Antagonism between lipid-derived reactive carbonyls and phenolic compounds in the Strecker degradation of amino acids

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ABSTRACT

The Strecker-type degradation of phenylalanine in the presence of 2-pentanal and phenolic compounds was studied to investigate possible interactions that either promote or inhibit the formation of Strecker aldehydes in food products. Phenylacetaldehyde formation was promoted by 2-pentenal and also by o- and p-diphenols, but not by m-diphenols. This is consequence of the ability of phenolic compounds to be converted into reactive carbonyls and produce the Strecker degradation of the amino acid. When 2-pentenal and phenolic compounds were simultaneously present, an antagonism among them was observed. This antagonism is suggested to be a consequence of the ability of phenolic compounds to either react with both 2-pentenal and phenylacetaldehyde, or compete with other carbonyl compounds for the amino acids, a function that is determined by their structure. All these results suggest that carbonyl-phenol reactions may be used to modulate flavor formation produced in food products by lipid-derived reactive carbonyls.

Keywords:
Carbonyl-amine reactions; Carbonyl-phenol reactions; Lipid oxidation; Maillard reaction; Phenolic compounds; Strecker degradation

Chemical compounds studied in this article:
Phenylalanine (PubChem ID: 994); phenylacetaldehyde (PubChem ID: 998); 2-pentenal (PubChem ID: 5364752); catechol (PubChem ID: 289); resorcinol (PubChem ID: 5054); hydroquinone (PubChem ID: 785); benzoquinone (PubChem ID: 4650); pyrogallol (PubChem ID: 1057); 1,2,4-trihydroxybenzene (PubChem ID: 10787); phloroglucinol (PubChem ID: 359).
1. Introduction

The Strecker degradation of amino acids is an oxidative decarboxylation reaction by which these compounds are transformed into decarboxylated deaminated carbonyl compounds in the presence of a variety of reagents under different reaction conditions (Yaylayan, 2003). This reaction is a source of important volatile constituents of food flavors, including Strecker aldehydes, pyrazines, pyridines, pyrroles, and oxazoles, among other compounds (see, for example, Kebede et al., 2014; Lu, Bruheim, Haugsgjerd, & Jacobsen, 2014).

In Maillard chemistry, the Strecker degradation is basically produced between $\alpha$-dicarbonyl compounds produced by carbohydrate dehydration or fragmentation (1- or 3-deoxyosones, glyoxal, 2,3-butanedione, 2-oxo-propanal, etc.) and amino acids (Guerra & Yaylayan, 2013; Zamora & Hidalgo, 2015). In addition, other carbonyl compounds, or their precursors, are also able to degrade amino acids. Thus, the ability of lipid-derived reactive carbonyls (Hidalgo & Zamora, 2004), amino acid-derived reactive carbonyls (Hidalgo, Alcón, & Zamora, 2013), polyphenol-derived quinones (Rizzi, 2006), and polyphenols (Delgado, Zamora, & Hidalgo, 2015) for producing the Strecker degradation of amino acids has also been described.

The fact that reactive carbonyls coming from very different origins, such as carbohydrates, lipids, amino acids, or polyphenols, can promote amino acid degradation, suggests the existence of many different alternative reaction pathways that contribute to the formation of a large variety of flavor compounds in addition to Strecker aldehydes. This would explain the seemingly endless source of flavor-significant compounds produced in the course of Strecker degradation (Rizzi, 2008). Furthermore, the existence of, at present, unknown interactions among all these routes might be either enhancing or inhibiting the formation of Strecker aldehydes as common...
products of all these routes. In an attempt to uncover possible interactions that either promote or inhibit the formation of Strecker aldehydes in food products, this manuscript studies the amino acid degradation produced in the presence of phenolic compounds or a lipid-derived reactive carbonyl, as well as in the simultaneous presence of both kinds of Strecker degradation promoters.

2. Materials and methods

2.1. Materials

Phenylalanine was selected as a model amino acid because its Strecker aldehyde phenylacetaldehyde has a high boiling point (195 ºC), can be easily determined by gas chromatography-mass spectrometry (GC-MS), and is a very powerful odorant (Delgado, Zamora, & Hidalgo, 2015).

2-Pentenal was employed as a model lipid-derived reactive carbonyl because its reaction with phenolic compounds, in addition to amino compounds, has been thoroughly studied (Hidalgo & Zamora, 2014).

