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Aqueous degradation of esculetin (6,7-dihydroxycoumarin) using gamma radiation

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ABSTRACT

The degradation by gamma radiation of esculetin (6,7-dihydroxycoumarin), an emerging contaminant present in olive mill and cork wastewaters, was studied using different irradiation atmospheres (aerated, N_2O and N_2+tert-butanol). The obtained results indicated that the highest degradation of esculetin was achieved in solutions saturated with N_2+tert-butanol, irradiated at 1 kGy. Therefore, these results demonstrated that this technology could be effective for the degradation of phenolic compounds present in industrial wastewaters. A tentative mechanism was proposed for esculetin degradation. From the results, it appeared that the solvated or aqueous electron dominated the removal of esculetin when compared with attack by the hydroxyl radical. These outcomes contribute to a better understanding of how these compounds degrade under radiation treatment and could provide better insight into the reaction mechanisms for other polyphenolic compounds.

Keywords: Esculetin; Fluorescence; Polyphenols; Radiolysis; Recalcitrant compounds

1. Introduction

In Portugal, the olive oil and cork industries are important contributors to the country economy. During the processing of olive oil, a highly contaminating olive mill wastewater is generated. This waste production in Mediterranean countries is estimated to be over 30 million m^3/year [1] and is a complex mixture of water (83%–96%), sugars, organic acids, tannins, lipids and inorganic substances [2]. The Portuguese cork industry exports around 70% of the world market and produces large quantities of wastewater during the cooking process. This wastewater is a dark liquor with high concentrations of tannins, lipids and organic acids [3]. In both processes (olive oil production and cork industry), wastewaters have high content in phenolic compounds which contributes for their low biodegradability and high phytotoxicity [4–6].

Advanced oxidation processes (AOPs) are considered efficient technologies to degrade complex compounds, such as pharmaceuticals [7], pesticides [8] and dyes [9]. The mechanism of radiolysis and its highly reactive species responsible for AOPs efficiency has been widely studied by several authors [10,11]. In particular, there are works reporting the treatment of olive mill and cork wastewaters, including

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ozonation [12–14], Fenton's reagent [14,15], membrane separation [16,17], electrochemical oxidation [18] and other methods using the combination of two or more processes [1,19–23]. Meanwhile, ionizing radiation has proven to be an effective technology in reducing the impact of chemical and biological pollution of effluents in the environment [24,25].

Among others, the most abundant phenolic compounds present in cork wastewater are gallic acid, protocatechuic acid, vanillic acid and syringic acid [26] while in olive oil wastewater the major compounds are hydroxytyrosol, tyrosol, p-coumaric acid, gallic acid and caffeic acid [4]. As mentioned above, these phenolic compounds are non-biodegradable pollutants, being a risk for environment and human health. In this context, some studies were performed using AOPs to study the degradation of these compounds. Baransi et al. [22] studied the synergetic effect between photocatalytic degradation and adsorption processes on the removal of p-coumaric acid and caffeic acid. The degradation of caffeic and p-coumaric acids was also studied in a mixture with vanillic and syringic acids by single UV radiation and the combination of ozone and UV radiation [27], being the combination of the processes more efficient due to the action of hydroxyl radicals generated from both oxidant agents. Also Benitez et al. [28] studied the degradation of gallic acid using UV/H_2O_2, Fenton's reagent and the combination of Fenton's reagent with UV radiation (photo-Fenton system) were also used, being photo-Fenton the most effective process for gallic acid removal from aqueous solution. The efficient use of gamma radiation on the degradation of phenolic acids was also demonstrated [29,30]. Madureira et al. [30] studied the degradation of phenolic acids present in cork wastewaters (gallic acid, protocatechuic acid, vanillic acid and syringic acid) in isolated and mixture aqueous solutions using gamma radiation and different conditions (pH and irradiation atmospheres). The authors observed higher degradation in isolated compounds solutions; thus indicating a protective effect in the quaternary mixture solution. The saturation with N_2O promoted the highest degradation for all phenolic acids in the mixture; however, at natural pH and in air the degradation was higher than 50% for gallic, vanillic and syringic acids at 20 kGy. The oxidation of these compounds by the hydroxyl radical seems to be the most important pathway for pollutants degradation [31]. Madureira et al. [30] and Melo et al. [29] proposed the fragmentation pathways for the studied phenolic acids, however, in many cases there is a lack of information about the by-products formed by AOPs. This information is important considering the possibility that the by-products might be as toxic as the parent compound.

