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

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Abbreviated running title: Antagonism between carbonyls and phenols for amino acid degradation

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 α-dicarbonyl compounds produced by carbohydrate dehydratation 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: cathecol (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

84 included for comparison purposes. Phenolic compounds, phenylalanine, 2-pentenal, and
85 other chemicals were purchased from Aldrich (Milwakee, WI), Sigma (St. Louis, MO),
86 Fluka (Buchs, Switzerland), or Merck (Darmstadt, Germany), and were of the highest
87 available quality.

88 *2.2. Formation of phenylacetaldehyde in binary and ternary mixtures of phenylalanine,*
89 *2-pentenal, and phenolic compounds*

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

96 *2.3. Phenylacetaldehyde and 2-pentenal concentration changes in the presence of*
97 *phenols*

98 Mixtures of phenylacetaldehyde (25 μmol), 2-pentenal (25 μmol), and the phenolic
99 compound (25 μmol) in 500 μL of 0.3 M citrate buffer, pH 3, were introduced in closed
100 test tubes and heated at 180 ºC for 1 h. After cooling (10 min at room temperature),
101 samples were diluted with 1 mL of acetonitrile and 50 μL of internal standard solution
102 (54.8 mg of methyl heptanoate in 25 mL of ethanol) added. Phenylacetaldehyde and 2-
103 pentenal were determined by GC-MS.

104 *2.4. GC-MS analyses*

105 GC-MS analyses were conducted with a Hewlett-Packard 6890 GC Plus coupled
106 with an Agilent 5973 MSD (mass selective detector, quadrupole type). A fused-silica
107 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 ºC; oven temperature programmed from 40 ºC (1 min) to 240 ºC at 5 ºC/min and then to 300 ºC at 10 ºC/min; transfer line to MSD, 280 ºC; ionization EI, 70 eV; ion source temperature, 230 ºC; 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 μmol of the phenolic compound were added and by 144–397% when 50 μmol 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 μmol of these trihydroxy derivatives were added and by 309–322% when 50 μmol 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 happened for resorcinol, 2,6-dihydroxybenzoic acid, and phloroglucinol.

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 μmol of hydroquinone, benzoquinone,

157 pyrogallol or 1,2,4-trihydroxybenzene, or 50 μmol of 3,4-dihydroxybenzoic acid,
158 benzoquinone or pyrogallol were added (Table 1). In addition, there was not a clear
159 difference in the amount of phenylacetaldehyde formed when either 25 or 50 μmol of
160 phenolic compound was employed. On the other hand, addition of 2,6-
161 dihydroxybenzoic acid or phloroglucinol at 25 μmol or phloroglucinol at 50 μmol,
162 significantly reduced the phenylacetaldehyde produced.

163 *3.3. Phenylacetaldehyde and 2-pentenal disappearance in the presence of phenols*

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

170 2-Pentenal was quite stable after 1 h heating at 180 ºC in sodium citrate buffer, pH 3
171 (Fig. 1A). About 80% of original 2-pentenal was recovered, and this recovering was
172 independent of the presence of phenylacetaldehyde in the reaction mixture. 2-Pentenal
173 recovering was fairly constant in the presence of resorcinol, hydroquinone, and 1,2,4-
174 trihydroxyphenol. However, it decreased significantly ($p < 0.05$) in the presence of
175 phloroglucinol. In fact, only 56% of the original 2-pentenal was recovered when heated
176 in the presence of this phenolic compound, and this percentage was similar when 2-
177 pentenal was heated only with the phenolic compound (binary mixture) or when the
178 mixture also contained phenylacetaldehyde (ternary mixture).

179 Differently to 2-pentenal, phenylacetaldehyde was less stable, and only 50% of
180 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 phenyalcetaldehyde 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

$$antagonism\ (\%) = \frac{expected\ phenylacetaldehyde - produced\ phenylacetaldehyde}{expected\ phenylacetaldehyde} * 100$$

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 *m*-di- or triphenol derivatives (Salazar, Arámbula-Villa, Hidalgo, & Zamora, 2014). *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 2*H*-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: 2*H*-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 *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, *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 phlorogucinol, 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 μmol of phenylacetaldehyde/mmol of phenylalanine) than in phenylalanine/benzoquinone mixtures (105.4 μmol 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

279 produced in phenylalanine/2-pentenal mixtures was quite similar to the
280 phenylacetaldehyde produced in mixtures of phenylalanine with *o*- and *p*-diphenols.

