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Strecker Type Degradation of Phenylalanine by 4-Hydroxy-2-nonenal in Model Systems

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The reaction of 4-hydroxy-2-nonenal, an oxidative stress product, with phenylalanine in acetonitrile−water (2:1, 1:1, and 1:2) at 37, 60, and 80 °C was investigated to determine whether 4-hydroxy-2-alkenals degrade amino acids, analogously to 4,5-epoxy-2-alkenals, and to compare the reactivities of both hydroxyalkenals and epoxyalkenals for production of Strecker aldehydes. In addition to the formation of *N*-substituted 2-pentylpyrrole and 2-pentylfuran, the studied hydroxyalkenal also degraded phenylalanine to phenylacetaldehyde with a reaction yield of 17%. The reaction mechanism is suggested to be produced through the corresponding imine, which is then decarboxylated and hydrolyzed. This reaction also produced a conjugated amine, which both may be one of the origins of the produced 2-pentyl-1*H*-pyrrole and may contribute to the development of browning in these reactions. 4-Hydroxy-2-nonenal and 4,5-epoxy-2-decenal degraded phenylalanine in an analogous extent, which is likely a consequence of the similarity of the degradation mechanisms involved. These results suggest that different lipid oxidation products are able to degrade amino acids; therefore, the Strecker type degradation of amino acids produced by oxidized lipids may be quantitatively significant in foods.

KEYWORDS: Carbonyl−amine reactions; epoxyalkenals; flavor production; hydroxyalkenals; lipid oxidation; Maillard reaction; nonenzymatic browning; phenylacetaldehyde; pyrroles; Strecker aldehydes

INTRODUCTION

Strecker degradation of amino acids is a very important route leading to final aroma compounds in the Maillard reaction (*1*−*3*). It is produced by reaction of an α-dicarbonyl compound with the amino group of the amino acid, which results in the formation of an α-amino carbonyl compound and the corresponding Strecker aldehyde of the amino acid (*2*).

In addition to α-dicarbonyl compounds derived from carbohydrates, both short chain aldehydes and long chain oxidized fatty acids having a 4,5-epoxy-1-oxo-2-pentene system have also been shown to degrade amino acids by a Strecker type mechanism (*4*, *5*). These lipid oxidation products degrade the amino acid to the corresponding Strecker aldehyde, and they are transformed into a hydroxyl amino derivative.

Lipid oxidation products having two oxygenated functions, such as the above cited epoxyalkenals and epoxyoxoene fatty esters, are commonly produced during lipid oxidation because hydroperoxides are converted to secondary oxidation products and many of these last compounds are very easily oxidized (*6*, *7*). Therefore, in addition to epoxyalkenals and epoxyoxoene fatty esters, other derivatives having hydroperoxy, hydroxy, epoxy, and oxo functions are also produced. Among them, 4-hydroxy-2-alkenals have been profusely studied because of their biological properties (*8*, *9*). These compounds might also contribute to the Strecker degradation of amino acids produced by oxidized lipids because their chemical structures are similar to those of 4,5-epoxy-2-alkenals.

The first objective of this study was to determine if 4-hydroxy-2-alkenals are able to degrade amino acids, analogously to 4,5-epoxy-2-alkenals, and to find out the mechanism of the reaction. The second objective was to compare the reactivities of hydroxyalkenals and epoxyalkenals for the Strecker type degradation of amino acids by quantifying the formation of the corresponding Strecker aldehyde in diverse systems containing these lipid oxidation products. All of these studies were carried out with 4-hydroxy-2-nonenal (**1**), which is the most common hydroxyalkenal, and phenylalanine (**8**). Compound **8** was employed because its aldehyde derivative phenylacetaldehyde (**9**) has a high boiling point (195 °C), can be easily determined by gas chromatography (GC), and is a very powerful odorant (*10*).

EXPERIMENTAL PROCEDURES

Materials. All chemicals were purchased from Aldrich (Milwaukee, WI), Sigma (St. Louis, MO), Fluka (Buchs, Switzerland), or Merck (Darmstadt, Germany). Compound **1** was prepared according to Gardner et al. (*11*). 4,5-Epoxy-2-decenal was prepared from 2,4-decadienal as described previously (*12*). 2-Pentyl-1-phenethyl-1*H*-pyrrole (**6**) was prepared by reaction of **1** and 2-phenylethylamine (**3**), as described previously (*13*).

