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Chemical Conversion of Phenylethylamine into Phenylacetaldehyde by Carbonyl−Amine Reactions in Model Systems

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ABSTRACT: The chemical conversion of phenylethylamine into phenylacetaldehyde in the presence of lipid oxidation products (LOPs) was studied to investigate the possibility that biogenic amines can be converted into Strecker aldehydes upon processing. Model systems of phenylethylamine and methyl 13-hydroperoxyoctadeca-9,11-dienoate (HP), 2,4-decadienal (DD), 4,5-epoxy-2-heptenal (EH), 4,5-epoxy-2-decenal (ED), 4-oxo-2-hexenal (OH), 4-oxo-2-nonenal (ON), or 4-hydroxy-2-nonenal (HN) were heated for 1 h at 180 °C and pH 3. Although HN and EH did not produce more phenylacetaldehyde than when phenylethylamine was heated alone, all other lipid oxidation products assayed increased the amount of phenylacetaldehyde produced by 300−900%, with ON being the most reactive compound for this reaction. The reaction was mainly produced at acidic pH values (<6) and was dependent upon the concentration of the LOPs involved, and the phenylacetaldehyde produced increased linearly as a function of the time and temperature. The E_a values for the reactions between phenylethylamine and DD and ON were 54.8 and 53.8 kJ/mol, respectively. The reaction is proposed to take place by the formation of an imine between the phenylethylamine and the LOPs, which is later converted into another imine by an electronic rearrangement. This new imine is the origin of phenylacetaldehyde by hydrolysis. These results show a new pathway for Strecker aldehyde formation. This route provides a potential way to reduce biogenic amine content in foods when they can be thermally processed before consumption.

KEYWORDS: *Biogenic amines, carbonyl−amine reactions, lipid oxidation, Maillard reaction, Strecker aldehydes*

INTRODUCTION

Biogenic amines are known to occur in many foods, especially in those that undergo a fermentation process.[1−4] Upon ingestion, these amines, which have been related to a number of physiological effects,[5] can be oxidatively deaminated by a monoamine oxidase to produce the corresponding Strecker aldehyde.[6] Thus, 2-phenylethylamine is metabolized by monoamine oxidase B to phenylacetaldehyde, which can then be converted to phenylacetic acid by either aldehyde dehydrogenase or aldehyde oxidase and xanthine oxidase.[6]

As an alternative mechanism, biogenic amines can also be produced chemically by carbonyl−amine reactions, although these last reactions require, at least, moderate heating.[7,8] On the other hand, the possibility that biogenic amines can undergo deamination to be converted chemically into Strecker aldehydes remains to be explored. Nevertheless, this conversion might take place because the formation of glycolaldehyde from aminoethanol in the presence of pyruvic acid has been observed using pyrolysis gas chromatography−mass spectrometry (GC−MS) at 250 °C.[9]

The present study was undertaken to determine whether biogenic amines, in particular phenylethylamine, can be converted into Strecker aldehydes by carbonyl−amine reactions initiated by lipid oxidation products. The existence of this pathway would provide a new route for flavor formation in foods.

MATERIALS AND METHODS

Materials. Methyl 13-hydroperoxyoctadeca-9,11-dienoate was prepared by oxidation of linoleic acid with lipoxygenase and later esterification with diazometane.[10] 4,5-Epoxy-2-heptenal and 4,5-epoxy-2-decenal were prepared by epoxidation of 2,4-heptadienal and 2,4-decadienal, respectively, with 3-chloroperoxybenzoic acid.[11,12] 4-Hydroxy-2-nonenal was synthesized according to the procedure by Gardner et al.[13] 4-Oxo-2-nonenal was prepared from 2-pentylfuran according to Shimozu et al.[14] 4-Oxo-2-hexenal was prepared analogously to 4-oxo-2-nonenal from 2-ethylfuran. Briefly, *N*-bromosuccinimide (1.9 g) and pyridine (10 mL) were added to 2-ethylfuran (1.6 g) in 11 mL of tetrahydrofuran (THF)/acetone/water (5:4:2) on an ice bath. The reaction mixture was stirred for 1 h at this temperature and then kept at ambient temperature. After 2 h, the mixture was diluted with water (10 mL) and extracted with chloroform (3 × 50 mL). The combined chloroformic extracts were dried (sodium sulfate) and concentrated under vacuo. The residue was subjected to silica gel chromatography using hexane/ethyl acetate (3:1, v/v) as the eluent, and 4-oxo-2-hexenal was obtained chromatographically pure. Its identity was confirmed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.79 (1H, d, J = 6.9 Hz, C-1), 6.90 (1H, d, J = 16.1 Hz, C-3), 6.79 (1H, dd, J = 6.9, 16.1 Hz, H-2), 2.75 (2H, c, J = 7.3 Hz, H-5), and 1.17 (3H, t, J = 7.3 Hz, H-6). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 200.4 (C-4), 193.5 (C-1), 144.8 (C-3), 137.3 (C-2), 34.5 (C-5), and 7.5 (C-6).