281 Independently of the positions of the hydroxyl groups, when phenols and 2-pentenal
282 were added simultaneously, an antagonism was mostly observed (Fig. 3). The reason for
283 this antagonism is clear in the case of *m*-diphenols because they remove the carbonyl
284 compounds responsible for amino acid degradation from the media. This effect was
285 clearly observed for phloroglucinol, which, according to the results shown in Fig. 2, is a
286 powerful phenylacetaldehyde scavenger and, to a lower extent, also a 2-pentenal
287 scavenger. For that reason, antagonism was very high between 2-pentenal and
288 phloroglucinol (66-72% as shown in Fig. 3). Contrarily to the antagonism between 2-
289 pentenal and *m*-di- and triphenols, the reason for the antagonism exhibited by *o*- and *p*-
290 diphenols is not so clear. This antagonism does not seem to be related to an inhibition of
291 the conversion of the phenolic compounds into quinones because hydroquinone and
292 benzoquinone exhibited a similar antagonism. On the contrary, it seems to be related to
293 a promotion of phenylacetaldehyde disappearance as observed in Fig. 2B. This
294 promotion of phenylacetaldehyde disappearance was similar for resorcinol,
295 hydroquinone, and 1,2,4-trihydroxybenzene. For that reason, cathecol, resorcinol,
296 hydroquinone, and 1,2,4-trihydroxybenzene exhibited a similar antagonism with 2-
297 pentenal (Fig. 3). Different to these phenolic derivatives, 3,4-dihydroxybenzoic acid,
298 2,5-dihydroxybenzoic acid, and pyrogallol, exhibited a reduced antagonism with 2-
299 pentenal (Fig. 3), which remains to be clarified.

300 All these results confirm that the Strecker degradation of amino acids is produced by
301 different carbonyl compounds. However, when several of them are present
302 simultaneously, there are interactions among them that mostly produce a reduction of
303 the amount of Strecker aldehyde that should have been produced. This reduction is

particularly important for *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 at 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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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 ºC. 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.

Table 1

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

	25 μmol of phenol		50 μmol of phenol	
Phenol tested	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.

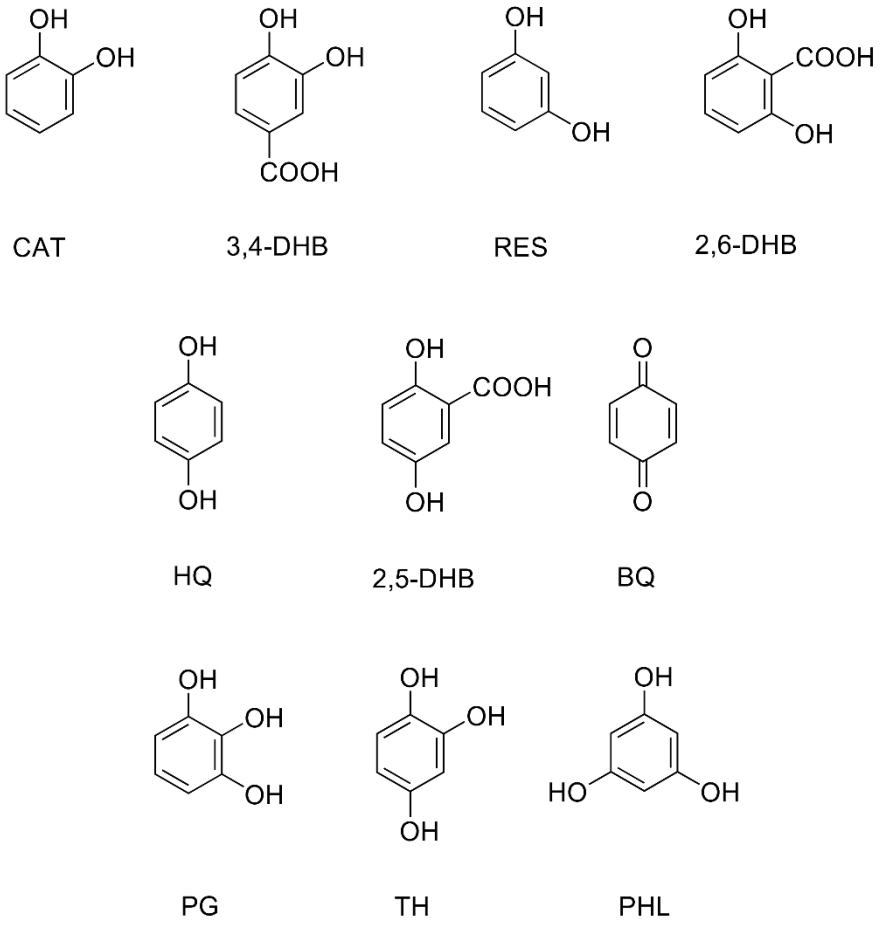
OH
OH
CAT
OH
OH
COOH
3,4-DHB
OH
OH
RES
OH
COOH
OH
2,6-DHB
OH
OH
HQ
OH
COOH
OH
2,5-DHB
O
O
BQ
OH
OH
OH
PG
OH
OH
OH
TH
OH
HO
OH
PHL