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Synthesis of 1-Nonyl-2-pentyl-1*H*-pyrrole (5). A solution of 0.5 mmol of nonylamine (**2**) in 4.5 mL of tetrahydrofuran was treated with 0.5 mmol of **1** and incubated for 16 h at 37 °C. After that, samples were taken to dryness and compound **5** was purified by preparative thin-layer chromatography (TLC) on aluminum oxide N-coated plates using isooctane as the solvent. ^{1}H NMR ($CDCl_3$): δ 0.9 (m, 6H, CH_3), 1.3 (m, 16H, CH_2), 1.5−1.7 (m, 4H, CH_2), 2.51 (dd, J = 7.3 Hz, J = 8.4 Hz, 2H, CH_2), 3.76 (dd, J = 7.3 Hz, J = 7.7 Hz, 2H, CH_2), 5.87 (m, 1H, H-3), 6.06 (t, J = 3.1 Hz, H-4), and 6.57 (dd, J = 1.9 Hz, J = 2.7 Hz, 1H, H-5). Their ^{13}C NMR pyrrole signals in $CDCl_3$ appeared at δ 104.95 (C-4), 106.42 (C-3), 119.54 (C-5), and 133.19 (C-2). GC-MS *m*/*z* (relative intensity, ion structure): 263 (28, M^+), 248 (2, M^+ − methyl), 234 (4, M^+ − ethyl), 220 (28, M^+ − propyl), 207 (19, 1-nonyl-2-methyl-1*H*-pyrrole), 206 (100, M^+ − butyl), 192 (47), 178 (5), 164 (10), 150 (18), 136 (16), 122 (19), 108 (23), 95 (32), 94 (54), 80 (25), 69 (6), and 55 (14).

Synthesis of 2-Pentyl-1*H*-pyrrole (11). A solution of 1 mmol of **1** and 10 mmol of ammonia (2 N in methanol) in tetrahydrofuran (9 mL) was incubated at 60 °C for 21 h. Compound **11** was purified by preparative TLC on aluminum oxide N-coated plates using isooctane−acetone (8:2) as the solvent. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, J = 6.7 Hz, 3H, CH_3), 1.25−1.33 (m, 4H, CH_2), 1.66 (m, 2H, CH_2), 2.60 (t, J = 7.7 Hz, 2H, CH_2), 5.92 (m, 1H, H-3), 6.14 (m, 1H, H-4), and 6.67 (ddd, J = 1.4 Hz, J = 2.7 Hz, and J = 4.1 Hz, 1H, H-5). ^{13}C NMR ($CDCl_3$): δ 14.05 (CH_3), 22.50 (CH_2), 27.68 (CH_2), 29.35 (CH_2), 31.56 (CH_2), 104.80 (CH), 108.20 (CH), 115.95 (CH), and 132.89 (C). GC-MS *m*/*z* (relative intensity, ion structure): 137 (19, M^+), 94 (6, M^+ − propyl), 81 (15, 2-methylpyrrole), 80 (100, M^+ − butyl), and 53 (12).

Reaction of Hydroxyalkenals or Epoxyalkenals with Amines or Amino Acids. Mixtures of 50 μmol of the aldehyde and 50 μmol of the amine or amino acid were incubated in 1 mL of acetonitrile−water (2:1, 1:1, or 1:2) at 37, 60, or 80 °C for 21 h. The reaction was carried out in 4 mL microreaction vessels, which were closed with a cap. The pH of samples was ∼5, and it did not change significantly upon incubation. After incubation, 300 μL of ethanol was added, and 10 μL of the resulting samples was diluted with 190 μL of acetonitrile−water (2:1, 1:1, or 1:2) and 25 μL of the internal standard solution [337 μg of 3-(*Z*)-nonenol in 1 mL of methanol], and either studied by GC-MS or **9** content determined by GC. Acetonitrile−water (2:1) was elected as the solvent because it guarantees the solubility of the starting aldehyde and amino acid as well as any possible intermediates and products. In addition, it has been proposed to be a reasonable compromise for modeling biochemical reactions, which could be occurring in relatively low dielectric microenviroments rather than the aqueous mileu (*13*).

The study of correlation between browning development and disappearance of compound **12** was carried out in a reaction mixture of 0.1 mmol of **1** and 0.1 mmol of **8** in 2 mL of acetonitrile−water (2:1) incubated for 2 h at 37 °C. After that time, 120 μL of 2 N KOH in methanol was added, and the sample was incubated for 5 days at 37 °C.

