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Model Studies on the Degradation of Phenylalanine Initiated by Lipid Hydroperoxides and Their Secondary and Tertiary Oxidation Products

ROSARIO ZAMORA, EMERENCIANA GALLARDO, AND FRANCISCO J. HIDALGO*

Instituto de la Grasa, Consejo Superior de Investigaciones Científicas, Avenida Padre García Tejero 4, 41012 Seville, Spain

The reaction of methyl 13-hydroperoxyoctadeca-9,11-dienoate (MeLOOH), methyl 13-hydroperoxyoctadeca-9,11,15-trienoate (MeLnOOH), methyl 13-hydroxyoctadeca-9,11-dienoate (MeLOH), methyl 13-oxooctadeca-9,11-dienoate (MeLCO), methyl 9,10-epoxy-13-hydroxy-11-octadecenoate (MeLEPOH), and methyl 9,10-epoxy-13-oxo-11-octadecenoate (MeLEPCO) with phenylalanine was studied to determine the comparative reactivity of primary, secondary, and tertiary lipid oxidation products in the Strecker degradation of amino acids. All assayed lipids were able to degrade the amino acid to a high extent, although the lipid reactivity decreased slightly in the following order: MeLEPCO $\geq$ MeLCO $>$ MeLEPOH $\geq$ MeLOH $>$ MeLOOH $\approx$ MeLnOOH. These data confirmed the ability of many lipid oxidation products to degrade amino acids by a Strecker-type mechanism and suggested that, once the lipid oxidation is produced, a significant Strecker degradation of surrounding amino acids should be expected. The contribution of different competitive mechanisms to this degradation is proposed, among which the conversion of the different lipid oxidation products assayed into the most reactive MeLEPCO and the fractionation of long-chain primary and secondary lipid oxidation products into short-chain aldehydes are likely to play a major role.

KEYWORDS: Carbonyl−amine reactions; hydroperoxides; hydroxydienes; ketodienes; lipid oxidation; lipid oxidation products; Maillard reaction; Strecker aldehydes

INTRODUCTION

Strecker degradation of amino acids is a very important route leading to final aroma compounds in the Maillard reaction (*1, 2*). Thus, it is the origin of significant flavor compounds such as Strecker aldehydes and pyrazines, for example (*3*). However, diverse studies have shown that Strecker aldehydes can also be produced by the reaction of amino acids with lipid oxidation products having two oxygenated functions including epoxyalkenals (*4*), unsaturated epoxyketo fatty esters (*5*), and hydroxyalkenals (*6*). These compounds react with the amino group of the amino acid to form the corresponding imine, which, after electronic rearrangement, decarboxylation, and hydrolysis, produces the corresponding Strecker aldehyde. Alternatively, this reaction can also take place without decarboxylation (*7*) and, therefore, suitable amines can also be converted into their corresponding aldehydes by this last mechanism (*8*).

Lipid oxidation products with only one oxygenated function also degrade amino acids. However, the oxidized lipid has to be oxidized as a step prior to its reaction with the amino acid. Thus, alkadienals and ketodienes degraded phenylalanine to phenylacetaldehyde when mixtures of the oxidized lipid and the amino acid were heated in the presence of oxygen (*9*). This reaction took place in two steps. First, alkadienals and ketodienes were oxidized to the corresponding epoxy derivatives (*10*) and, then, the produced compounds reacted directly with the amino acid as described above.

Furthermore, recent studies have shown that Strecker degradation of amino acids can also be produced by unoxidized lipids. Thus, when unoxidized lipids were heated in the presence of amino acids, the Strecker degradation of these last compounds was produced to an extent that depended on the presence of other compounds, that is, carbohydrates, which contributed to the lipid oxidation (*11*). The Strecker degradation observed in this last study was hypothesized to be produced by reaction of the produced lipid oxidation products with the amino acid following one of the mechanisms described in previous studies (*4*−*6*). However, although alkadienals and ketodienes are only a small part of the lipid oxidation products formed, the yield of the reaction obtained with unoxidized lipids was not much lower than the yield obtained with alkadienals or ketodienes, therefore suggesting that other lipid oxidation products, in addition to alkadienals and ketodienes, are likely to be contributing to the Strecker degradation of the amino acids observed.