Figure 1

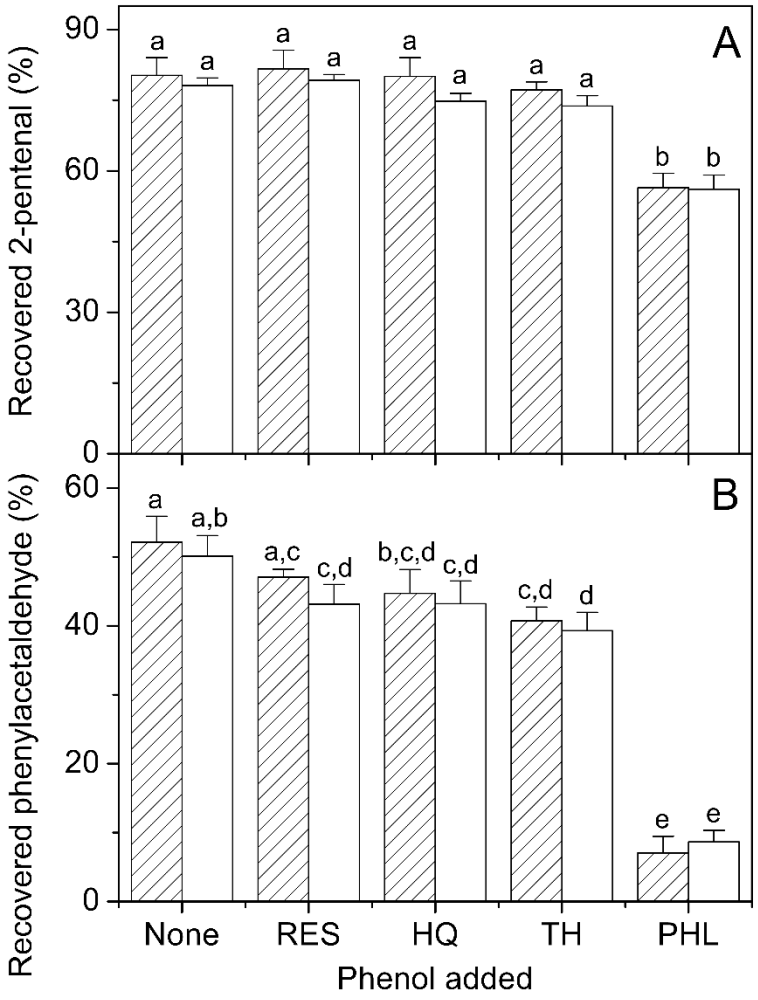
A
B
Recovered 2-pentenal (%)
Recovered phenylacetaldehyde (%)
90
60
30
0
60
40
20
0
a
a
a
a
a
a
a
a
b
b
a
a,b
a,c
c,d
b,c,d
c,d
c,d
d
e
e
None
RES
HQ
TH
PHL
Phenol added