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 mm × 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, 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 9 Content by GC. GC analyses were conducted with an Aligent 6890 GC Plus. Column and working conditions were analogous to the above-described for the GC-MS analyses, and compounds were detected with a flame ionization detector. Quantification of **9** was carried out by preparing standard curves over a concentration range of 5−90 nmol of **9** in the 225 μL of solution prepared for GC injection (see above). For each curve, five different concentration levels of the aldehyde were used. The compound **9** content was directly proportional to the **9**/internal standard area ratio ($r > 0.99$, $p < 0.0001$). The coefficients of variation within this range were lower than 5%.

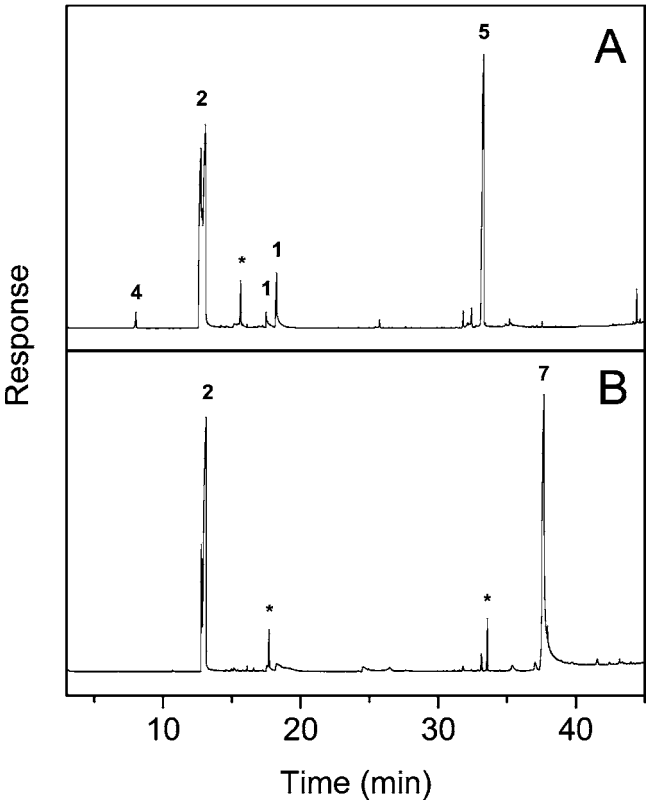


Figure 1. Total ion chromatograms of GC-MS analysis for the reaction of **1** with **2** after (**A**) 1 h of reaction in acetonitrile–water (2:1) at 37 °C and (**B**) reduction with $NaBH_4$ of the nonincubated reaction mixture. The structures for the identified compounds are given in **Scheme 1**. Unidentified peaks are marked with *.

^{1}H and ^{13}C NMR. ^{1}H and ^{13}C NMR spectra at 300 and 75.4 MHz, respectively, were determined in a Bruker AC-300P (Karlsruhe, Germany), with Me_4Si as an internal standard. Two-dimensional NMR was used to assign the ^{13}C NMR spectra.

Browning. Browning of samples was determined spectrophotometrically using a Shimadzu UV-2401 PC UV−vis spectrophotometer. Color differences (ΔE) at the different periods of time were calculated from the determined CIELAB L^* a^* b^* values according to Hunter (*14*):

$$\Delta E = [(L^* - 100)^2 + (a^*)^2 + (b^*)^2]^{1/2}$$

by referring the determined values to an ideal colorless solution of $L^* = 100$ and $a^* = b^* = 0$ (*15*).

Statistical Analysis. Compound **9** determinations are expressed as mean values ± standard deviations (SDs) of at least three determinations. Statistical comparisons among different groups were made using analysis of variance. When significant F values were obtained, group differences were evaluated by the Student−Newman−Keuls test (*16*). All statistical procedures were carried out using Primer of Biostatistics: The Program (McGraw-Hill, Inc., New York). The significance level is $p < 0.05$ unless otherwise indicated.