In an attempt to uncover the routes by which unoxidized lipids produce the Strecker degradation of amino acids, this study analyzes the reaction of the primary lipid oxidation products

* Author to whom correspondence should be addressed [telephone +(34) 954 611 550; fax +(34) 954 616 790; e-mail fhidalgo@ig.csic.es].

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(the lipid hydroperoxides) with amino acids. Lipid hydroperoxides are very rapidly produced under the oxidizing conditions in which amino acids are degraded. Therefore, the study of lipid hydroperoxide/amino acid reaction mixtures may add to the understanding of the Strecker aldehyde formation in complex mixtures including unoxidized lipids, carbohydrates, and amino acids, for example (*11*). These studies were carried out in model systems of lipid hydroperoxides (derived from both linoleic and linolenic acids as major *n*6 and *n*3 fatty acids, respectively) and phenylalanine (as a model amino acid that produces the important flavor phenylacetaldehyde). In addition, studies with the hydroxydiene and the ketodiene derived from linoleic acid, as major secondary oxidation products of linoleic acid hydroperoxide, and studies with epoxyhydroxy and epoxyketo unsaturated fatty esters, as tertiary lipid oxidation products, have also been included for comparison.

EXPERIMENTAL PROCEDURES

Materials. All chemicals were purchased from Aldrich (Milwaukee, WI), Sigma (St. Louis, MO), Fluka (Buchs, Switzerland), or Merck (Darmstadt, Germany) and were of analytical grade. In particular, the following compounds were purchased to be employed in the identification of lipid/phenylalanine reaction products by GC-MS: hexanal, 2-hexenal, benzaldehyde, 2-pentylfuran, phenylacetaldehyde, 2-octenal, methyl octanoate, and 2,4-decadienal. 1-Phenethyl-1*H*-pyrrole and 2-pentyl-1-phenethyl-1*H*-pyrrole were prepared as described previously (*12*). Methyl 13-hydroxyoctadeca-9,11-dienoate (MeLOH) and methyl 13-oxooctadeca-9,11-dienoate (MeLCO) were prepared as described below. The techniques employed to confirm the purity of the prepared compounds were mostly thin layer chromatography (TLC) and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. In addition, when prepared compounds were sufficiently stable to be analyzed by gas chromatography (GC), this technique was also employed.

Methyl 13-hydroperoxyoctadeca-9,11-dienoate (MeLOOH) and methyl 13-hydroperoxyoctadeca-9,11,15-trienoate (MeLnOOH) were prepared by oxidation of the corresponding fatty acids with lipoxygenase following a previously described procedure (*13*). The obtained hydroperoxides were esterified with diazomethane and purified by column chromatography on silica gel using hexane/diethyl ether (7:3) as the eluent. MeLOOH and MeLnOOH were obtained chromatographically pure. Additional confirmations of identity and purity were obtained by 1D and 2D NMR. ^{13}C NMR ($CDCl_3$, 75.4 MHz) of MeLOOH: δ 174.49 (C1), 133.96 (C9), 131.23 (C12), 130.11 (C11), 127.51 (C10), 86.85 (C13), 51.54 (OCH_3), 34.06 (C2), 32.49 (C14), 31.72 (C16), 29.35, 29.03, 29.00, 28.87 (C4−C7), 27.69 (C8), 24.98 (C15), 24.85 (C3), 22.51 (C17), and 14.04 (C18). This spectrum was identical to that previously described by Dussault et al. (*14*). ^{13}C NMR ($CDCl_3$, 75.4 MHz) of MeLnOOH: δ 174.53 (C1), 134.35, 134.11 (C9,C16), 130.37 (C12), 130.20 (C11), 127.50 (C10), 123.09 (C15), 86.21 (C13), 51.56 (OCH_3), 34.07 (C2), 30.58 (C14), 29.34, 29.03, 29.00, 28.87 (C4−C7), 27.69 (C8), 24.85 (C3), 20.70 (C17), and 14.12 (C18).