All other chemicals were purchased from Aldrich (Milwakee, WI), Sigma (St. Louis, MO), Fluka (Buchs, Switzerland), or Merck (Darmstadt, Germany) and were analytical-grade.

Phenylethylamine/Lipid Reaction Mixtures. Mixtures of phenylethylamine (10 μmol) and 0−10 μmol of lipid derivative in 0.5 mL of buffer were introduced in Schott Duran test tubes (16 × 1.5 cm), which were closed and heated at 120−180 °C for 0−1 h. The atmosphere of the test tube was air, unless otherwise indicated. The buffers employed for controlling the reaction pH were 0.3 M sodium citrate buffer at pH 2.15−6.0 and 0.3 M sodium phosphate buffer at pH 6.0−8.0. At the end of the heating period, samples were cooled,

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diluted with 1 mL of acetonitrile and 50 μL of internal standard solution (54.8 mg of methyl heptanoate in 25 mL of methanol), and analyzed by GC−MS.

GC−MS Analyses. GC−MS analyses were conducted with a Hewlett-Packard 6890 GC Plus coupled with an Agilent 5973 mass selective detector (MSD, quadrupole type). A fused-silica HP5-MS capillary column (30 m × 0.25 inner diameter, with a coating thickness of 0.25 μm) was used. Working conditions were as follows: carrier gas, helium (1 mL/min at constant flow); injector, 250 °C; oven temperature programmed from 70 °C (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 electron ionization (EI), 70 eV.

Determination of the Phenylacetaldehyde Content. Quantification of phenylacetaldehyde was carried out, as described previously,[15] by preparing standard curves of the aldehyde in the 1.55 mL of solution prepared for GC−MS injection (see above). For each curve, eight different concentration levels of the aldehyde were used. The phenylacetaldehyde content was directly proportional to the aldehyde/internal standard area ratio ($r = 0.999$; $p < 0.0001$). The coefficients of variation were <10%.

Statistical Analysis. All data given are the mean ± standard deviation (SD) values of at least three independent experiments. Statistical comparisons among different groups were made using analysis of variance. When significant F values were obtained, group differences were evaluated by the Tukey test.[16] Statistical comparisons were carried out using Origin version 7.0 (OriginLab Corporation, Northampton, MA). The significance level is $p < 0.05$, unless otherwise indicated.

RESULTS

Formation of Phenylacetaldehyde in the Reaction of Phenylethylamine with Lipid Oxidation Products. When phenylethylamine was heated at 180 °C for 1 h, the formation of a small amount of phenylacetaldehyde was observed (Figure 1). Nevertheless, the addition of lipid oxidation products increased significantly ($p < 0.05$) the amount of phenylacetaldehyde produced for most of the lipid oxidation products assayed.

The addition of the primary lipid oxidation product methyl 13-hydroperoxyoctadeca-9,11-dienoate increased the amount of phenylacetaldehyde produced by 326%. When the phenylethylamine was heated in the presence of the secondary lipid oxidation product 2,4-decadienal, an increase of 420% in the formation of phenylacetaldehyde was observed.