RESULTS

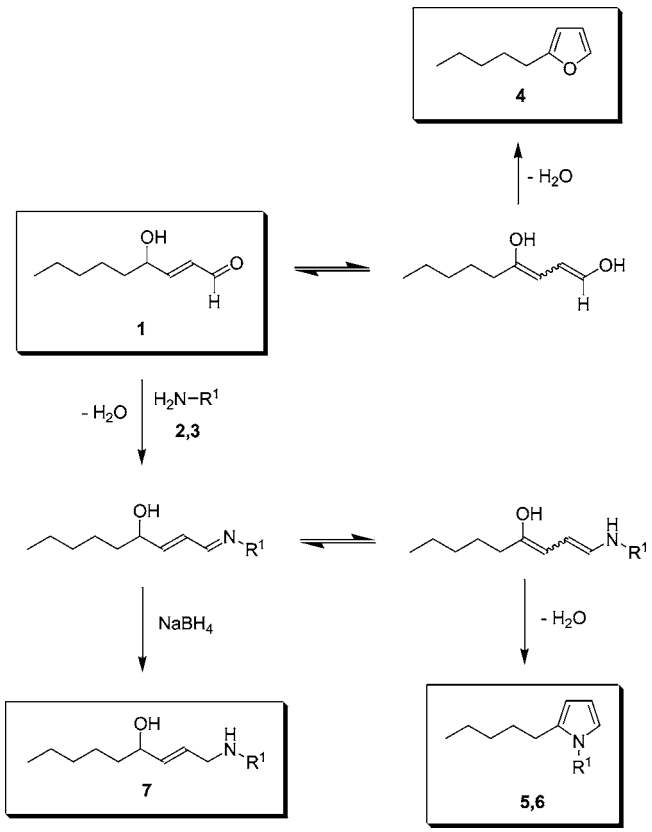
Reaction between 1 and Primary Amines. The reaction between hydroxyalkenals and amino acids is complex, and diverse compounds are produced. In an attempt to facilitate the characterization of the diverse compounds produced in these reactions, the reaction between **1** and primary amines was studied as a previous step. **Figure 1A** shows the total ion chromatogram of GC-MS analysis obtained for a reaction of **1** and **2** in acetonitrile−water (2:1) after 1 h at 37 °C. **Table 1** collects the retention indices of compounds described in this

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

number	compound	retention index
1	**1**	1290/1316
2	**2**	1141/1150
3	**3**	1094
4	**4**	993
5	**5**	1945
6	**6**	1887
7	**7**	2172
9	**9**	1049
10	**10**	1132
11	**11**	1198
12	unidentified	2118

[a] Structures for these compounds are given in **Schemes 1** or **2**.

Scheme 1. Reaction of **1** with Primary Amines[a]



[a] For **2**, **5**, and **7**: $R^1 = CH_3(CH_2)_8$. For **3** and **6**: $R^1 = PhCH_2CH_2$.

study. As observed, the reaction produced a major product, which was isolated by preparative TLC and characterized by ^1H and ^{13}C NMR and MS, as **5**. The reaction also produced as a minor product 2-pentylfuran (**4**), which was identified on the basis of its retention time and mass spectra.

Previous studies have shown the formation of pyrrole derivatives in the reaction between **1** and amines (*17*). It is believed that they are produced by a reaction mechanism similar to that described in **Scheme 1**. Thus, the reaction between the hydroxyalkenal and the primary amine produces in a first step an imine, which then cycles to the corresponding pyrrole **5**. This reaction may be accompanied by the cyclization of the hydroxyalkenal to produce the corresponding **4**.

Although it has not been described, the reduction of the imine produced between the hydroxyalkenal and the amine should produce the secondary amine **7**. Thus, when the mixture of **1** and **2** was reduced with sodium borohydride and studied by GC-MS, the appearance of one major compound was observed

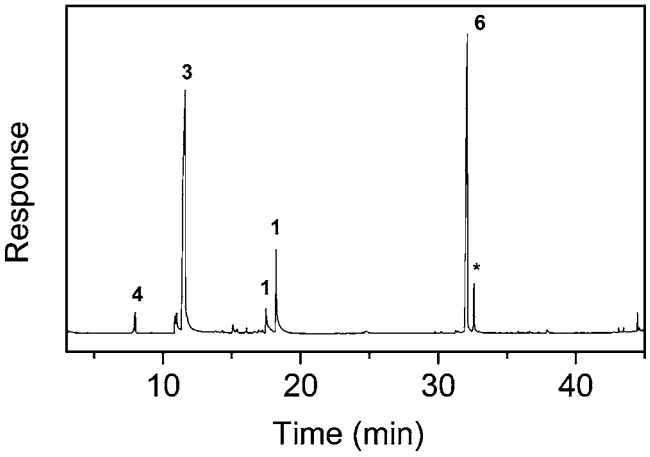


Figure 2. Total ion chromatogram of GC-MS analysis for the reaction of **1** with **3** in acetonitrile–water (2:1) after 1 h at 37 °C. The structures for the identified compounds are given in **Scheme 1**. Unidentified peaks are marked with *.