Ten simple phenolic compounds having two or three hydroxyl groups at different positions of the aromatic ring were employed to understand also the role of the relative positions of hydroxyl groups in the aromatic ring for producing the Strecker degradation of the amino acid. Some of these compounds also contained one carboxylic group. The chemical structures of these phenolic compounds are shown in Fig. 1. The selected phenols included o-diphenols: catechol (CAT) and 3,4-dihydroxybenzoic acid (3,4-DHB); m-diphenols: resorcinol (RES) and 2,6-dihydroxybenzoic acid (2,6-DHB); p-diphenols: hydroquinone (HQ) and 2,5-dihydroxybenzoic acid (2,5-DHB); and trihydroxyphenols: pyrogallol (PG), 1,2,4-trihydroxybenzene (TH), and phloroglucinol (PHL). In addition, although benzoquinone (BQ) is not a phenol derivative, it was
included for comparison purposes. Phenolic compounds, phenylalanine, 2-pentenal, and other chemicals were purchased from Aldrich (Milwaukee, WI), Sigma (St. Louis, MO), Fluka (Buchs, Switzerland), or Merck (Darmstadt, Germany), and were of the highest available quality.

2.2. Formation of phenylacetaldehyde in binary and ternary mixtures of phenylalanine, 2-pentenal, and phenolic compounds

Mixtures of phenylalanine (25 µmol), the phenolic compound (0, 25 or 50 µmol), and/or 2-pentenal (0 or 25 µmol) in 500 µL of 0.3 M citrate buffer, pH 3, were introduced in closed test tubes and heated at 180 ºC for 1 h. After cooling (10 min at room temperature) samples were diluted with 1 mL of acetonitrile and 50 µL of internal standard solution (54.8 mg of methyl heptanoate in 25 mL of ethanol) added. Samples were analyzed for phenylacetaldehyde formation by GC-MS.

2.3. Phenylacetaldehyde and 2-pentenal concentration changes in the presence of phenols

Mixtures of phenylacetaldehyde (25 µmol), 2-pentenal (25 µmol), and the phenolic compound (25 µmol) in 500 µL of 0.3 M citrate buffer, pH 3, were introduced in closed test tubes and heated at 180 ºC for 1 h. After cooling (10 min at room temperature), samples were diluted with 1 mL of acetonitrile and 50 µL of internal standard solution (54.8 mg of methyl heptanoate in 25 mL of ethanol) added. Phenylacetaldehyde and 2-pentenal were determined by GC-MS.

2.4. 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, and
1 μL of sample was injected in the pulsed splitless mode. Working conditions were as follows: carrier gas, helium (1 mL/min at constant flow); injector, 250 °C; oven temperature programmed from 40 °C (1 min) to 240 °C at 5 °C/min and then to 300 °C at 10 °C/min; transfer line to MSD, 280 °C; ionization EI, 70 eV; ion source temperature, 230 °C; mass range, 28–550 amu.

2.5. Determination of phenylacetaldehyde and 2-pentenal contents

Quantification of phenylacetaldehyde and 2-pentenal was carried out as described previously for phenylacetaldehyde (Zamora, Gallardo, & Hidalgo, 2007) by preparing standard curves of both aldehydes in the 1.55 mL of the solution prepared for GC-MS injection. Then, different concentration levels of both aldehydes were used. Aldehyde content was directly proportional to the aldehyde/internal area ratio ($r = 0.999$, $p < 0.0001$). The coefficients of variation were < 10%.

2.6. Statistical analysis

All data given are mean or mean ± 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 (Snedecor & Cochran, 1980). Statistical comparisons were carried out using Origin v. 7.0 (OriginLab Corp., Northampton, MA, USA). The significance level is $p < 0.05$ unless otherwise indicated.