Among the ternary lipid oxidation products assayed, the 4-hydroxy-2-nonenal did not increase significantly the amount of phenylacetaldehyde produced. On the contrary, both epoxyalkenals and oxononenals increased the amount of phenylacetaldehyde, and the longer the chain length, the higher the amount of phenylacetaldehyde produced. In addition, epoxyalkenals were less reactive than oxoalkenals. Thus, 4,5-epoxy-2-heptenal did not increase significantly the amount of phenylacetaldehyde produced. On the contrary, 4,5-epoxy-2-decenal increased it by 425%. Oxoalkenals were much more reactive for this reaction. 4-Oxo-2-hexenal increased the amount of phenylacetaldehyde produced by 388%, and 4-oxo-2-nonenal increased the amount of phenylacetaldehyde produced by 887%. This compound produced the highest amount of phenylacetaldehyde among the different compounds assayed.

All of these results showed that lipid oxidation products were able to convert phenylethylamine into phenylacetaldehyde to some extent. To study how this reaction was produced, 4-oxo-2-nonenal, as the most reactive lipid oxidation product for this reaction, and 2,4-decadienal, as a major lipid oxidation product formed during oxidation of ω-6 fatty acid chains and having relevant aroma properties,[17,18] were selected.

Effect of the Reaction Conditions (pH, Concentration of the Lipid Oxidation Product, Time, and Temperature) on the Amount of Phenylacetaldehyde Produced in the Reaction of Phenylethylamine with Either 2,4-Decadienal or 4-Oxo-2-nonenal. The conversion of phenylethylamine into phenylacetaldehyde was produced at acidic pH values, and this behavior was similar for the two lipid oxidation products assayed (Figure 2). Thus, phenylacetaldehyde was produced to the highest extent at pH 2.15−3 and decreased at higher pH values. 4-Oxo-2-nonenal but no 2,4-decadienal still produced phenylacetaldehyde at pH 5, and no phenylacetaldehyde formation was observed at pH ≥ 6. For this

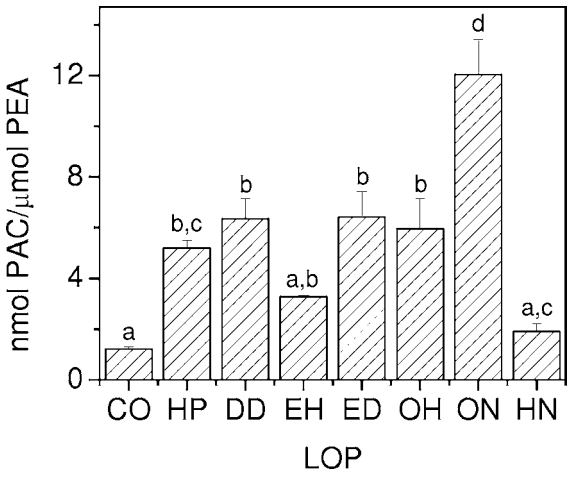

Figure 1. Formation of phenylacetaldehyde (PAC) in phenylethylamine (PEA)/lipid oxidation product (LOP) reaction mixtures. Samples were heated at 180 °C for 1 h at pH 3. Lipid oxidation products assayed were CO, none; HP, methyl 13-hydroperoxyoctadeca-9,11-dienoate; DD, 2,4-decadienal; EH, 4,5-epoxy-2-heptenal; ED, 4,5-epoxy-2-decenal; OH, 4-oxo-2-hexenal; ON, 4-oxo-2-nonenal; and HN, 4-hydroxy-2-nonenal. Bars with different letters are significantly different ($p < 0.05$).

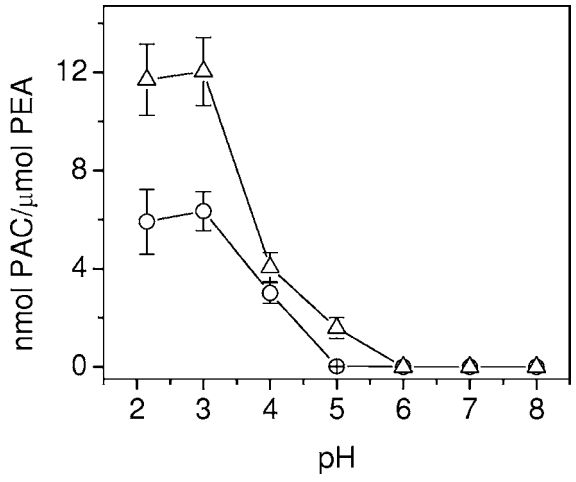

Figure 2. Effect of reaction pH on the formation of phenylacetaldehyde (PAC) in the reaction of phenylethylamine (PEA) with either 4-oxo-2-nonenal (△) or 2,4-decadienal (○) at 180 °C for 1 h. The employed buffers were sodium citrate for pH 2.15−6 and sodium phosphate for pH 6−8. Identical results were obtained for both citrate and phosphate buffers at pH 6.