Figure 2

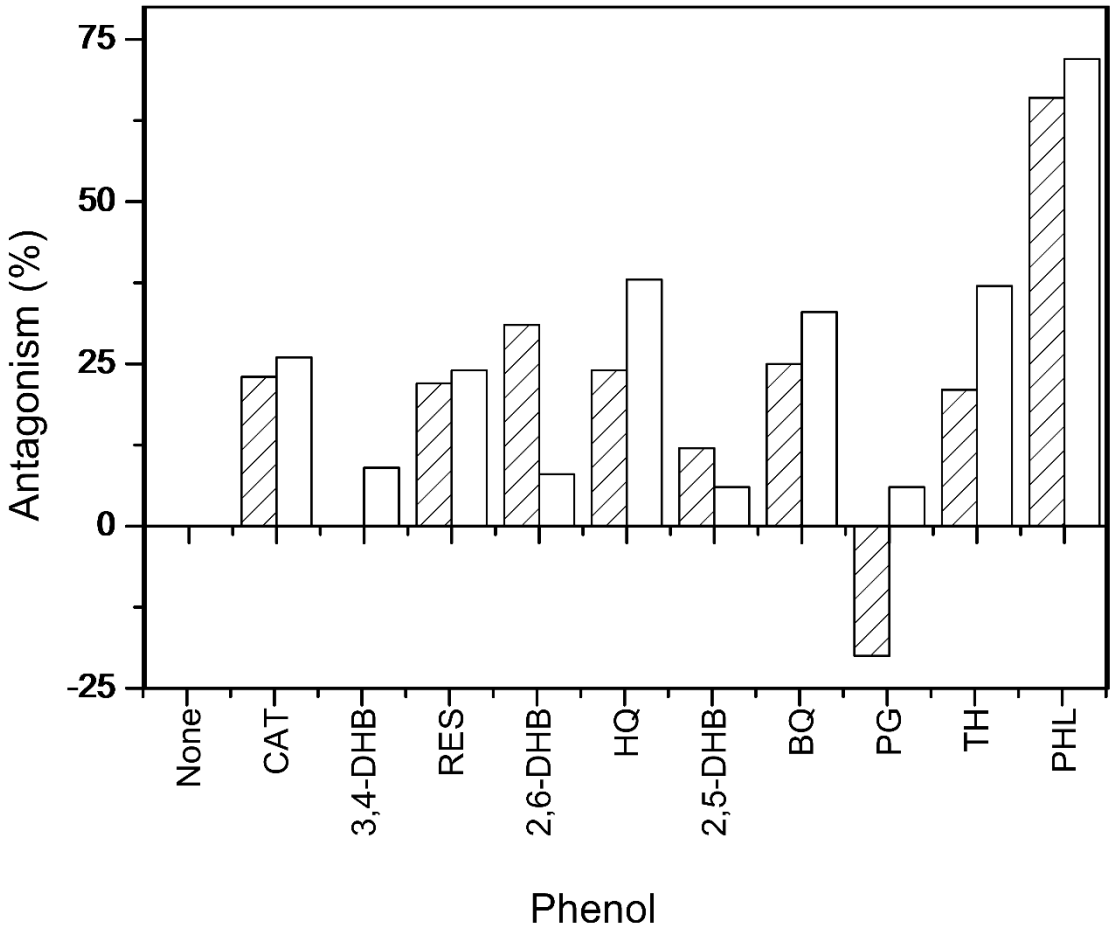
75
50
25
0
-25
Antagonism (%)
None
CAT
3,4-DHB
RES
2,6-DHB
HQ
2,5-DHB
BQ
PG
TH
PHL
Phenol