Esculetin (6,7-dihydroxycoumarin; Fig. 1) is one of the representative compounds reported in both cork cooking water and olive oil wastewater. Acero et al. [32] studied the chemical oxidation of esculetin with single oxidants (ozone, UV radiation, hydroxyl radicals) but the corresponding degradation mechanism is still unexplained.

The aim of this work was to study the degradation of esculetin using gamma radiation as a clean AOP, determining the formed stable by-products in order to propose its degradation mechanism [33]. Esculetin decomposition was followed by UV-Vis spectrophotometry and excitation-emission matrix (EEM) fluorescence spectroscopy. The reactions of hydroxyl radical ($^{\bullet}OH$) and hydrated electron (e^-_{aq}) were considered to a deeper understanding of the esculetin degradation mechanism, saturating the solutions with N_2O and N_2+tert-butanol, respectively. These studies were conducted at lower esculetin concentrations than observed in natural wastewaters to enable the use of water as solvent, since esculetin is only slightly soluble in water. In the complex wastewater, however, its solubility is modified by the presence of co-solutes (organic compounds) or by higher temperatures associated with the treatment and/or processing [34].

2. Materials and methods

2.1. Chemicals

Esculetin (6,7-dihydroxycoumarin; Fig. 1) was obtained from Sigma-Aldrich (St. Louis, USA) and used as received. Acetic acid with >99.8% purity was supplied by Riedel-de Haën (Seelze, Germany) and HPLC grade acetonitrile (CH_3CN) was acquired from Carlo Erba (Val-de-Reuil, France). Water was treated in a Milli-Q water purification system (Merck Millipore, USA).

2.2. Sample preparation

The esculetin solution (0.1 mmol/dm^3) was prepared with extra pure water and all experiments were carried out at pH (6.63). At this pH value, esculetin is mainly in the protonated form (pKa = 7.34) [32]. The reaction mediated by hydrated electron (e^-_{aq}) with esculetin was studied in N_2 saturated 5% by volume tert-butanol containing solution. The reaction involving only hydroxyl radicals ($^{\bullet}OH$) was achieved by presaturating the solution with N_2O [35]. N_2 and N_2O gases were supplied by Air Liquide (Lisbon, Portugal).

2.3. Irradiation experiments

To study reaction by-products and to determine the degradation efficiency, steady-state experiments were conducted in a ^{137}Cs source (662 keV gamma irradiation, J.L. Shepherd Mark I Model A68 irradiator). The system has a fixed central source rod in a cavity (30 cm diameter and 33 cm high). Samples in glass test tubes were placed in a rack with a specific distance from the source guide tube to provide dose rate of 2 kGy h^{-1} and varying the irradiation time to obtain absorbed dose from 0.5 kGy up to 50 kGy. The local dose rate had been previously determined by Fricke method [36].

2.4. Analytical procedures

The degradation efficiency was evaluated by UV-Vis absorbance using a Shimadzu 1603 double beam spectrophotometer (Kyoto, Japan). Besides UV-Vis spectrophotometry, EEM fluorescence spectroscopy was used to follow the behavior of esculetin under gamma irradiation. Thus, EEM spectra of the non-irradiated and irradiated solutions were recorded using a FluoroMax-4 (Horiba-Jobin Yvon , Kyoto, Japan). The fluorometer was set up as follows: the excitation wavelength was incrementally increased from 230 to 500 nm in

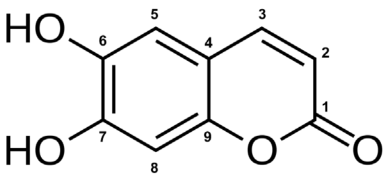

Fig. 1. Chemical structure of esculetin (6,7-dihydroxycoumarin).