Methyl 13-hydroxyoctadeca-9,11-dienoate (MeLOH) was prepared by reducing the 13-hydroperoxide of linoleic acid with sodium borohydride and later esterification with diazomethane (*13*). MeLOH was purified by column chromatography on silica gel using hexane/diethyl ether (7:3) as the eluent. This compound was obtained chromatographically pure. Additional confirmations of identity and purity were obtained by 1D and 2D NMR. ^{13}C NMR ($CDCl_3$, 75.4 MHz) of MeLOH: δ 174.36 (C1), 135.84 (C12), 132.80 (C9), 127.71 (C10), 125.69 (C11), 72.87 (C13), 51.47 (OCH_3), 37.21 (C14), 34.00 (C2), 31.72 (C16), 29.40 (C6), 28.99, 28.99, 28.89 (C4−C6), 27.61 (C8), 25.08 (C15), 24.82 (C3), 22.56 (C17), and 14.03 (C18). This spectrum was identical, for example, to that previously collected by Hämäläinen and Kamal-Eldin (*15*).

Methyl 13-oxooctadeca-9,11-dienoate (MeLCO) was prepared by oxidation of 13-hydroxyoctadeca-9,11-dienoic acid with chromium trioxide and later esterification with diazomethane (*13*). MeLCO was purified by column chromatography on silica gel using hexane/diethyl ether (4:1) as the eluent. This compound was obtained chromatographically pure and exhibited the previously described ^{1}H and ^{13}C NMR spectra (*13*).

Methyl 9,10-epoxy-13-oxo-11-octadecenoate (MeLEPCO) was prepared by epoxidation of MeLCO with 3-chloroperoxybenzoic acid (*16*). MeLEPCO was purified by column chromatography on silica gel using hexane/diethyl ether (4:1) as the eluent. This compound was obtained chromatographically pure and exhibited the previously described ^{1}H and ^{13}C NMR spectra (*13*).

Methyl 9,10-epoxy-13-hydroxy-11-octadecenoate (MeLEPOH) was prepared by reduction of MeLEPCO with sodium borohydride (*13*). MeLEPOH was purified by column chromatography on silica gel using hexane/diethyl ether (3:2) as the eluent. This compound was obtained chromatographically pure and exhibited the previously described ^{1}H and ^{13}C NMR spectra (*13*).

Lipid/Amino Acid Reaction Mixtures. Mixtures of 0−25 μmol of lipid derivative and 25 μmol of phenylalanine in 0.5 mL of buffer were introduced in Schott Duran test tubes (16 × 1.5 cm), which were closed and heated at 180 °C. 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, pH 2.15−6.0; 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 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 MSD (mass selective detector, quadrupole type). A fused-silica HP5-MS capillary column (30 m × 0.25 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 programmed from 70 (1 min) to 240 at 5 °C/min and then to 325 at 10 °C/min; transfer line to MSD, 280 °C; and ionization EI, 70 eV.

Determination of Phenylacetaldehyde Content. Quantification of phenylacetaldehyde was carried out, as described previously (*9*), 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. Phenylacetaldehyde content was directly proportional to the aldehyde/internal standard area ratio ($r = 0.999$, $p < 0.0001$). The coefficients of variation were <10%. All data are mean values of, at least, two independent experiments.

