



## Properties of the humic-like material arising from the photo-transformation of L-tyrosine



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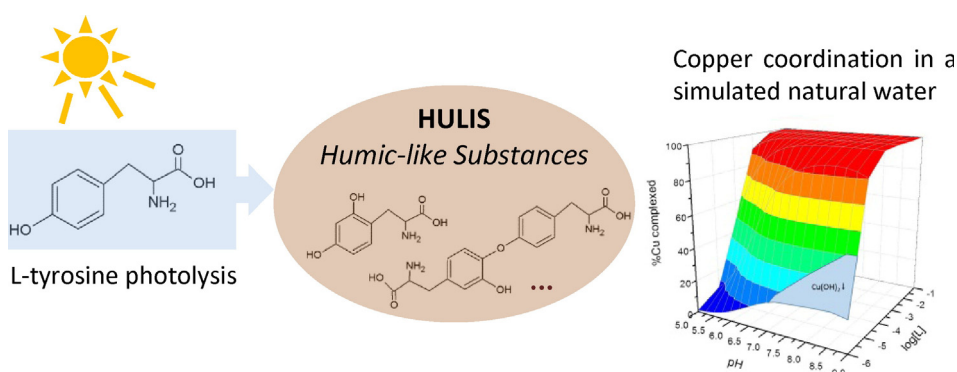
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### HIGHLIGHTS

- Tyrosine photolysis proceeds through deamination, hydroxylation and dimerization.
- Dimerization could be linked to the photoinduced formation of tyrosyl radicals.
- New protogenic sites are formed by irradiation, compared to the parent amino acid.
- The irradiated material has higher copper complexation capacity than tyrosine.
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- Humic-like substances derived from tyrosine could complex Cu in surface waters.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The UVB photolysis of L-tyrosine yields species with fluorescence and absorption spectra that are very similar to those of humic substances. By potentiometric measurements, chemical modeling and the application of NMR, mass spectrometry and laser flash photolysis, it was possible to get insights into the structural and chemical properties of the compounds derived by the L-tyrosine phototransformation. The photolytic process follows aromatic-ring hydroxylation and dimerization. The latter is presumably linked with the photoinduced generation of tyrosyl (phenoxy-type) radicals, which have a marked tendency to dimerize and possibly oligomerize. Interestingly, photoinduced transformation gives compounds with protogenic and complexation capabilities similar to those of the humic substances that occur naturally in surface waters. This finding substantiates a new and potentially important abiotic (photolytic) pathway for the formation of humic compounds in surface-water environments.

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## 1. Introduction

Humic substances (HS) are important components of the chromophoric dissolved organic matter (CDOM) that occurs in surface waters (Ma et al., 2010; Xiao et al., 2013). HS play key roles in surface-water ecosystems because, as major sunlight absorbers, they can limit the penetration of harmful UVB radiation into the water column (Sommaruga and Augustin, 2006; Piccini et al., 2009; Uusikivi et al., 2010). Moreover, HS may act as solvents for water-insoluble organic pollutants and as ligands for metals and even inorganic nanoparticles. In all these cases, HS can allow the aqueous-phase transport of otherwise insoluble harmful species (Senesi, 1992; Westerhoff and Nowack, 2013; Prado et al., 2014). An additional issue is that the absorption of sunlight by HS causes the production of photoactive transients: the hydroxyl radical,  $^{\bullet}\text{OH}$ ; singlet oxygen,  $^1\text{O}_2$ ; CDOM triplet states,  $^3\text{CDOM}^*$  and, in the presence of inorganic carbon, the carbonate radical,  $\text{CO}_3^{\bullet-}$ . These transients are involved into the indirect photodegradation of many priority and emerging pollutants, but they can also induce the formation of harmful by-products (Latch and McNeill, 2006; Cavani et al., 2009; Minella et al., 2013; Cawley et al., 2015).

HS are usually thought to originate from the microbial decomposition of organic material that occurs in soil (allochthonous HS, which reach water bodies by e.g. runoff) and surface waters (autochthonous HS) (Xu and Zheng, 2003; Su et al., 2015). However, recent research suggests that compounds with fluorescence properties that are very similar to those of humic and fulvic acids can be formed by photolysis (or photoinduced oxidation) of phenolic compounds and of amino acids such as tyrosine and tryptophan (De Laurentiis et al., 2013a,b,c; Bianco et al., 2014). In the latter case, the amino acids have been irradiated by UVB light and their direct photolysis has induced the formation of compounds with fluorescence emission in the HS region, as suggested by their excitation–emission matrix (EEM) fluorescence spectra. Moreover, the irradiated material was able to photoproduce reactive transient species ( $^1\text{O}_2$ ,  $^3\text{CDOM}^*$ ), which was not the case for the original amino acids (Bianco et al., 2014). Despite these analogies, the extent to which the photogenerated compounds can be assimilated to HS and, therefore, the significance of the possible abiotic pathway leading to HS production have been scarcely clarified. Indeed, it is essential to assess whether the photogenerated material may have further properties in common with HS.