5 nm intervals, with emission monitoring from 280 to 600 nm at 5 nm intervals for each excitation wavelength. All esculetin solutions samples were diluted 10 times using Optima LC/MS water to avoid internal absorption. The intensity of all EEM spectra was normalized by dividing by the area of the Raman water line obtained using 350 nm excitation and 397 nm emission wavelengths. The FL Tool Box software was used to correct the spectra for Raman and Raleigh scattering and to calculate EEM peak integrals [37].

Esculetin and its by-products were analyzed by LC-MS according to the method described by Razavi et al. [38].

3. Results and discussion

The effects of gamma radiation on esculetin solutions (0.1 mmol/dm^3) irradiated at different conditions were analyzed by UV-Vis spectrometry (Fig. 2).

The results of the UV-Vis showed that esculetin had two major absorption peaks, a broad peak between 285 and 300 nm and another one at 348 nm. The lower wavelength peak could be attributed to absorption by the benzene moiety and hydroxyl groups in C6 and C7 positions in the ring, respectively (Fig. 1). The peak at 348 nm was related with C2-C3 double bond in the esculetin molecule [39]. The overall spectra (Fig. 2) showed that the absorbance of the peaks decreased with the increase of absorbed doses. This behavior, however, seemed to be more pronounced in the 348 nm peak than in 300 nm peak. Also, for esculetin solution irradiated without gas saturation (Fig. 2a), the obtained results demonstrated a complete degradation of this compound at an absorbed dose of 5 kGy. Moreover, it was observed higher degradation under saturated N_2O and N_2+tert-buitanol solutions (Fig. 2b). In fact, the higher degradation was achieved in solutions saturated with N_2+tert-butanol, irradiated at 1 kGy (Fig. 2b), which proposed the hypothesis that the hydrated electron could be the most important reactive species in the degradation of esculetin. In order to validate these findings, the "dose constant" values were calculated for each set of experiments (Table 1).

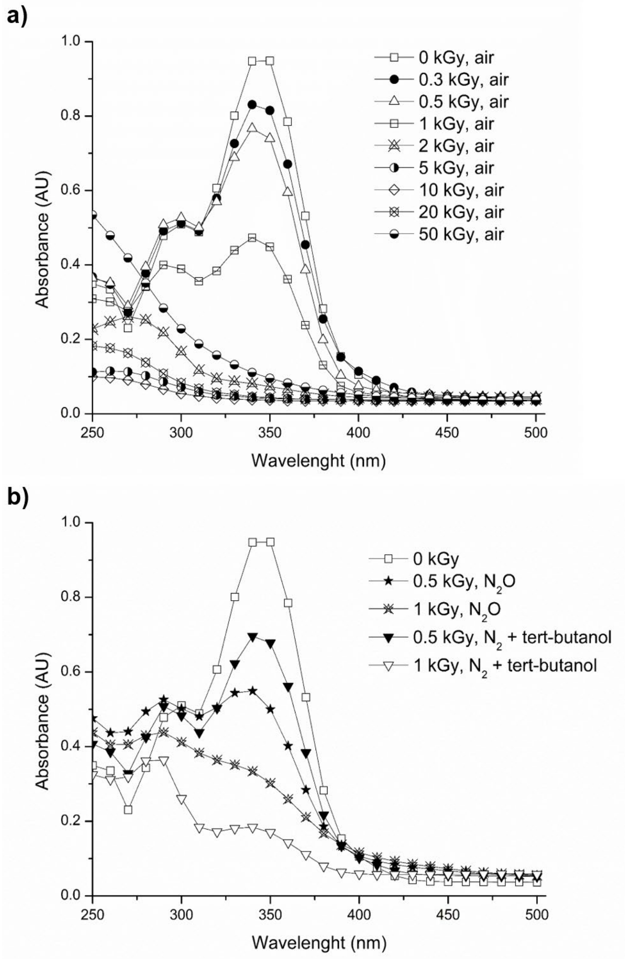

Fig. 2. Optical absorption spectra of 0.1 mmol/dm^3 esculetin solutions non-irradiated and irradiated in aerated conditions (a) and in N_2O saturated solutions and N_2 with tert-butanol (b).

