being oxidized during heating and the reaction between this oxidized lipid and the amino acid was occurring. Therefore, analogous pyrroles, furans, pyridines, and aldehydes to those collected in **Scheme 1** should be expected. However, pyrroles and furans were only detected in trace amounts in these systems under the assayed conditions. In addition, methyl 9-oxononanoate (the aldehyde equivalent to the hexanal produced in decadienal/phenylalanine systems) was also detected in small amounts. The main reaction products in the ketodiene/phenylalanine reaction mixtures were phenylacetaldehyde (**10**) and the pyridine derivative methyl 8-(6-pentylpyridin-2-yl)octanoate (**18**), therefore suggesting that the Strecker-type degradation indicated in the pathway a2 was preferred in these systems (**Scheme 2**). Nevertheless, pyrrole derivatives were also produced because they could be determined spectrophotometrically (**Figure 1C**). These compounds should have polymerized under the assayed conditions. However, the absence of a proton at the α-position of the pyrrole ring in the hydroxyalkyl pyrroles derived from the epoxyketo fatty ester impeded the pyrrole polymerization responsible for developing browning and fluorescence described for hydroxyalkyl pyrroles with this α-position free (*18*).

**Scheme 2.** Formation of Phenylacetaldehyde in the Reaction of Methyl 13-Oxooctadeca-9,11-dienoate with Phenylalanine



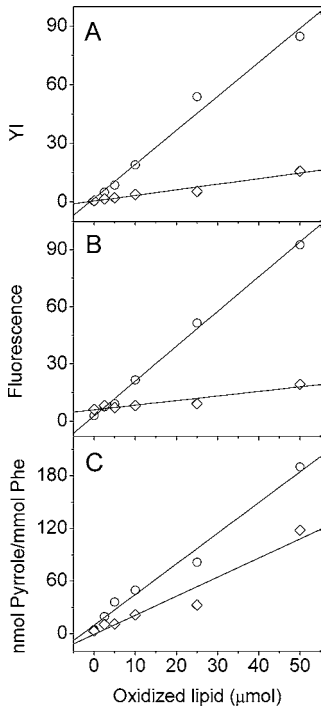



**Figure 3.** Effect of the concentration of the oxidized lipid on (**A**) yellowness index (YI), (**B**) fluorescence development, and (**C**) pyrrolization of phenylalanine (Phe) in 2,4-decadienal/phenylalanine (○) and methyl 13-oxooctadeca-9,11-dienoate/phenylalanine (◇) reaction mixtures. Reactions were carried out in acetonitrile/sodium citrate (2:1), pH 3, after 1 h at 180 °C.

**Figure 2A** collects the amounts of phenylacetaldehyde produced in the ketodiene/phenylalanine systems as a function of reaction pH. Analogous to the observed in decadienal/phenylalanine reactions, phenylacetaldehyde content decreased exponentially ($r^2 = 0.96$) in the range pH 3−12 when reaction pH increased, therefore confirming that Strecker-type degradation of the amino acid was produced to a higher extent at acid pHs.

**Effect of Oxidized Lipid/Amino Acid Ratio in the Reactions Produced in Decadienal/Phenylalanine and Methyl 13-Oxooctadeca-9,11-dienoate/Phenylalanine Reaction Mixtures.** The different reactions discussed above were produced by the assayed oxidized lipids, and the amount of decadienal or ketodiene present in the reaction mixture determined the browning, fluorescence, and pyrrolyzation produced as well as the amounts of the aldehydes formed. **Figure 3** shows the browning, fluorescence, and pyrrolization determined after heating phenylalanine in the presence of different amounts of decadienal or methyl 13-octadeca-9,11-dienoate in sodium citrate buffer, pH 3, for 1 h at 180 °C. [This pH was selected because it was the pH at which phenylacetaldehyde was produced to a higher extent (**Figure 2A**).] Browning, fluorescence, and pyrrolization increased linearly ($r > 0.95$, $p < 0.005$) as a function of decadienal or ketodiene concentration. A similar behavior was also observed for the formation of phenylacetaldehyde (**Figure 4A**) and hexanal (**Figure 4B**) in decadienal/phenylalanine systems and phenyacetaldehyde (**Figure 4A**) in methyl 13-oxooctadeca-9,11-dienoate/phenylalanine reaction mixtures.