RESULTS

Reaction of Lipid Hydroperoxides with Phenylalanine. The reaction between lipid hydroperoxides and phenylalanine is complex, and numerous compounds were formed. These compounds were produced both by hydroperoxide and, to a lesser extent, by amino acid decomposition and also by reaction of the oxidized lipid with the amino acid. Thus, the formation of hexanal, benzaldehyde, 2-pentylfuran, 2-octenal, methyl octanoate, 2,4-decadienal, methyl 9-oxononanoate, methyl 8-(2-furyloctanoate), MeLOH, and MeLCO could be easily identified in the total ion chromatograms of MeLOOH and phenylalanine reaction mixtures on the basis of their retention indices and mass spectra (**Table 1**). Some reaction mixtures also produced the pyrrole derivatives 1-phenethyl-1*H*-pyrrole and 2-pentyl-1-phenethyl-1*H*-pyrrole, which were previously shown to be produced in the reaction between alkadienals, hydroxyalkenals, or epoxyalkenals with phenylalanine (*9, 12*). The major reaction product detected by GC-MS in samples heated for very short time periods (5−10 min) was MeLOH. However, when these samples were heated for longer periods, the major reaction product was the Strecker aldehyde phenylacetaldehyde.

Analogous results were also obtained when MeLnOOH/phenylalanine reactions were analyzed by GC-MS, although some of the produced lipid derivatives were different. Particu-

Table 1. Retention Indices of Compounds Identified in Phenylalanine/MeLOOH and Phenylalanine/MeLnOOH Mixtures

compd name	retention index
hexanal	801
2-hexenal	854
benzaldehyde	960
2-pentylfuran	993
phenylacetaldehyde	1053
2-octenal	1060
methyl octanoate	1125
2,4-decadienal	1306
methyl 8-oxooctanoate[a]	1316
methyl 9-oxononanoate[a]	1418
1-phenethyl-1*H*-pyrrole	1428
methyl 8-(2-furyl)octanoate [a]	1612
2-pentyl-1-phenethyl-1*H*-pyrrole	1885
methyl 13-hydroxyoctadeca-9,11-dienoate	2252/2263/2293
methyl 13-oxooctadeca-9,11-dienoate	2421

[a] These compounds were only tentatively identified on the basis of their mass spectra.

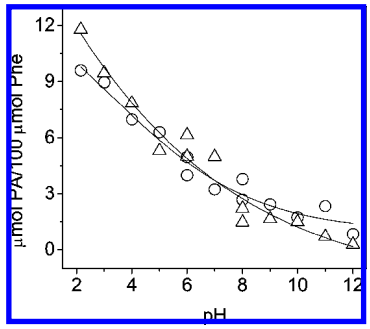

Figure 1. Effect of pH on phenylacetaldehyde (PA) formation in the reaction of MeLOOH (○) or MeLnOOH (△) with phenylalanine (Phe) at 180 °C for 1 h. The buffers employed were 0.3 M sodium citrate for pH 2.15−6, 0.3 M sodium phosphate for pH 6−8 and 11−12, and 0.3 M sodium borate for pH 8−10. The chemical structure for MeLOOH is given in **Figure 5**. MeLnOOH is the corresponding analogous hydroperoxide of methyl linolenate.

larly, a major product of the decomposition of the employed MeLnOOH was 2-hexenal, which was also identified in the total ion chromatograms of MeLnOOH/phenylalanine mixtures on the basis of its retention index and mass spectrum (**Table 1**). Nevertheless, and analogously to the observed MeLOOH/phenylalanine mixtures, the major reaction product in most heated MeLnOOH/phenylalanine reactions was the Strecker aldehyde phenylacetaldehyde.

Effect of Reaction Conditions in the Formation of Phenylacetaldehyde in Phenylalanine/Lipid Hydroperoxide Reaction Mixtures. The yield of the Strecker-type degradation of the amino acid depended on the reaction conditions. **Figure 1** collects the amount of phenylacetaldehyde produced after heating for 1 h at 180 °C equimolecular mixtures of MeLOOH (or MeLnOOH) and phenylalanine as a function of pH. As observed, the amount of Strecker aldehyde produced decreased exponentially ($r^2 > 0.96$) as a function of reaction pH, and the reaction yield decreased from 12 to 0.25% when the reaction pH increased from 2.15 to 12. This behavior was similar to that observed for the different secondary and tertiary lipid oxidation products analyzed previously (*4*−*6, 9*) and suggests that this reaction is always favored at acid pH values independent of the involved lipid. In addition, both hydroperoxides exhibited very similar behaviors, therefore suggesting that *n*6 and *n*3 fatty acids have an analogous reactivity for the Strecker degradation of the amino acids.