3. Results

3.1. Phenylacetaldehyde formation in binary and ternary mixtures of phenylalanine, 2-pentenal and phenolic compounds

As described previously, both lipid-derived reactive carbonyls (Hidalgo & Zamora, 2004) and some phenolic compounds (Delgado, Zamora, & Hidalgo, 2015) are able to
produce the Strecker degradation of amino acids. Thus, addition of 2-pentenal, analogously to other lipid-derived reactive carbonyls, increased phenylacetaldehyde formation by 274% in relation to the phenylacetaldehyde produced in the absence of an added carbonyl compound (Table 1). Analogously, addition of \( o \)- and \( p \)-diphenols also increased phenylacetaldehyde formation by 68–391% when 25 \( \mu \)mol of the phenolic compound were added and by 144–397% when 50 \( \mu \)mol of the phenolic compound were added. An analogous increase in phenylacetaldehyde formation was observed when either pyrogallol or 1,2,4-trihydroxybenzene were added. Thus, phenylacetaldehyde content increased by 227–247% when 25 \( \mu \)mol of these trihydroxy derivatives were added and by 309–322% when 50 \( \mu \)mol of these trihydroxy derivatives were added. Differently to the increases observed for all these compounds, no significant increases were observed when \( m \)-diphenols were added (Table 1). This different behavior between \( m \)-diphenols and \( o \)- and \( p \)-diphenols is consequence of the ability of carbonyl compounds, including the quinones formed by oxidation of \( o \)- and \( p \)-diphenols, to produce the Strecker degradation of phenylalanine. For that reason, when benzoquinone was employed in the place of phenolic derivatives, phenylacetaldehyde was produced to a higher extent than when the phenolic compound was added (about 500–600% higher than the phenylacetaldehyde produced by hydroquinone in relation to control reaction).

When both 2-pentenal and phenolic compounds were added simultaneously to phenylalanine, the obtained results were different to those described above and much lower increases in the phenylacetaldehyde produced were observed. Thus, phenylacetaldehyde only increased significantly (\( p < 0.05 \)) in relation to the control of phenylalanine and 2-pentenal, when 25 \( \mu \)mol of hydroquinone, benzoquinone,
pyrogallol or 1,2,4-trihydroxybenzene, or 50 µmol of 3,4-dihydroxybenzoic acid, 
benzoquinone or pyrogallol were added (Table 1). In addition, there was not a clear 
difference in the amount of phenylacetaldehyde formed when either 25 or 50 µmol of 
phenolic compound was employed. On the other hand, addition of 2,6-
dihydroxybenzoic acid or phloroglucinol at 25 µmol or phloroglucinol at 50 µmol, 
significantly reduced the phenylacetaldehyde produced.

3.3. Phenylacetaldehyde and 2-pentenal disappearance in the presence of phenols

To understand this different behavior in the presence and in the absence of 2-
pentenal, the disappearance of phenylacetaldehyde and 2-pentenal in the presence of 
phenolic compounds was studied. Four phenols were selected as model compounds for 
these studies. They included resorcinol, hydroquinone, 1,2,4-trihydroxybenzene, and 
phloroglucinol, as model m-diphenol, p-diphenol, triphenol having ortho and para 
substitutions, and triphenol having meta substitutions, respectively.

2-Pentenal was quite stable after 1 h heating at 180 ºC in sodium citrate buffer, pH 3 
(Fig. 1A). About 80% of original 2-pentenal was recovered, and this recovering was 
independent of the presence of phenylacetaldehyde in the reaction mixture. 2-Pentenal 
recovering was fairly constant in the presence of resorcinol, hydroquinone, and 1,2,4-
trihydroxyphenol. However, it decreased significantly (p < 0.05) in the presence of 
phloroglucinol. In fact, only 56% of the original 2-pentenal was recovered when heated 
in the presence of this phenolic compound, and this percentage was similar when 2-
pentenal was heated only with the phenolic compound (binary mixture) or when the 
mixture also contained phenylacetaldehyde (ternary mixture).

Differently to 2-pentenal, phenylacetaldehyde was less stable, and only 50% of 
original phenylacetaldehyde was recovered after 1 h heating at 180 ºC in sodium citrate
buffer, pH 3 (Fig. 1B). This percentage was similar for phenylacetaldehyde heated in
the presence or in the absence of 2-pentenal. However, it decreased when heated in the
presence of most phenols. Thus, resorcinol, hydroquinone, and 1,2,4-trihydroxybenzene
decreased slightly the amount of phenylacetaldehyde recovered (the phenylacetaldehyde
recovered in the presence of these phenols was 39–47%), and there were not significant
differences when 2-pentenal was, or not, present. The decrease in the amount of
phenylacetaldehyde recovered after heating was much higher in the presence of
phloroglucinol. In the presence of this phenolic compound, only 7–9% of the original
phenylacetaldehyde was recovered at the end of the heating process.

3.2. Antagonism between 2-pentenal and phenolic compounds for phenylacetaldehyde
formation in ternary mixtures of phenylalanine, 2-pentenal and phenolic compounds.