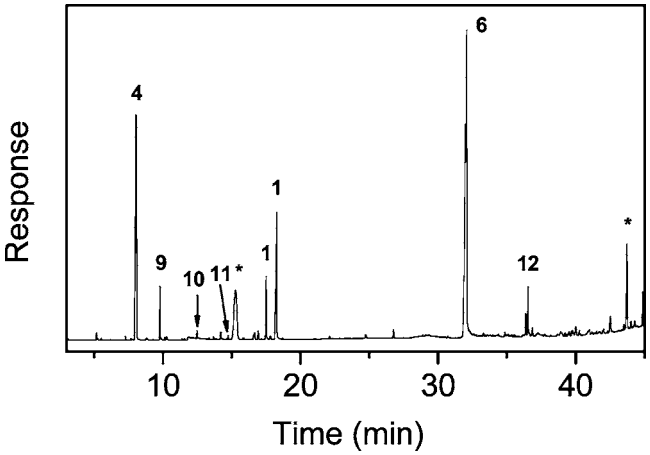


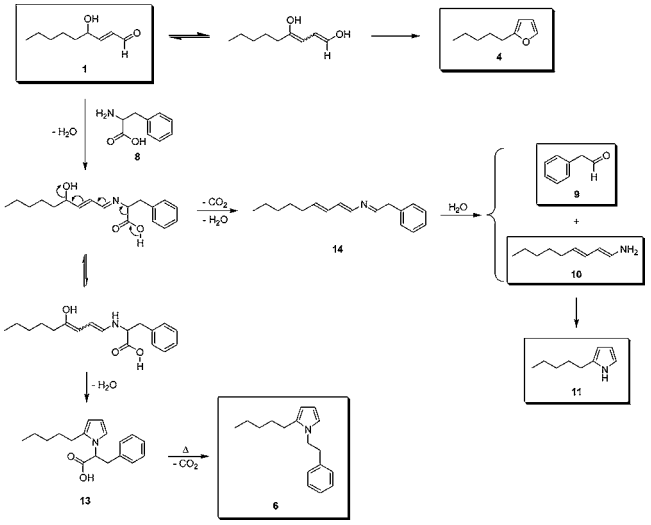
Figure 3. Total ion chromatogram of GC-MS analysis for the reaction of **1** with **8** in acetonitrile–water (2:1) after 24 h at 37 °C. The structures for the identified compounds are given in **Scheme 2**. Unidentified peaks are marked with *.

(**Figure 1B**). This compound was tentatively identified as 1-(nonylamino)non-2-en-4-ol (**7**) on the basis of its mass spectra. GC-MS *m/z* (relative intensity, ion structure): 283 (0.2, M^+), 282 (2, $M^+ - 1$), 265 (2, $M^+ - H_2O$), 222 (2, $M^+ - H_2O$ − propyl), 212 (10, M^+ − pentyl), 208 (7, $M^+ - H_2O$ − butyl), 182 (22), 170 (90, M^+ − octyl), 152 (15, $M^+ - H_2O$ − octyl), 144 (100, $CH_3(CH_2)_8NH_3^+$), 140 (22), 99 (42), 84 (20), 71 (27), 69 (23), and 55 (30).

Analogously to the reaction between **1** and **2**, the reaction of the aldehyde with **3** also produced the corresponding pyrrole as the major product. **Figure 2** shows the total ion chromatogram of GC-MS analysis obtained for a reaction of **1** and **3** in acetonitrile−water (2:1) after 1 h at 37 °C. The major product of the reaction was identified, on the basis of its retention time and mass spectra, as **6**. Analogously to the observed for **2**, the reaction also produced **4** as a minor product.

Reaction of 1 with 8. When a mixture of **8** and **1** was incubated for 24 h in acetonitrile−water (2:1) at 37 °C, the formation of different products was observed (**Figure 3**). The number of the products formed in this reaction was higher than those produced in the reaction between the hydroxyalkenal and the primary amines, suggesting that other reactions than the above-described for primary amines were also produced.

Scheme 2. Strecker Type Degradation of **8** by **1**



As expected, the major reaction product was identified as **6**. This compound should be produced by a mechanism similar to that described for primary amines, which is shown in **Scheme 2**. The reaction of the hydroxyalkenal and the amino acid should produce the corresponding imine, which would evolve into the corresponding pyrrole (**13**) by cyclization through an intermediate amine. The thermal decarboxylation of this acid, which is produced in the injector port of the chromatograph (*4*), is the origin of pyrrole **6**. In addition, the cyclization of compound **1** should be responsible for the appearance of **4**. This compound was always produced in a major extent in the presence of amino acids than in the presence of amines.