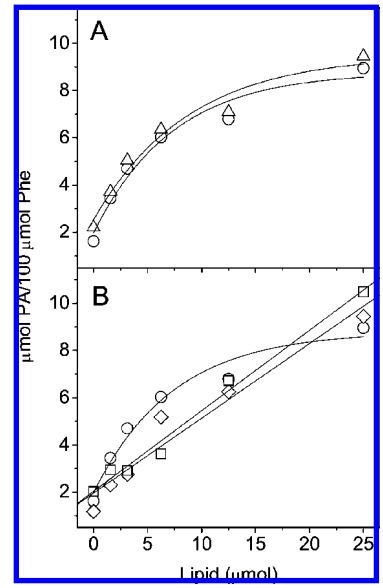

Figure 2. Effect of lipid concentration on phenylacetaldehyde (PA) formation in the reaction of (**A**) MeLOOH (○) or MeLnOOH (△) with phenylalanine (Phe) and (**B**) MeLOOH (○), MeLOH (◇), or MeLCO (□) with phenylalanine (Phe) at 180 °C for 1 h. Samples were heated in 0.3 M sodium citrate buffer. The chemical structures of MeLOOH, MeLOH, and MeLCO are given in **Figure 5**. MeLnOOH is the corresponding analogous hydroperoxide of methyl linolenate.

Previous studies in the Strecker degradation initiated by different lipid oxidation products were carried out at pH 3. Although the Strecker degradation initiated by lipid hydroperoxides seemed to be produced at pH 2.15 to a higher extent than at pH 3, a pH of 3 was selected for the rest of this study to obtain results comparative to those previously obtained with the different secondary and tertiary lipid oxidation products assayed.

The yield of the Strecker degradation of the amino acid increased with the amount of hydroperoxide added, therefore confirming that, in hydroperoxide/phenylalanine systems, the Strecker degradation of the amino acid was mostly a consequence of the presence of the oxidized lipid (**Figure 2A**). However, the amount of the produced phenylacetaldehyde did not increase linearly with the amount of hydroperoxide present, and the highest increases in phenylacetaldehyde were observed when small amounts of hydroperoxide were added. This behavior was different from the linear increases observed for epoxyalkenals (*4*), epoxyketo fatty esters (*5*), alkadienals, and ketodienes (*9*) and similar to that observed for hydroxyalkenals (*6*). The yield of phenylacetaldehyde as a function of hydroperoxide concentration could be described using a Boltzmann fit ($r^2 > 0.97$) for both MeLOOH and MeLnOOH.

The yield of the Strecker degradation also depended on the incubation time, and the amount of the Strecker aldehyde increased linearly ($r > 0.98$, $p < 0.02$) for the first 30 min until achieving a maximum, which seemed to increase slowly afterward (**Figure 3A**). This behavior was similar to that observed previously for other lipid oxidation products (*4*−*6, 9*).