Although 2-pentenal and phenolic compounds converted phenylalanine into
phenylacetaldehyde, the simultaneous presence of both kinds of compounds usually
reduced the amount of phenylacetaldehyde that should have been produced considering
the phenylacetaldehyde produced by both kinds of compounds when added
independently. This antagonism was calculated from the data shown in Table 1
according to the following equation

\[
\text{antagonism (\%)} = \frac{\text{expected phenylacetaldehyde} - \text{produced phenylacetaldehyde}}{\text{expected phenylacetaldehyde}} \times 100
\]

where the produced phenylacetaldehyde was the phenylacetaldehyde determined
experimentally in the ternary mixtures and the expected phenylacetaldehyde was
calculated by adding the phenylacetaldehyde produced by each component in the binary
mixtures.

The exhibited antagonism is shown in Fig. 3. In general, most of the determined
antagonisms between 2-pentenal and the assayed phenols was about 25%. This occurred
for catechol, resorcinol, 2,6-dihydroxybenzoic acid, hydroquinone, benzoquinone, and 1,2,4-hydroxybenzene. However, three of the assayed phenols clearly exhibited a reduced antagonism. They were 3,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, and pyrogallol. On the other hand, the antagonism exhibited between 2-pentenal and phloroglucinol was clearly higher: around 70%.

4. Discussion

Strecker-type degradation of amino acids is produced by a number of carbonyl compounds, including carbohydrates (Guerra & Yaylayan, 2013), lipid-derived reactive carbonyls (Hidalgo & Zamora, 2004), amino acid-derived reactive carbonyls (Hidalgo, Alcón, & Zamora, 2013), polyphenol-derived quinones (Rizzi, 2006), and polyphenols (Delgado, Zamora, & Hidalgo, 2015), among others. A pathway for phenylalanine degradation in the presence of 2-pentenal is suggested in Fig. 4. This pathway is based on the studies of amino acid degradation in the presence of carbonyl compounds discussed by Rizzi (2008). As can be observed, the first step is the formation of the corresponding imine between the amino group of the amino acid and the carbonyl group. This imine undergoes then a thermally induced, irreversible decarboxylation. The reason for this decarboxylation can be better understood from the zwitterionic form of the imine. Finally, the produced azomethine ylide undergoes addition of water to produce the Strecker aldehyde (phenylacetaldehyde) and an unstable enamine. The easiness of the imine decarboxylation in relation to the analogous decarboxylation of the amino acid is the responsible for the much higher yield of phenylacetaldehyde produced in phenylalanine/2-pentenal mixtures than in phenylalanine heated alone (Table 1).

The presence of phenolic compounds introduces alternative routes in this reaction pathway. Fig. 4 shows the reactions with resorcinol, but analogous reactions also take
place with other \textit{m-di-} or triphenol derivatives (Salazar, Arámbula-Villa, Hidalgo, &
Zamora, 2014). \textit{m-Diphenols} are able to react with both 2-pentenal and
phenylacetaldehyde. The reaction with 2-pentenal was studied by Hidalgo & Zamora
(2014). These authors found that a number of carbonyl-phenol adducts are produced,
including $2H$-chromenols, chromandiols, chromanols, and dihydropyrano[3,2-
g]chromenes, some of which are only intermediates in the formation of polymeric
structures. Fig. 4 shows only the structures of two of the simplest produced adducts:
$2H$-chromenols and chromandiols.

Phenylacetaldehyde also reacts with phenolic compounds. This reaction was studied
by Chen et al. (2009). The reaction takes place by addition of the aromatic CH group in
\textit{ortho} to one of the hydroxyl groups of the phenolic compound to the carbonyl carbon of
the aldehyde. The produced adduct can suffer then a dehydration to produce the
conjugated structure shown in Fig. 4.