reason, the rest of the experiments in this study were carried out at pH 3.

Phenylacetaldehyde formation was a consequence of the presence of the lipid oxidation product and increased with its concentration (Figure 3). This increase was not linear, and a phenylethylamine/lipid oxidation product ratio of 4:4 or 4:3 produced the same amount of phenylacetaldehyde.

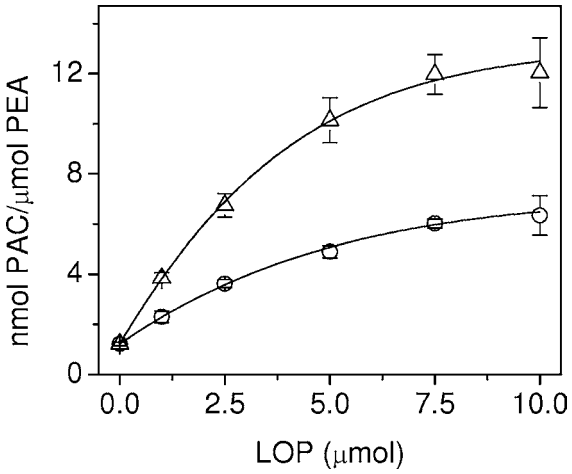

Figure 3. Effect of the lipid oxidation product (LOP) concentration on the formation of phenylacetaldehyde (PAC) in the reaction of phenylethylamine (PEA) with either 4-oxo-2-nonenal (△) or 2,4-decadienal (○) at 180 °C for 1 h and pH 3.

Phenylacetaldehyde formed also depended upon time and temperature (Figure 4). Thus, the amount of phenylacetaldehyde increased linearly ($r > 0.98$; $p < 0.0001$) as a function of the time between 120 and 190 °C when phenylethylamine was heated in the presence of either 2,4-decadienal or 4-oxo-2-nonenal. In addition, the reaction rate increased with the temperature.

Reaction rates at the different assayed temperatures were calculated using the equation

$$[\text{phenylacetaldehyde}] = [\text{phenylacetaldehyde}]_0 + kt$$

where $[\text{phenylacetaldehyde}]_0$ represents the intercept, 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 phenylacetaldehyde formation from phenylethylamine in the presence of either 2,4-decadienal or 4-oxo-2-nonenal (Figure 5). The determined E_a values were 54.8 kJ/mol for the formation of phenylacetaldehyde in the reaction of phenylethylamine with 2,4-decadienal and 53.8 kJ/mol for the reaction with 4-oxo-2-nonenal.

Effect of the Atmosphere on the Conversion of Phenylethylamine into Phenylacetaldehyde Initiated by Either 2,4-Decadienal or 4-Oxo-2-nonenal. Oxygen promotes further reactions and transformations in lipid oxidation products, which later influences the reactions of these compounds.[19] For this reason, the effect of the atmosphere was studied in the formation of phenylacetaldehyde as a consequence of the reaction of phenylethylamine with either 2,4-decadienal or 4-oxo-2-nonenal. As observed in Figure 6, when the air was replaced by nitrogen, the amount of phenylacetaldehyde produced by both 2,4-decadienal and 4-oxo-2-nonenal was reduced similarly (about 40%) for both lipid oxidation products. Nevertheless, phenylacetaldehyde was still produced to a significant extent in the absence of oxygen.