Comparative Reactivity of Primary, Secondary, and Tertiary Lipid Oxidation Products in the Formation of Phenylacetaldehyde in Phenylalanine/Oxidized Lipid Reaction Mixtures. The comparative reactivity of different lipid oxidation products was studied in an attempt to understand the mechanism by which lipid hydroperoxides are able to produce the Strecker degradation of the amino acids. **Figure 2B** shows

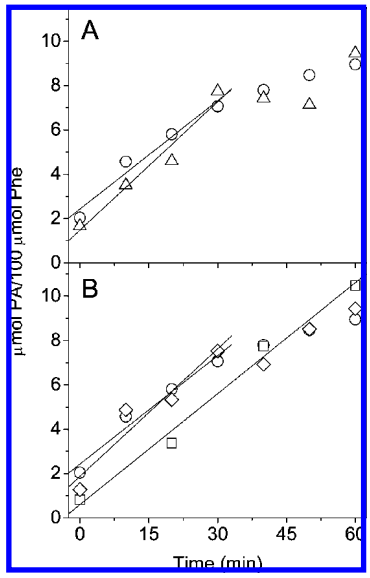

Figure 3. Time course of phenylacetaldehyde (PA) formation in the reaction of (**A**) MeLOOH (○) or MeLnOOH (△) with phenylalanine (Phe) and (**B**) MeLOOH (○), MeLOH (◇), or MeLCO (□) with phenylalanine (Phe) at 180 °C. Samples were heated in 0.3 M sodium citrate buffer. The chemical structures of MeLOOH, MeLOH, and MeLCO are given in **Figure 5**. MeLnOOH is the corresponding analogous hydroperoxide of methyl linolenate.

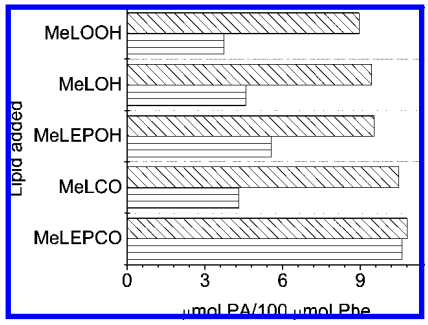

Figure 4. Reactivity of different lipid oxidation products in the Strecker degradation of phenylalanine to produce phenylacetaldehyde (PA). Binary reaction mixtures of the lipid and the amino acid were heated in 0.3 M sodium citrate buffer for 1 h at 180 °C in the presence of air (slashed bars) or nitrogen (horizontally striped bars). The chemical structures of the different lipid oxidation products are given in **Figure 5**.

the effect of lipid concentration in the formation of Strecker aldehydes in mixtures of phenylalanine with MeLOOH, MeLOH, and MeLCO. The three assayed lipids exhibited similar behaviors, although the amount of phenylacetaldehyde seemed to increase linearly ($r > 0.97$, $p < 0.001$) as a function of the lipid concentration when mixtures of phenylalanine with either MeLOH or MeLCO were assayed, and it was better described using a Boltzmann fit ($r^2 = 0.97$) when the oxidized lipid was MeLOOH.

Similar results were obtained when the effect of reaction time was studied (**Figure 3B**). Thus, the three assayed lipids degraded analogously to the amino acid, although MeLOOH and MeLOH seemed to produce higher amounts of phenylacetaldehyde at shorter reaction times.

When the reactivities of different primary, secondary, and tertiary lipid oxidation products for this reaction were compared after 1 h of heating at 180 °C, a small increase in the reactivity of the assayed lipids was observed: MeLOOH < MeLOH ≤ MeLEPOH < MeLCO ≤ MeLEPCO (**Figure 4**). This reactivity changed when reaction mixtures were heated under nitrogen. Thus, the amount of phenylacetaldehyde produced by MeLEPCO did not change, but the amounts of phenylacetaldehyde produced by the other lipid oxidation products were much reduced. In the absence of oxygen, the reactivity of the assayed lipids was as follows: MeLEPCO ≫ MeLEPOH > MeLOH ≈ MeLCO > MeLOOH.

DISCUSSION

Until very recently, lipids have not been considered as contributors to the formation of Strecker aldehydes during food processing. However, oxidized lipids exhibit a behavior very similar to that of carbohydrates for carbonyl−amine reactions, and analogous products and reaction mechanisms are frequently found in both carbohydrate/amino acid and oxidized lipid/amino acid reaction mixtures (*17*). Furthermore, recent studies have shown that lipid oxidation and Maillard reaction are so interrelated that they should be considered simultaneously to understand their consequences in foods when lipids, carbohydrates, and amino acids or proteins are simultaneously present (*18*).