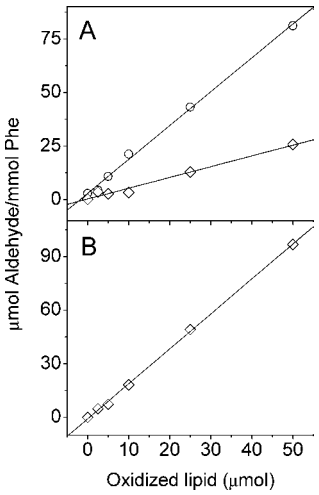



**Figure 4.** Effect of the concentration of the oxidized lipid on (**A**) phenylacetaldehyde and (**B**) hexanal formation in 2,4-decadienal/phenylalanine (○) and methyl 13-oxooctadeca-9,11-dienoate/phenylalanine (◇) reaction mixtures. Reactions were carried out in acetonitrile/sodium citrate (2:1), pH 3, after 1 h at 180 °C.

**Effect of Incubation Time in the Reactions Produced in Decadienal/Phenylalanine and Methyl 13-Oxooctadeca-9,11-dienoate/Phenylalanine Reaction Mixtures.** Browning, fluorescencence, pyrrolization, phenylacetaldehyde formation, and production of hexanal followed zero-order kinetics in both decadienal/phenylalanine and methyl 13-oxooctadeca-9,11-dienoate/phenylalanine reaction mixtures. However, maximum values were usually achieved earlier in decadienal/phenylalanine reaction mixtures than in methyl 13-oxooctadeca-9,11-dienoate/phenylalanine reaction mixtures. Thus, browning, fluorescence, and pyrrolization increased linearly ($r > 0.997$, $p < 0.06$) for the first 40 min in decadienal/phenylalanine reaction mixtures (**Figure 5**). After that, either the increases were produced at a lower reaction rate or these increases were not observed. When methyl 13-oxooctadeca-9,11-dienoate/phenylalanine reaction mixtures were studied, browning increased linearly during 1.5 h ($r = 0.986$, $p = 0.0019$), and fluorescence and pyrrolization increased linearly during the whole studied period ($r > 0.98$, $p < 0.0002$).

A similar behavior was observed when formation of both phenylacetaldehyde and hexanal was studied. Thus, formation of both phenylacetaldehyde (**Figure 6A**) and hexanal (**Figure 6B**) increased linearly ($r > 0.997$, $p < 0.003$) for the first hour in decadienal/phenylalanine reaction mixtures incubated at pH 3 and 180 °C. On the contrary, a linear increase ($r = 0.990$, $p < 0.0001$) in the formation of phenylacetaldehyde was observed during the whole studied period in methyl 13-oxooctadeca-9,11-dienoate/phenylalanine reaction mixtures (**Figure 6A**).

## DISCUSSION

Lipid oxidation is the origin of a broad range of compounds, traditionally associated with the development of paintlike, fatty, metallic, papery, and candlelike flavors in foods. Some of these lipid oxidation products are stable, and they will contribute to food flavors. However, others are unstable, are able to react with other food constituents, and may contribute to the generation of new flavors in processed foods. In this context, previous studies showed that secondary lipid oxidation products having two oxygenated functions were able to degrade amino acids to the corresponding Strecker aldehydes and α-oxo acids (*3*−*7*). These lipid oxidation products having two oxygenated functions

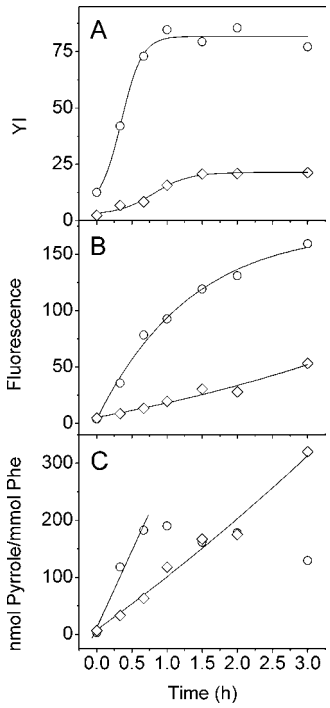



**Figure 5.** Time course of (**A**) yellowness index (YI), (**B**) fluorescence development, and (**C**) pyrrolization of phenylalanine (Phe) in 2,4-decadienal/phenylalanine (○) and methyl 13-oxooctadeca-9,11-dienoate/phenylalanine (◇) reaction mixtures. Reactions were carried out in acetonitrile/sodium citrate (2:1), pH 3, at 180 °C.