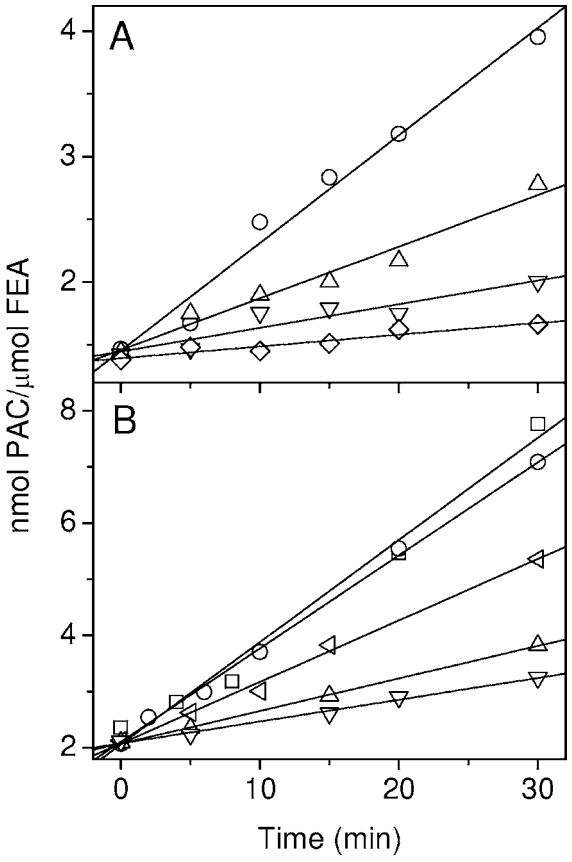

Figure 4. Effect of the time and temperature on the formation of phenylacetaldehyde (PAC) in the reaction of phenylethylamine (PEA) with either (A) 2,4-decadienal or (B) 4-oxo-2-nonenal at pH 3. Temperatures assayed were 190 °C (□), 180 °C (○), 170 °C (◁), 160 °C (△), 140 °C (▽), and 120 °C (◇).

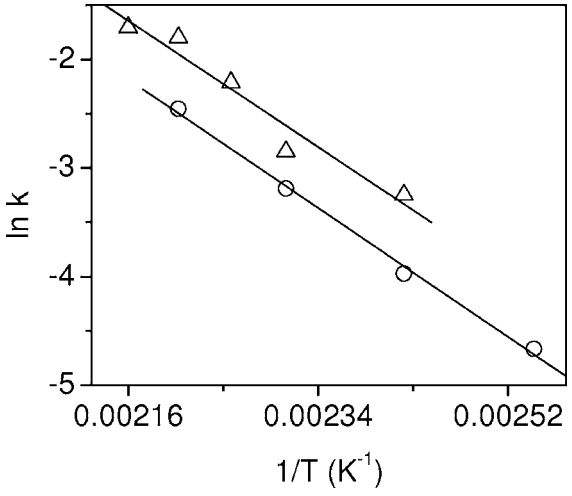

Figure 5. Arrhenius plot for phenylacetaldehyde formation in the reaction of phenylethylamine with either 4-oxo-2-nonenal (△) or 2,4-decadienal (○).

DISCUSSION

Recent studies have shown that amino acids are degraded by lipid oxidation products in multiple ways. Thus, they can suffer

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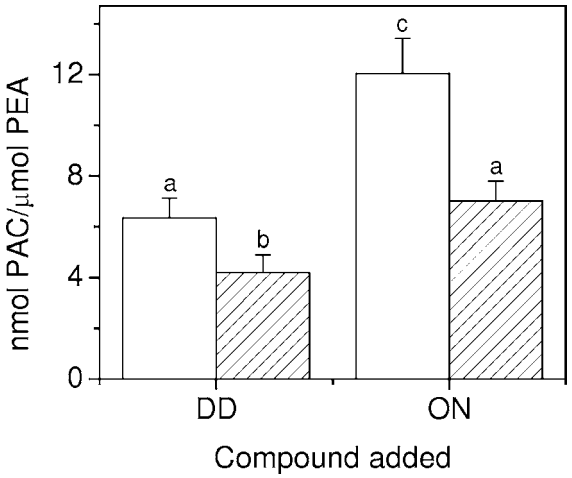