Therefore, \textit{m}-diphenols should inhibit the reaction between phenylalanine and 2-
pentenal by scavenging either the initial aldehyde or the final phenylacetaldehyde. For
that reason, when the reaction between phenylalanine and 2-pentenal was carried out in
the presence of resorcinol, 2,6-dihydroxybenzoic acid and phloroglucinol, the amount of
phenylacetaldehyde determined was lower than when the phenolic compounds were
absent (Table 1). In particular, the phenylacetaldehyde formed in the presence of
phloroglucinol was similar to the phenylacetaldehyde formed by phenylalanine in the
absence of carbonyl compounds (Table 1). The reason for that was the high carbonyl-
scavenging power of phloroglucinol. As shown in Fig. 2, phloroglucinol exhibited a
significant 2-pentenal-scavenging power, but it was especially good for removing
phenylacetaldehyde, which almost disappeared when mixtures of phenylacetaldehyde
and phloroglucinol were heated either in the presence or in the absence of 2-pentenal.
The effect of \(o\)- and \(p\)-diphenols was different. These compounds are oxidized upon heating and the formed quinones are able to produce the Strecker degradation of amino acids (Delgado, Zamora, & Hidalgo, 2015). As shown in Fig. 5, catechol, as an example of \(o\)-diphenol, is converted into 1,2-benzoquinone upon heating and this quinone reacts with amino acids analogously to other carbonyl compounds. Thus, it forms the corresponding imine, which can be decarboxylated through the zwitterionic form of the imine. Finally, the produced azomethine ylide undergoes addition of water to produce the Strecker aldehyde (phenylacetaldehyde) and an aminophenol. Therefore, \(o\)- and \(p\)-diphenols and analogous triphenols increased the formation of phenylacetaldehyde in comparison to the aldehyde produced by decomposition of phenylalanine in the absence of carbonyl compounds (Table 1).

The differences observed in the phenylacetaldehyde produced in either the presence of phenols or 2-pentenal is likely related to both the stability of the azomethine ylide formed and the yield of the conversion of the phenol into quinone. Thus, the azomethine ylide produced in the reaction with quinones is highly delocalized because of the aromatic ring, and should be more stable than the corresponding azomethine ylide formed from 2-pentenal. For that reason, it should be expected that the decarboxylation of the imine would be easier with quinones than with 2-pentenal. In fact, phenylacetaldehyde was produced to a lower extent in phenylalanine/2-pentenal mixtures (43.7 \(\mu\)mol of phenylacetaldehyde/mmol of phenylalanine) than in phenylalanine/benzoquinone mixtures (105.4 \(\mu\)mol of phenylacetaldehyde/mmol of phenylalanine). However, when reactions were carried out with phenols and not with the quinone, the yields were lower more likely because of the limited conversion of the phenol into the corresponding quinone (Table 1). In fact, the phenylacetaldehyde
produced in phenylalanine/2-pentenal mixtures was quite similar to the phenylacetaldehyde produced in mixtures of phenylalanine with \( o \)- and \( p \)-diphenols.

Independently of the positions of the hydroxyl groups, when phenols and 2-pentenal were added simultaneously, an antagonism was mostly observed (Fig. 3). The reason for this antagonism is clear in the case of \( m \)-diphenols because they remove the carbonyl compounds responsible for amino acid degradation from the media. This effect was clearly observed for phloroglucinol, which, according to the results shown in Fig. 2, is a powerful phenylacetaldehyde scavenger and, to a lower extent, also a 2-pentenal scavenger. For that reason, antagonism was very high between 2-pentenal and phloroglucinol (66-72% as shown in Fig. 3). Contrarily to the antagonism between 2-pentenal and \( m \)-di- and triphenols, the reason for the antagonism exhibited by \( o \)- and \( p \)-diphenols is not so clear. This antagonism does not seem to be related to an inhibition of the conversion of the phenolic compounds into quinones because hydroquinone and benzoquinone exhibited a similar antagonism. On the contrary, it seems to be related to a promotion of phenylacetaldehyde disappearance as observed in Fig. 2B. This promotion of phenylacetaldehyde disappearance was similar for resorcinol, hydroquinone, and 1,2,4-trihydroxybenzene. For that reason, cathecol, resorcinol, hydroquinone, and 1,2,4-trihydroxybenzene exhibited a similar antagonism with 2-pentenal (Fig. 3). Different to these phenolic derivatives, 3,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, and pyrogallol, exhibited a reduced antagonism with 2-pentenal (Fig. 3), which remains to be clarified.

All these results confirm that the Strecker degradation of amino acids is produced by different carbonyl compounds. However, when several of them are present simultaneously, there are interactions among them that mostly produce a reduction of the amount of Strecker aldehyde that should have been produced. This reduction is
particularly important for \textit{m}-diphenols, which are able to scavenge both the carbonyl compounds responsible for the Strecker degradation of the amino acid and also the produced Strecker aldehydes. These results are in agreement with the reduction of off-flavor development in Maillard chemistry produced when using phenols (Kokkinidou & Peterson, 2014) and with the aromas developed during cooking of vegetables with different culinary techniques due to the large amount and variety of phenolic compounds and the possible interactions with other food components (Kebede et al., 2013). They also point out to carbonyl-phenol reactions as a way to modulate flavor formation produced by lipid-derived carbonyl compounds in food products.