The results obtained in the present study confirm the ability of lipid oxidation products to produce the Strecker degradation of amino acids and suggest that the reactivity of oxidized lipids for this reaction is much more general than previously believed because hydroperoxides, hydroxydienes, ketodienes, unsaturated epoxyhydroxy derivatives, and unsaturated epoxyketo derivatives, in addition to different short-chain aldehydes (*4, 6, 9*), are able to degrade phenylalanine to phenylacetaldehyde to a great extent.

Lipid oxidation is a very complex process in which, by decomposition of the lipid hydroperoxides, many different compounds are formed (*19*). In fact, lipid oxidation can take place at different reaction rates in separate positions of the same food product (*20*), therefore producing distinct lipid oxidation products that can coexist simultaneously. In addition, many of these produced compounds are only intermediates in the formation of more stable products. Furthermore, some of the formed products can also react with the surrounding amino compounds to produce new compounds. Because of the many lipid oxidation products simultaneously present, it is frequently very difficult to identify which of these lipid derivatives reacts with the amino compound. Thus, in the reactions analyzed in the present study, the action of different compounds by diverse mechanisms is likely to be contributing to the formation of the Strecker aldehyde.

One possible reaction pathway is an interconversion among the different lipid oxidation products to achieve the lipid oxidation product that would react with the amino acid. This reaction pathway is schematically shown in **Figure 5**. The decomposition of the hydroperoxides would produce hydroxydienes and ketodienes, as major degradation products, following, for example, a Russell mechanism (*21*). However, these compounds are not final products. In fact, previous studies have shown that ketodienes are oxidized to unsaturated epoxyketo derivatives, and these last products are the compounds responsible for the amino acid degradation (*9*). Furthermore, under the reaction conditions employed, MeLOH can be either oxidized to MeLCO or epoxidized to MeLEPOH. The formation of MeLCO was observed in MeLOH/phenylalanine reaction mixtures (data not shown). However, MeLEPOH, like MeLEPCO, is more reactive than the corresponding dienes and could not be detected by GC-MS under the assayed conditions. In any case, the final compound seems to be the MeLEPCO,