However, compounds **4** and **6** were not the unique reaction products. Among the different compounds produced, some of which could not be identified, the presence of **9** was significant because it is the Strecker aldehyde derived from **8**. The formation of **9** should be produced by a mechanism analogous to that described for epoxyalkenals (*4*), which is shown in **Scheme 2**. As an alternative to the dehydration of the imine to produce the pyrrole **13**, its decarboxylation should produce the intermediate imine **14**, which is the origin of **9** and the unsaturated amine **10**. This amine, which appeared in the chromatogram as a minor product, was tentatively identified as nona-1,3-dien-1-amine (**10**) on the basis of its mass spectrum. GC-MS *m*/*z* (relative intensity, ion structure): 138 (2, $M^+ - 1$), 124 (1, M^+ − methyl), 110 (14, M^+ − ethyl), 96 (31, M^+ − propyl), 83 (100, penta-1,3-dien-1-amine), 82 (26, M^+ − butyl), and 55 (13). In addition, its retention time was similar to that of **2**, as should be expected. Nevertheless, compound **10** was reactive, and at least one peak in the chromatogram is related to it. Thus, the intramolecular addition of the amino group to the γ,δ carbon−carbon double bond followed by aromatization should produce **11**. This compound, which appeared as a minor product in the reaction mixture, was identified on the basis of its retention time and mass spectrum.

Another important peak in the chromatogram is compound **12**. Although its structure is unknown at present, its mass spectrum suggests that it was produced by condensation of one molecule of the amine **10** with one molecule of hydroxyalkenal **1**. GC-MS *m*/*z* (relative intensity, ion structure): 277 (16, M^+), 220 (16, M^+ − propyl), 206 (6, M^+ − butyl), 202 (7), 177 (15), 176 (100), 139 (21), 138 (44), 120 (34), 118 (16), 106 (20), and 80 (70). Different attempts were carried out to isolate this compound, but all of them were unsuccessful. In fact, this compound seemed to be an intermediate in the browning

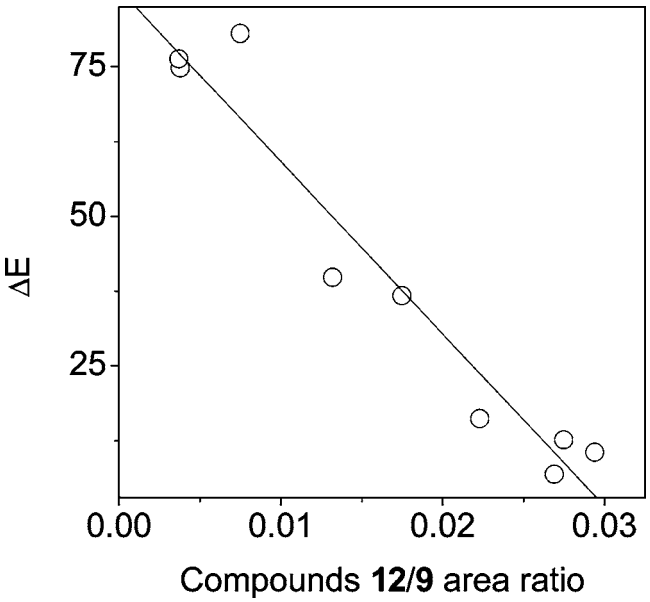


Figure 4. Correlation observed between the decrease in the area of compound **12** produced as a function of incubation time and the development of browning in the reaction of **1** and **8**. Once formed, **9** content remained constant during browning development. Total ion chromatogram of GC-MS analysis for the reaction of **1** with **8** is given in **Figure 3**. The structures for the identified compounds are given in **Scheme 2**.

produced in the reaction because a linear relationship ($r = -0.97$, $p < 0.0001$) was observed between the disappearance of this peak and the development of browning observed as a function of the incubation time (**Figure 4**). The development of browning was followed during 5 days at 37 °C and pH 9. Differently to compound **12**, once **9** was produced, content of **9** remained constant during these 5 days.

Formation of 9 in the Reaction Mixtures of 1 and 8. The effects of hydroxyalkenal concentration, reaction temperature, and polarity of the solvent in the formation of **9** were studied by employing diverse mixtures of **1** and **8** (0−50 μmol of hydroxyalkenal and 50 μmol of the amino acid), dissolved in acetonitrile−water (2:1, 1:1, or 1:2) and heated a 37, 60, or 80 °C. As expected and with independence of the temperature or the polarity of the solvent employed, an increase in the concentration of the hydroxyalkenal produced an increase in the formation of **9** (**Figure 5**). However, this increase was not linear, and the higher increases were observed in the range of 0−5 μmol of **1**. On the contrary, phenylacetaldehyde production was analogous when 25 or 50 μmol of **1** was employed.