Table 1
Dose constants (kGy^{-1}) of esculetin irradiated solution at different conditions

Experimental conditions	At 348 nm	At 300 nm
All radicals (aerated)	0.671	0.427
$^{\bullet}$OH (N_2O saturated)	0.704	0.304
e^-_{aq} (tert-BuOH + N_2 saturated)	0.833	0.559

The "dose constant" or the overall efficiency of the compound decomposition is the slope obtained from fitting straight lines to removal data plotted as $(ABS_0\text{-}ABS_{dose})/ABS_{dose}$ against absorbed dose [40]. The higher the value of the "dose constant", the more efficient the process mediated by that reactive species. Independently of the experimental condition used, the dose constant was higher at 348 nm than at 300 nm, suggesting that the attack of reactive species on esculetin lead, preferentially, to the break of the C2-C3 double bond. In addition, the hydrated electron reaction seemed to be the most efficient way to degrade esculetin with the highest "dose constant" among the three different experimental conditions (0.833 kGy^{-1} at 348 nm) (Table 1). Thus, the radiation-chemical degradation of esculetin seems to be due to its interaction with the hydrated electron in line with Antropova et al. [39]. Furthermore, as the dose and the concentration of reactive radical species increased, the benzene ring could be destroyed.

Based on the previous results and thinking in a potential application scenario, the proposed mechanism will take into consideration only the degradation at aerated conditions and irradiated at 20 kGy. Tentative structural assignments were based on the analysis of the total ion chromatogram and the corresponding mass spectra obtained by negative ion electrospray LC-MS. To our knowledge, this is the first study trying to identify the radiolytic products of esculetin and its degradation mechanism. The masses of the products were determined from (M-H)/z peaks corresponding to the molecular ion, referred as molecular weight (MW) of esculetin (MW 178) which was detected at a concentration high enough to assign a structure. Analysis by LC-MS only identified one radiolytic product with MW of 164. This proposed radiolytic product (MW 164) and respective reaction pathway are illustrated in Fig. 3.

The structure was consistent with the mass spectra, which confirmed previous studies of the radiolytic degradation mechanism of simple coumarin [41]. Considering the dose constants, the by-product seemed to result from the two main reactive species (hydroxyl radical and hydrated electron) attacks and, the compound with MW 164 was formed with hydrogen peroxide release.

With the increasing doses and considering the initial low concentration of esculetin solution (0.1 mmol/dm^3), the concentration of fragmentation products was probably below LC-MS detection limits. The lack of detection of other reaction products could be related to several factors: (1) A great variety of products were formed, all with very low concentration making detection difficult with LC-MS; (2) The non-aromatic compounds were retained in the LC chromatography column; or (3) a combination of the two reasons.

One of the main physical properties of coumarin derivatives is the intense fluorescence that they display under ultraviolet or visible region. This feature frequently has been employed for detection of coumarins such as scopoletin (6-methoxy-7-hydroxy-coumarin) and esculetin [42]. The EEM fluorescence spectra of diluted non-irradiated and irradiated solutions are presented in Fig. 4.