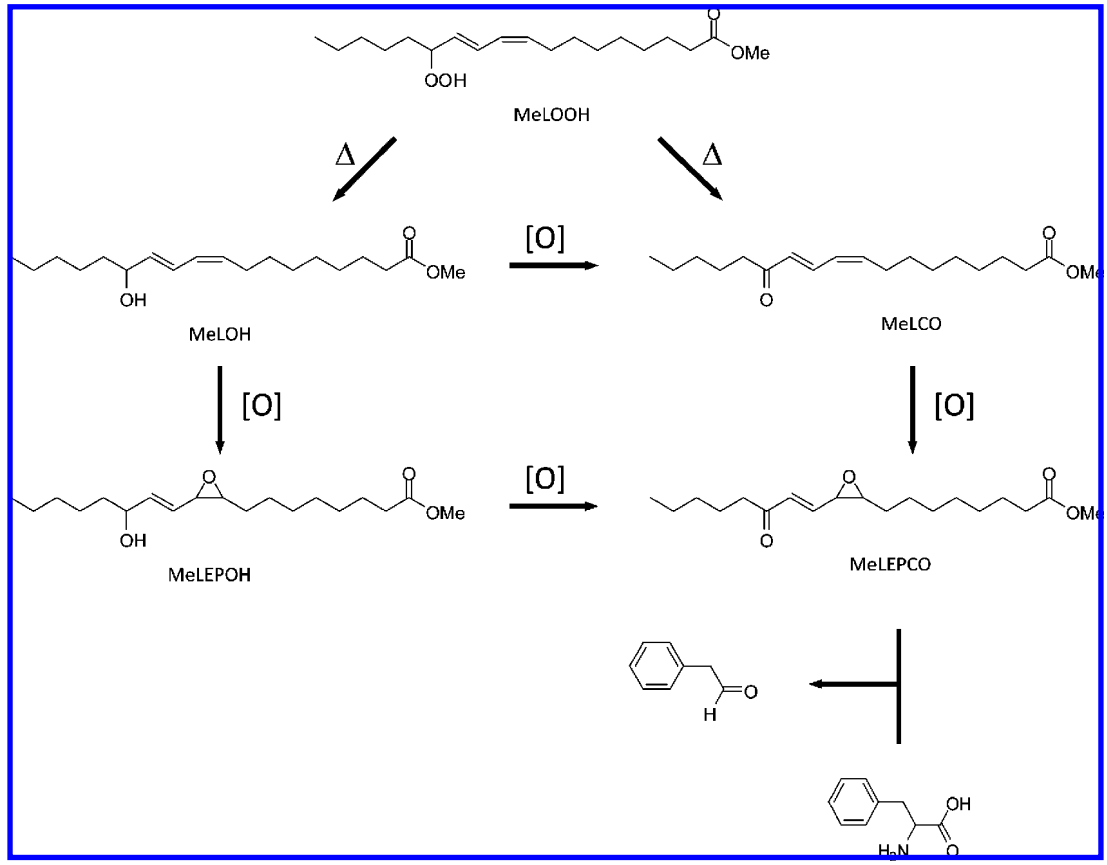

Figure 5. Proposed interconversion, under oxidative conditions, among the different lipid oxidation products included in this study to produce MeLEPCO as a major compound responsible for the observed Strecker degradation of phenylalanine.

which would react with the amino acid by the previously described mechanism (*5*). This hypothesis is supported by the relative reactivities of the different oxidized lipids assayed (**Figure 4**). The highest reactivity was observed for the MeEPCO, and this reactivity decreased as a function of the number of lipid intermediates needed for the formation of MeLEPCO. In addition, when oxygen was not present, the oxidative steps in the lipid interconversion were not favored and the yield of phenylacetaldehyde was much reduced except for MeLEPCO.

However, this is not likely the only mechanism involved because all assayed lipids degraded phenylalanine even under nonoxidative conditions (**Figure 4**). Thus, other mechanisms can be assumed to take part to some extent, including those that involve lipid fractionation. These last mechanisms would be related to the fractionation of the oxidized lipids to produce compounds able to react directly with the amino acid. Thus, the formation of hydroxyalkenals from hydroxydienes has been described (*22*), and hydroxyalkenals are able to produce the Strecker degradation of the amino acid (*6*). The major reactivity of MeLOOH and MeLOH compared with MeLCO at short reaction times (**Figure 3B**) supports the contribution of alternative mechanisms like this one to the Strecker degradation of amino acids.

Other reaction pathways might be initiated by the oxidation of the primary oxidation products to produce epoxyhydroperoxy fatty esters (*22*). These last compounds would suffer a thermal fractionation to yield epoxyalkenals, among other compounds (*23*), and epoxyalkenals were previously shown to convert amino acids into their corresponding Strecker aldehydes (*4*).

Additional studies are needed to evaluate the real contribution of the above-proposed mechanisms to the Strecker degradation of amino acids as a function of the reaction conditions. However, the results obtained in the present study suggest that, once the lipid oxidation is produced, a significant Strecker degradation of surrounding amino acids should be expected, therefore explaining the significant contribution of lipids to the Strecker aldehydes formed in complex mixtures of unoxidized lipids, carbohydrates, and amino acids (*11*). Furthermore, the much lower reactivity of unoxidized lipids compared with lipid hydroperoxides in binary mixtures of lipids and amino acids (*11*) suggests that the limiting step of the Strecker degradation of amino acids by unoxidized lipids is the formation of the lipid oxidation products.

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