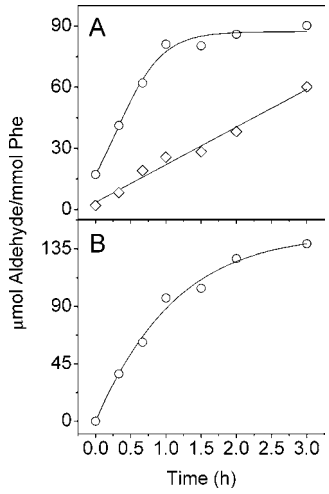



**Figure 6.** Time course of (**A**) phenylacetaldehyde and (**B**) hexanal formation in 2,4-decadienal/phenylalanine (○) and methyl 13-oxooctadeca-9,11-dienoate/phenylalanine (◇) reaction mixtures. Reactions were carried out in acetonitrile/sodium citrate (2:1), pH 3, at 180 °C.

are very reactive and their reaction with amino acids is produced very rapidly at low or moderate temperatures. However, the results obtained in this study show that secondary lipid oxidation products having two oxygenated functions are not the unique lipid oxidation products that may contribute to generate food flavors by Strecker-type degradation of amino acids. Thus, both decadienal and methyl 13-oxooctadeca-9,11-dienoate degraded phenylalanine to phenylacetaldehyde to a significant extent. The yield of phenylacetaldehyde was ∼8% when an equimolecular mixture of decadienal and phenylalanine was heated for 1 h at 180 °C, and the yield of phenylacetaldehyde was ∼6% after 3 h at 180 °C when starting from methyl 13-oxooctadeca-9,11-dienoate. This yield depended on the amount of the lipid present in the media, and the Strecker-type degradation of the amino acid was almost absent in the absence of the lipid.

Strecker-type degradation of amino acids was always accompanied, in part, by cyclization of the unsaturated hydroxylamine produced from the lipid to a pyridine derivative. This derivative was 2-pentylpyridine, when starting from decadienal, and methyl 8-(6-pentylpyridin-2-yl)octanoate, when starting from methyl 13-oxooctadeca-9,11-dienoate. Formation of 2-alkylpyridines in reactions involving alkadienals has been previously communicated (*19*−*21*). However, this is the first time in which the formation of long-chain pyridine fatty acids from ketodienes is described.

Although phenylacetaldehyde was one of the major reaction products, amino acid degradation was not the only reaction produced in the alkadienal (or ketodiene)/amino acid reaction mixtures assayed. In fact, several competitive reactions were produced, and the yield of each of these reactions seemed to depend on the reaction conditions. All these reactions were initiated by the oxidation of the lipid and were not produced if the lipid could not be oxidized. Furthermore, the corresponding epoxyalkenals and long-chain unsaturated epoxyketones were detected by GC−MS, and these new oxidized lipids reacted with the amino group of the amino acid forming different pyrrole and furan derivatives (**Scheme 1**), all of which could be identified. In addition, 9−14% of the decadienal was converted into hexanal, therefore suggesting that, in the presence of amino acids, the formation of hexanal from decadienal through an intermediate epoxydecenal may be a significant pathway for the formation this important flavor, which may be produced by both decadienal autoxidation and in the pyrrolization of the amino group of the amino acid. Different from hexanal, the corresponding aldehyde of methyl 13-oxooctadeca-9,11-dienoate degradation (methyl 9-oxononanoate) was not detected as a major product.

The results obtained in this and in previous studies suggest that a significant number of lipid oxidation products, some of which are quantitatively important, can degrade amino acids to their corresponding Strecker aldehydes. Therefore, secondary lipid oxidation products are not necessarily final products of the lipid oxidation process. Some of these products can either suffer further oxidations or react with other food components to produce new compounds. In this aspect, lipid oxidation should be considered only the first step in the production of reactive carbonyls that compete with those formed in the Maillard reaction of carbohydrates for producing carbonyl−amine reactions in foods (*22*).

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## LITERATURE CITED

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