Compound **9** was produced in the same extent at 37 or 60 °C (8.7 ± 0.4 μmol/50 μmol of **8**) (**Figure 5A**,**B**). However, when reaction mixtures were heated at 80 °C, lower values of the Strecker aldehyde were determined (between 4.9 and 7.4 μmol of **9**/50 μmol of **8** depending on the polarity of the employed solvent) (**Figure 5C**). This may be related to the volatility of acetonitrile (bp 82 °C) at this temperature that might produce losses of **9**. In fact, when acetonitrile−water (1:2) was employed, the results were close to those obtained at 37 or 60 °C (7.4 ± 1.2 μmol/50 μmol of **8**). However, when the solvent was rich in acetonitrile [acetonitrile−water (2:1)], the amount of **9** determined was significantly lower (4.9 ± 0.8 μmol/50 μmol of **8**).

Analogously to the reaction temperature, the polarity of the solvent did not seem to influence the amount of **9** produced at 37 or 60 °C (**Figure 5A**,**B**). However, **9** was produced in a

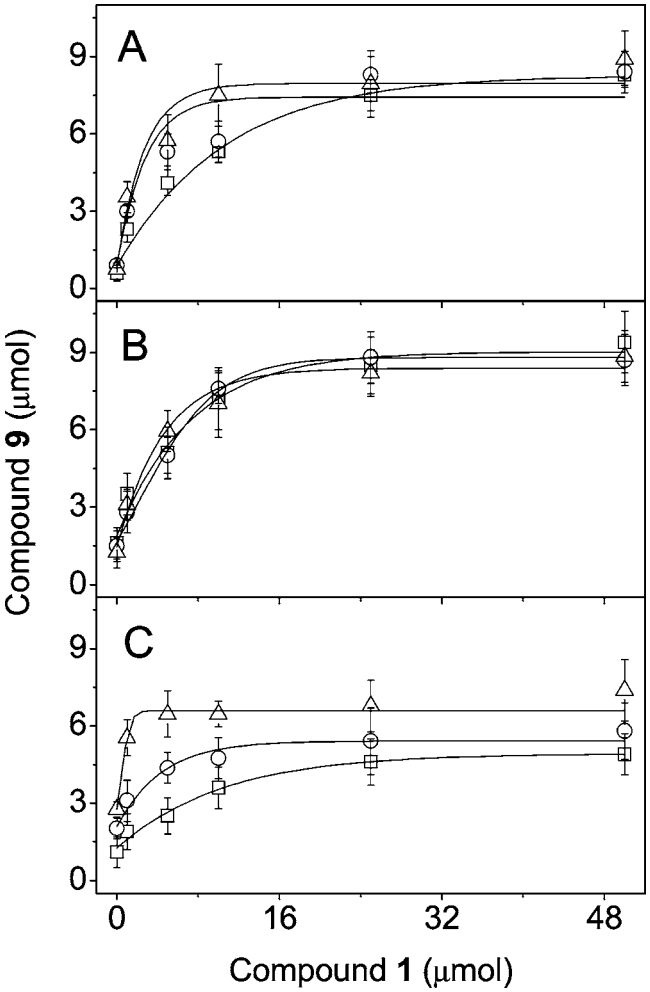


Figure 5. Effect of **1** content on **9** formation in mixtures of **1** and **8** incubated at (**A**) 37, (**B**) 60, and (**C**) 80 °C. The solvent employed was acetonitrile–water (2:1) (□), acetonitrile–water (1:1) (○), or acetonitrile–water (1:2) (△). Fifty micromoles of **8** was employed in all of the assays. Values are means ± SD of at least three experiments.

lower extent at acetonitrile−water (2:1), followed by acetonitrile−water (1:1) and by acetonitrile−water (1:2) when the reaction temperature was 80 °C. As discussed above, these results may be a consequence of volatility of acetonitrile at the reaction temperature employed.

Comparative Formation of 9 in the Reactions of Hydroxyalkenals and Epoxyalkenals with 8. In an attempt to compare the relative reactivities of hydroxyalkenals and epoxyalkenals for producing Strecker type degradation of amino acids, the formation of **9** was studied in the reaction of **1** and 4,5-epoxy-2-decenal with **8**. **Table 2** collects the results obtained in diverse mixtures of hydroxyalkenal and epoxyalkenal incubated for 21 h at 37 or 60 °C in acetonitrile−water (2:1 or 1:2). As observed, **1** and 4,5-epoxy-2-decenal degraded **8** in an analogous proportion (about 17% of initial **8** was converted into **9**) and no significant differences were observed among most of them. Only the reaction between 4,5-epoxy-2-decenal and **8** in acetonitrile−water (1:2) at 37 °C produced a significantly higher degradation of **8** (conversion yield 25%).