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References


**Figure legends**

**Fig. 1.** Chemical structures of phenolic compounds, and analogous compounds, employed in this study.

**Fig. 2.** 2-Pentenal and phenylacetaldehyde recovered from mixtures of 2-pentenal, phenylacetaldehyde, and phenolic compounds heated for 1 h at 180 °C. 2-Pentenal recovering (panel A) was determined in binary mixtures of 2-pentenal and phenolic compounds (striped bars) and in ternary mixtures of 2-pentenal, phenylacetaldehyde and phenolic compounds (open bars). Phenylacetaldehyde recovering (panel B) was determined in binary mixtures of phenylacetaldehyde and phenolic compounds (striped bars) and in ternary mixtures of phenylacetaldehyde, 2-pentenal and phenolic compounds (open bars).

**Fig. 3.** Antagonism among 2-pentenal and phenolic compounds in the formation of phenylacetaldehyde in ternary mixtures of phenylalanine, 2-pentenal, and phenolic compounds heated for 1 h at 180 ºC. Two amounts of phenolic compounds were employed in the mixtures: 25 µmol (striped bars) and 50 µmol (open bars).

**Fig. 4.** Reaction pathway for phenylacetaldehyde formation by phenylalanine degradation in the presence of 2-pentenal and inhibition by m-diphenols.

**Fig. 5.** Competitive reaction pathways for phenylacetaldehyde formation by phenylalanine degradation in the presence of 2-pentenal and o- and p-diphenols.
| Phenol tested                        | 25 µmol of phenol | 50 µmol of phenol |  |  |
|-------------------------------------|--------------------|--------------------|  |  |
|                                     | Without 2-pentenal | With 2-pentenal    | Without 2-pentenal | With 2-pentenal |
| None                                | 11.7 ± 1.4         | 43.7 ± 7.4         | 11.7 ± 1.4         | 43.7 ± 7.4      |
| Catechol                            | 26.0 ± 6.0 *       | 44.8 ± 11.5        | 28.6 ± 5.4 **      | 44.7 ± 9.6      |
| 3,4-Dihydroxybenzoic acid           | 19.7 ± 6.6         | 51.9 ± 12.7        | 36.2 ± 1.5 ***     | 61.8 ± 15.1 *   |
| Resorcinol                          | 11.2 ± 2.1         | 33.9 ± 8.0         | 16.1 ± 2.9         | 36.5 ± 1.0      |
| 2,6-Dihydroxybenzoic acid           | 12.9 ± 3.0         | 31.0 ± 6.6 *       | 12.0 ± 2.7         | 40.4 ± 10.8     |
| Hydroquinone                        | 57.4 ± 7.9 ***     | 68.1 ± 15.3 **     | 58.1 ± 1.4 ***     | 56.1 ± 9.6      |
| 2,5-Dihydroxybenzoic acid           | 27.0 ± 1.7 **      | 52.2 ± 4.8         | 29.2 ± 1.0 ***     | 57.3 ± 14.2     |
| Benzoquinone                        | 105.4 ± 17.8 ***   | 103.2 ± 19.0 ***   | 126.3 ± 12.2 ***   | 106.0 ± 4.1 *** |
| Pyrogallol                          | 38.3 ± 4.5 ***     | 84.5 ± 7.7 ***     | 47.9 ± 11.7 **     | 74.9 ± 11.8 **  |
| 1,2,4-Trihydroxybenzene             | 40.6 ± 10.2 **     | 57.2 ± 9.6 *       | 49.4 ± 9.1 **      | 50.9 ± 12.9     |
| Phloroglucinol                      | 12.8 ± 3.4         | 15.2 ± 2.0 ***     | 12.6 ± 2.9         | 12.3 ± 2.7 ***  |

Values are mean ± SD (in µmol of phenylacetaldehyde/mmol of phenylalanine) for, at least, three independent experiments. Means in the same column with an asterisk are significantly different from its control: * \((p < 0.05)\), ** \((p < 0.01)\), *** \((p < 0.001)\). Reaction mixtures contained 25
µmol of phenylalanine, 25 µmol of 2-pentenal, and the indicated amount of phenolic compound. Benzoquinone is not a phenol, but it was assayed for comparison purposes.
Figure 1
Figure 2
Figure 3
Figure 4