Figure 3

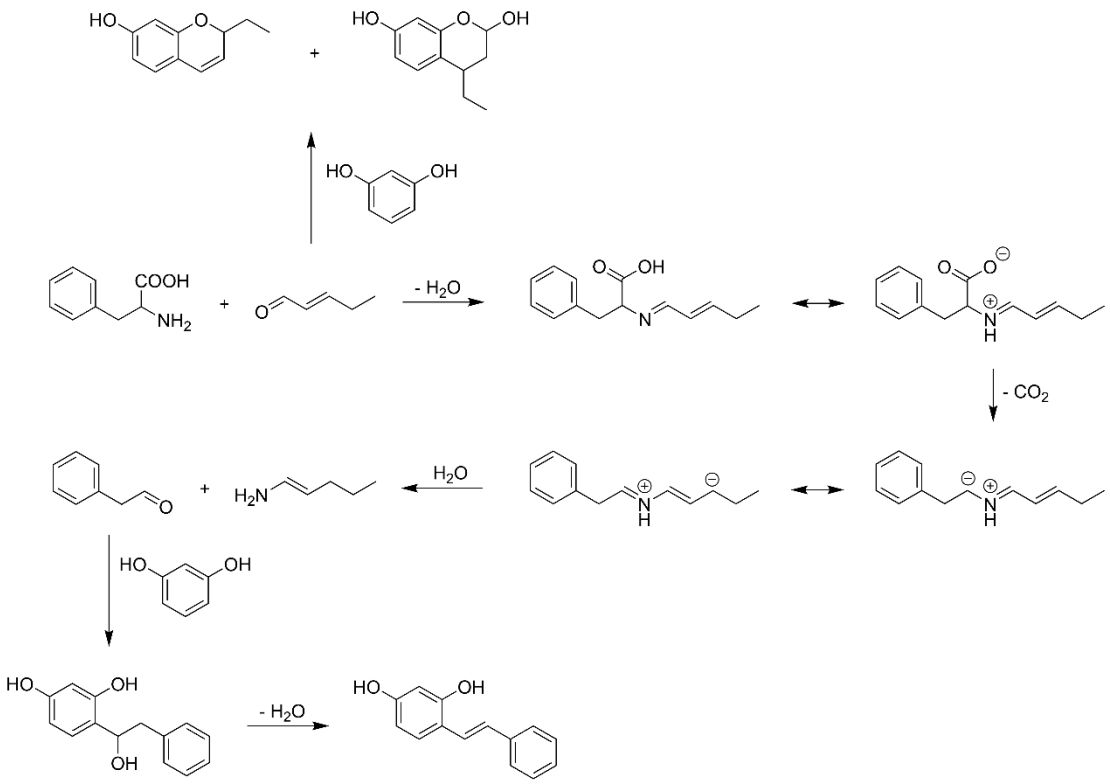
HO
O
OH
+
HO
OH
COOH
NH2
+
O
- H2O
OH
O
N
O
O
N
H
- CO2
O
+
H2N
H2O
N
H
N
H
HO
OH
HO
OH
OH
- H2O
HO
OH

Figure 4

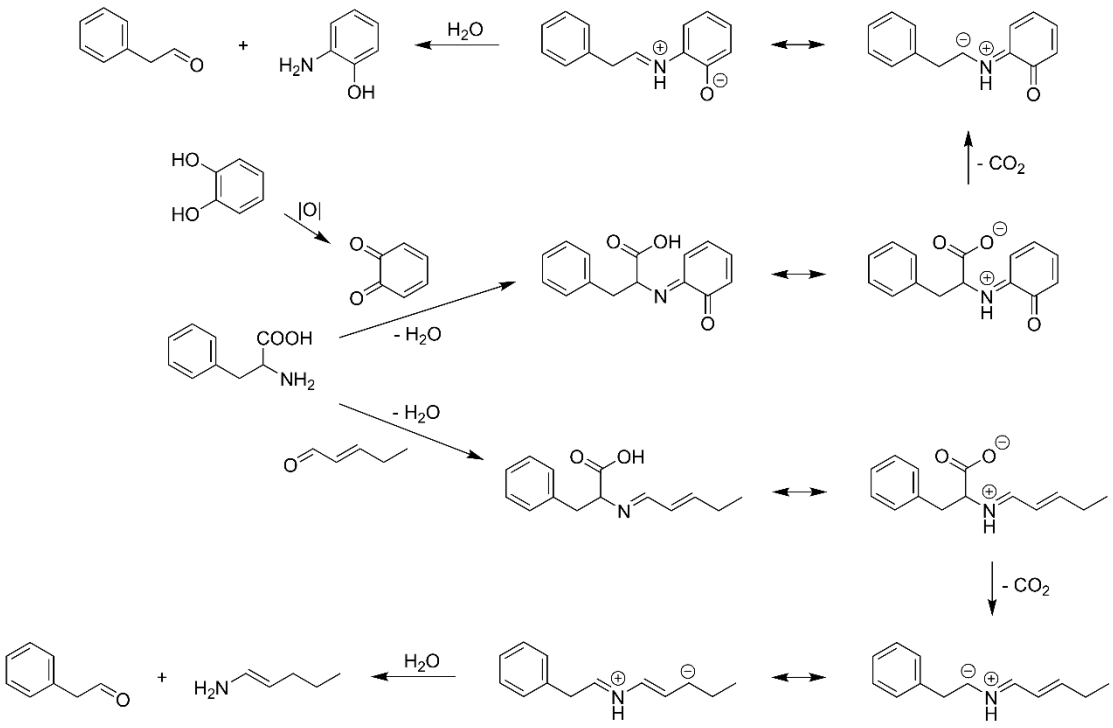

Figure 5