Table 2. Formation of **9** in Mixtures of **1** or 4,5-Epoxy-2-decenal and **8**[a]

lipid	A/W ratio[b]	temperature 37 °C	temperature 60 °C
1	2:1	166 ± 8 a	188 ± 24
	1:2	178 ± 22 a	178 ± 20
4,5-epoxy-2-decenal	2:1	174 ± 18 a	170 ± 6
	1:2	248 ± 12 b	160 ± 12

[a] Values are given in micromoles of **9** per millimole of **8**. Means in the same column with different letters are significantly different ($p < 0.05$). [b] A/W = acetonitrile/water.

DISCUSSION

Lipid oxidation is a major cause of deterioration in foods and feeds, both in those containing substantial amounts of fats, such as lard or edible oils, and in those where only minor amounts of lipids occur, as in several vegetable products (*18*−*21*). It is a complex process in which hydroperoxides are the initial products, and then, they enter into numerous interlaced reactions involving substrate degradation and interaction, which results in myriad compounds of various molecular weights, flavor thresholds, and biological significance (*22*). When this oxidation takes place in the presence of amino compounds, including amino phospholipids, amino acids, and proteins, the formation of oxidized lipid/amino compound reaction products is an unavoidable process, which should be considered as a last step in the lipid oxidation (*23*−25) and that contributes to the changes of colors, flavors, and antioxidative activities produced in foods during processing and storage (*4*, *5*, *26*−*28*).

Lipid oxidation has been traditionally related to the production of off-flavors in foods (*3*). On the other hand, the Maillard reaction is considered very important to the production of desirable food flavors. However, recent studies from this and other laboratories have shown that this separation between lipid oxidation and Maillard reaction is not so clear, and lipid oxidation may produce analogous products to Maillard oxidation by the same mechanisms (*29*, *30*). In fact, this and the previous (*4*, *5*) studies have shown that Strecker aldehyde production is not an exception and both carbohydrates and oxidized lipids are able to degrade amino acids analogously. In addition, this is not a property of only one type of lipid oxidation products, like those having a 4,5-epoxy-1-oxo-2-pentene system previously described, but it has to be extended to hydroxyalkenals and, more likely, to other lipid oxidation products having two oxygenated functions. Therefore, Strecker type degradation of amino acids produced by oxidized lipids may be quantitatively significant in foods. Furthermore, the relative importance of both carbohydrates and lipids in the formation of these compounds should be determined. In this context, Strecker degradation of amino acids produced by lipids may be very important at low temperature because the obtained results (**9** was produced in the same extent at 37 or 60 °C) suggest that heating at high temperature is not a requisite for this reaction when it is produced by lipids.

Nevertheless, Strecker aldehydes are not the unique flavor compounds produced in these reactions. If the previous studies on epoxyalkenals indicated that this reaction is likely the origin of 2-alkylpyridines and pyridine-containing long chain fatty esters, some of which have been determined in processed foods (*31*−*34*), hydroxyalkenals seem to be related both to the origin of other flavors, like **11**, and to the development of browning. Compound **11** has been found, for example, among flavor components of roasted filberts (*35*), roasted chufa-tubers (*36*), and dried squids (*37*).

Compound **1** and 4,5-epoxy-2-decenal have been found to degrade amino acids in an analogous extent. This may be a consequence of both the similarity of the degradation mecha-

nisms produced by both aldehydes and the similar chain length of the assayed aldehydes. These results are in agreement with the results found in a previous study comparing the reactivities of epoxyalkenals and epoxyoxoene fatty esters (*5*) and confirm that the chain length of the oxidized lipid plays an important role in the reaction yield. According to the results obtained in this and in the previous study, oxidized lipids derived from *n*-6 fatty acids (**1**, 4,5-epoxy-2-decenal, methyl 9,10-epoxy-13-oxo-11-octadecenoate, and methyl 12,13-epoxy-9-oxo-11-octadecenoate) have been found to produce the Strecker type degradation of **8** in a higher extent than oxidized lipids derived from *n*-3 fatty acids (4,5-epoxy-2-heptenal). Additional studies should confirm these results and might reveal a different contribution of different types of fatty acids to flavor formation by the Strecker type mechanism.

ACKNOWLEDGMENT

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