Figure 6. Effect of the atmosphere on the formation of phenylacetaldehyde (PAC) in the reaction of phenylethylamine (PEA) with either 2,4-decadienal (DD) or 4-oxo-2-nonenal (ON) at 180 °C for 1 h and pH 3. The atmosphere was air (open bars) or nitrogen (striped bars). Bars with different letters are significantly different ($p < 0.05$).

a Strecker degradation to be converted in Strecker aldehydes or α-keto acids.[12,20] In addition, amino acids can also be decarboxylated to the corresponding amines.[8,21] However, these new compounds are not always final compounds, and they can suffer additional degradations or transformations. Thus, Strecker aldehydes have been shown to be degraded to shorter aldehydes.[22] In addition, amines can be deaminated to produce the corresponding vinylogous derivatives of the initial amino acids.[23,24] The results obtained in this study show the existence of a new reaction produced in the amino acid degradation by lipid oxidation products: the conversion of the amines derived from amino acids into Strecker aldehydes.

The analogy of the results obtained with both 2,4-decadienal and 4-oxo-2-nonenal is likely related to an analogous reaction mechanism for both reactions. The conversion of phenylethylamine into phenylacetaldehyde promoted by 4-oxo-2-nonenal may follow a pathway similar to that shown in Figure 7. Phenylethylamine reacts with the aldehyde to produce the corresponding Schiff base (in this case, two imines can be formed). This imine has been labeled as imine A in the figure. An electronic rearrangement of imine A, which does not have to be necessarily concerted, would produce imine B. Analogous imine isomerizations have been described in the Maillard reaction pathway. A review of these imine isomerizations has been recently published.[25] Finally, the later hydrolysis of imine B would produce phenylacetaldehyde.

The difficulty of the interconversion between imine A and imine B shown in Figure 7 is likely related to the different reactivities observed for the different lipid oxidation products assayed. Figure 8 shows the chemical structures of the corresponding imines A and B formed with the different lipid oxidation products assayed (the hydroperoxide has not been included because it is likely decomposed upon heating, and phenylacetaldehyde formation will be related to the compounds formed in this decomposition). As observed in Figure 8, the formation of phenylacetaldehyde is clearly favored for 4-oxo-2-alkenals because the interconversion between imines A and B can be considered a keto−enol tautomerism. This interconversion is likely more difficult for 2,4-alkadienals or 4,5-epoxy-2-alkenals and, specially, for 4-hydroxy-2-nonenal. The formation of phenylacetaldehyde with 4-hydroxy-2-nonenal would be produced with elimination of water, which might not be favored under the reaction conditions employed in this study.

This new reaction is expected to compete with the elimination reaction that produce vinylogous derivatives of amino acids.[24] However, both reactions seem to require very different reaction conditions. Thus, the elimination is produced mainly at neutral or basic pH values, and the conversion into

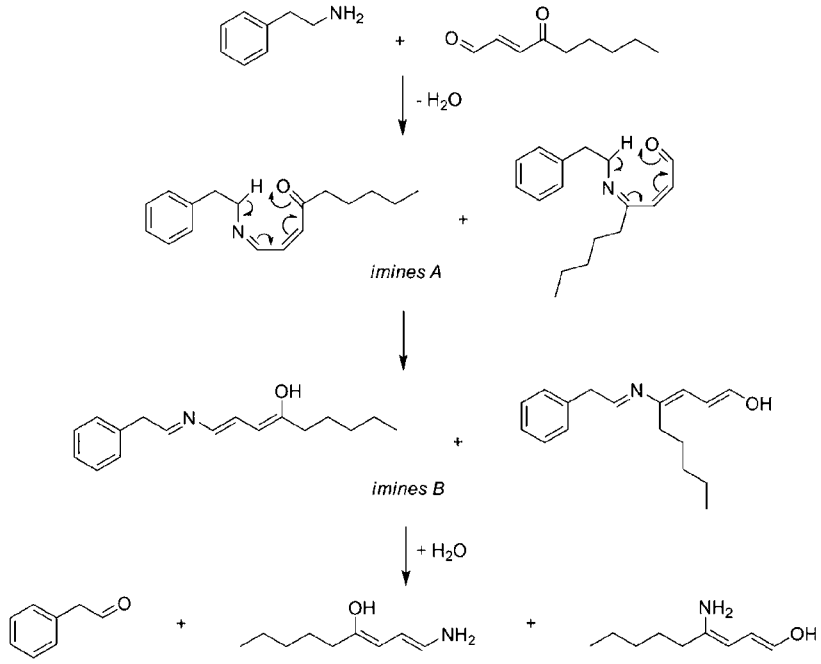

Figure 7. Proposed pathways for the conversion of phenylethylamine into phenylacetaldehyde in the presence of lipid oxidation products (4-oxo-2-nonenal is shown as the lipid oxidation product that produces this reaction to the highest extent).