Comparing the EEM fluorescence spectra, the esculetin signal was faint at 2 kGy (Fig. 4c) and its degradation was almost complete at 5 kGy (Fig. 4d), corroborating the decrease of the absorption peak at 348 nm in Fig. 2. The reduction of fluorescence at 5 kGy could be connected with the disappearance of oxygen double bond on pyrone ring. A new fluorophore appeared at 2 kGy (Fig. 4c) and seemed to disappear at higher absorbed doses. This fluorophore could be related to the new peak that was detected by LC-MS at 2 kGy. The hydroxyl groups are responsible for the aromatic molecules fluorescence [39]. Thus, these results are in accordance with the proposed mechanism (Fig. 3). Fluorescence spectrum at 50 kGy (Fig. 4f) showed that there was a low concentration of fluorophores in the irradiated solution that could indicate a complete degradation of the esculetin structure. Fluorescence spectra could give a comprehensive overall picture of esculetin degradation in aerated solutions.

As far as the authors know, this is the first work reporting the use of gamma radiation for esculetin degradation. Acero et al. [32] studied different single oxidants on esculetin degradation demonstrating that only the combination of two or more processes (photo-Fenton, UV/H_2O_2, O_3/UV/H_2O_2) was effective. Similar degradation efficiencies were obtained in the present study using only one AOP, as gamma radiation, without requiring the addition of any chemicals. Considering the obtained results, ionizing radiation (5 kGy) could be an alternative treatment for industrial wastewater with phenolic content.

4. Conclusions

The degradation of esculetin by gamma radiation was studied. The saturation with N_2+tert-butanol promoted the highest degradation, although the absorbed dose of 5 kGy was enough to achieve the complete decomposition of esculetin in aerated solutions. The obtained results demonstrated that gamma radiation could be applied as an efficient process in the degradation of esculetin and as an alternative technology for the elimination or reduction of recalcitrant compounds in industrial wastewaters. Based on EEM spectroscopy

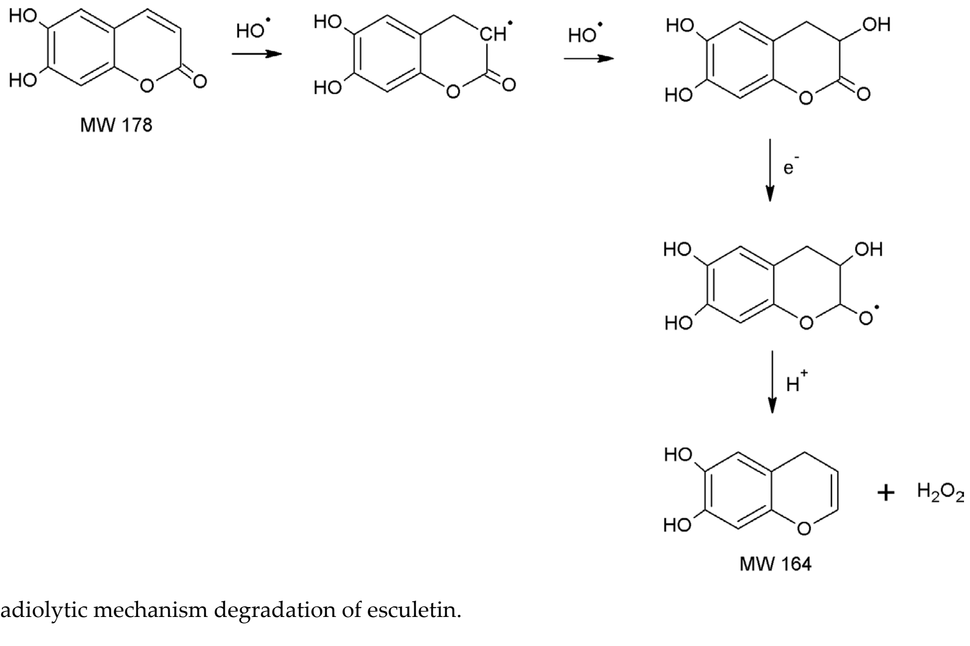

Fig. 3. Proposed radiolytic mechanism degradation of esculetin.