The definition of HS is currently an operational one, (i) because they are not compounds of definite chemical structure (which can vary depending on the environment), and (ii) because their structure is still insufficiently elucidated despite recent important advances in the so-called humeomics science (Piccolo, 2001; Nebbioso and Piccolo, 2011; Nebbioso et al., 2014). Nevertheless, some chemical properties such as the presence of carboxylic and phenolic groups, the acid–base behavior and the ability to form complexes with metal cations are distinctive features of HS. While previous work reveals that compounds sharing some HS-like properties can be formed upon irradiation of amino acids, some important chemical properties that could substantiate their assimilation to HS have not been elucidated so far: they include the occurrence of relevant functional groups, the protogenic properties and the metal complexation capabilities.

Therefore, the present paper is aimed at better characterizing the compounds formed upon irradiation of the amino-acid L-tyrosine. Amino acids may be present in surface waters as components of proteins and peptides at concentrations ranging within 20–6000  $\mu\text{g L}^{-1}$  (Thurman, 1985) or in the free form, in which case they can account for about 6% of the DON (Dissolved Organic Nitrogen) (Bronk, 2002). Previous works studied the indirect photodegradation of amino acids, or dipeptides, evaluating the effect of pH (Saprygina et al., 2014), Reactive Oxygen Species (ROS) and Dissolved Organic Matter (DOM) (Boreen et al., 2008; Plowman et al., 2013; Posadaz et al., 2004) on the photooxidation kinetics. Besides, it is known that the tyrosine is one of the photosensitive amino acids and it is subjected to direct

photodegradation under solar-simulated conditions (Boreen et al., 2008). However, information on the nature of the tyrosine photooxidation products is still lacking. Early work has suggested that the transformation of tyrosine might proceed in a similar way as the biosynthesis of melanin, through the intermediate formation of 3,4-dihydroxyphenylalanine (DOPA) (Bosetto et al., 1997). However, recent research has shown that a possible DOPA pathway cannot account for the formation of substances with humic fluorescence (Bianco et al., 2014). In any case, the phototransformation of amino acids has an environmental interest in addition to the mechanistic one, because of its important but variable consequences on the bacterial communities (Amado et al., 2015), also concerning the chemistry and the photochemistry of surface waters. For the reported reasons, additional investigations on this topic should provide insight into the environmental significance of possible abiotic (photochemical) processes of HS formation. Moreover, amino acids, and tyrosine in particular, are involved in Cu(II) complexation (He et al., 2014), and also the binding of Cu(II) to HS is thought to occur through nitrogenous ligands similar to those of amino acids (Croue et al., 2003).

This work aims at providing additional insight into the photochemical formation of humic-like substances from tyrosine, with particular emphasis on the reaction pathways (how is tyrosine phototransformed) and on the humic nature of the photogenerated material. In the latter case, the ability of the irradiated solutions to undergo acid–base chemistry and to complex metal ions (Cu) will be assessed, as these are important features of natural humic substances.

## 2. Experimental section

### 2.1. Chemicals

Tetraethyl ammonium chloride (TEACl,  $\geq 98.5\%$ ), copper chloride (99%), potassium carbonate ( $>99\%$ ), sodium acetate ( $>98\%$ ), disodium hydrogen phosphate ( $>99\%$ ), formic acid ( $\sim 98\%$ ), trifluoroacetic acid (99%), methanesulfonic acid ( $>99.5\%$ ), perchloric acid (70%) and methanol ( $>99.8\%$ ) were from Sigma Aldrich (St. Louis, Missouri, US). Phosphoric acid (85%) and acetic acid (100%) were provided by Carlo Erba Reagents (Cornaredo, Italy). L-Tyrosine ( $>99\%$ ) was from Merck (Darmstadt, Germany). Deuterated dimethyl sulfoxide, DMSO- $d_6$ , was from Eurisotop, France. Standard KOH and HCl solutions were prepared by diluting Merck or Sigma Aldrich concentrated products, and they were standardized against potassium hydrogen phthalate (Sigma Aldrich,  $\geq 99.5\%$ ) and sodium carbonate (Sigma Aldrich,  $\geq 99.5\%$ ), respectively. Grade-A glassware and ultra-pure water (Milli-Q, Millipore) were used for all the solutions.

### 2.2. Irradiation experiments

To evaluate the transformation kinetics, a solution (80 mL) of L-tyrosine 1.0  $\text{mmol L}^{-1}$  was placed into a square Pyrex glass bottle (capacity 100 mL) and irradiated under a solar simulator (Solarbox, CO.FO.ME.GRA., Milan, Italy) equipped with a 1500 W Philips xenon lamp and a 320 nm cut-off filter. This filter transmits 50% of radiation at 320 nm, its transmittance being lower (and reaching up to zero) below 320 nm and higher above it. The concentration and the volume of the irradiated solutions were chosen in order to allow the successive potentiometric investigation. Each bottle was placed so as to lie down horizontally on one of its flat sides, and irradiation occurred through the opposite side that acted as optical window. Lamp radiation was vertically incident over the solutions and the optical path length was 1.95 cm. The UV irradiance reaching the bottles was  $28.0 \pm 1.6 \text{ W m}^{-2}$ , measured with a CO.FO.ME.GRA. (Milan, Italy) multimeter equipped with a UV probe that is sensitive to radiation in the 295–400 nm interval. The photon flux in solution was actinometrically determined with the ferrioxalate method (Kuhn et al. 2004), taking into account the wavelength-dependent quantum yield of  $\text{Fe}^{2+}$

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