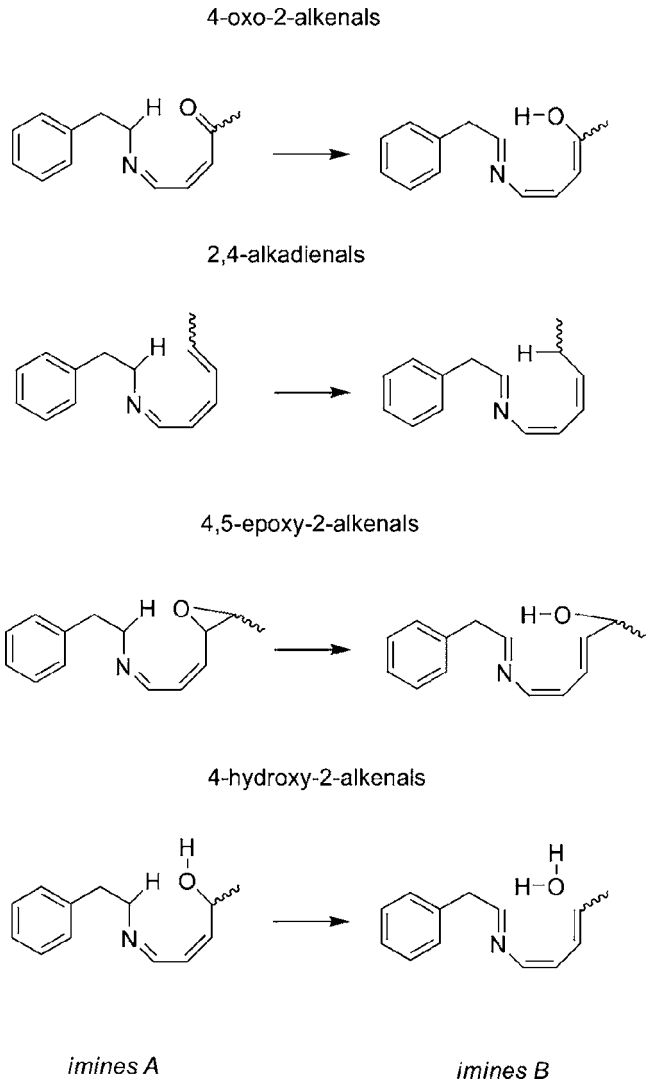

Figure 8. Chemical structures of imines A and B formed between phenylethylamine and the different lipid oxidation products assayed (only the functional groups of the lipid oxidation products are shown).

the Strecker aldehydes is produced at acid pH values. In addition, the elimination reaction is mainly produced at low water activity, and the formation of Strecker aldehydes described in this study was produced in aqueous solution. Furthermore, anaerobic conditions favor the elimination reaction, and Strecker aldehydes are produced to a higher extent under aerobic conditions (Figure 6). Therefore, condition reactions are likely to determine whether an olefin or a Strecker aldehyde is going to be produced to a higher extent. Thus, the conditions employed in this study did not favor the formation of styrene from phenylethylamine. An analogous strategy might also be employed in foods to direct these reactions in the desired sense when processing conditions allow for such changes.

All of these results confirm and expand our present knowledge of the complexity of the reactions responsible for the formation of flavors in foods and how processing conditions and food formulation play a major role in the flavors formed. These results show a new pathway for Strecker aldehyde formation that may be contributing to the formation of these aroma active compounds. In addition, this route provides a potential way to reduce to some extent the biogenic amines produced in some food products, which can lately be thermally processed before consumption.

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Notes

The authors declare no competing financial interest.

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