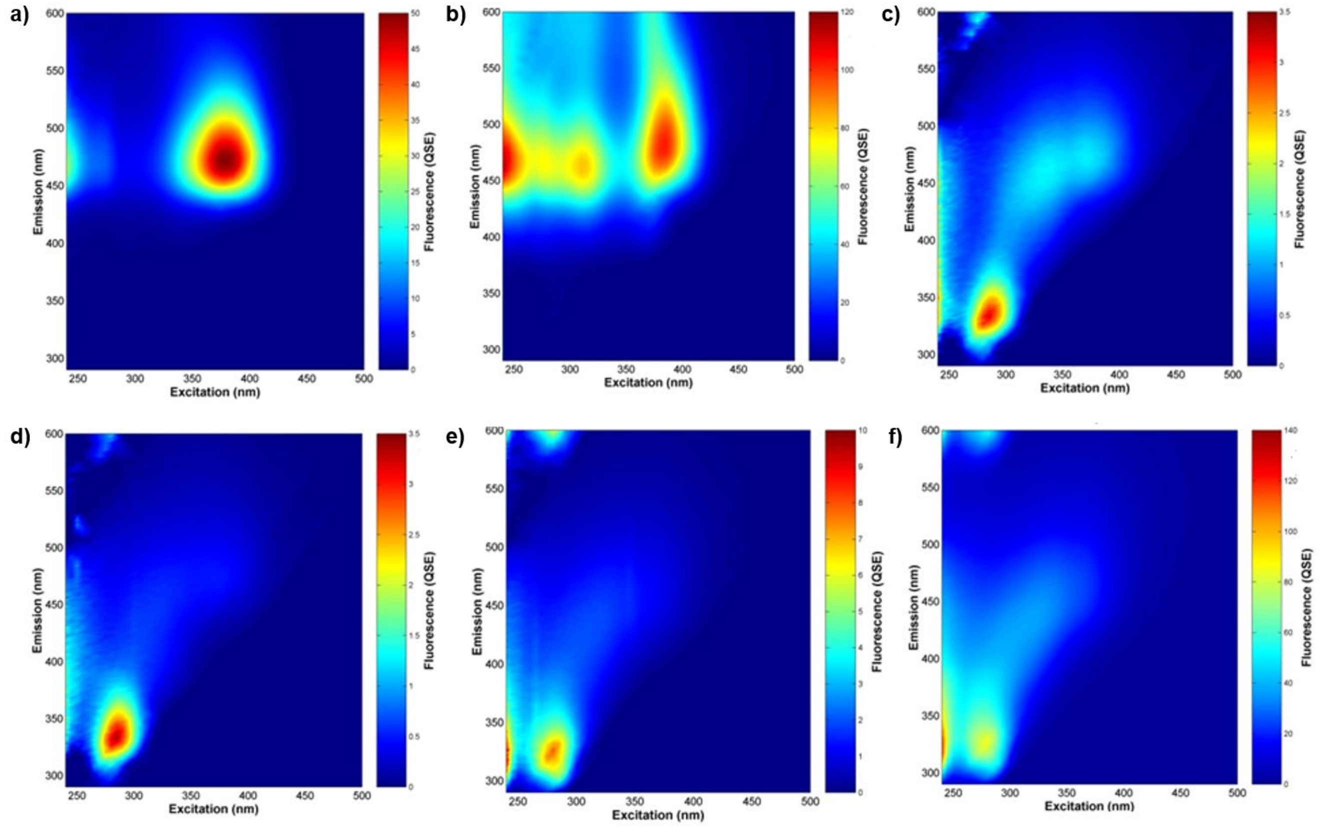

Fig. 4. Excitation-emission fluorescence spectra of non-irradiated and irradiated esculetin solutions: (a) non-irradiated (0 kGy); (b) 1 kGy; (c) 2 kGy; (d) 5 kGy; (e) 20 kGy and (f) 50 kGy.

and LC-MS results, a possible degradation mechanism for esculetin was proposed with the identification of a radiolytic product with MW of 164.

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Declarations of interest

None

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