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## Electrochemical Characterization of the Marine Antioxidant Gadusol

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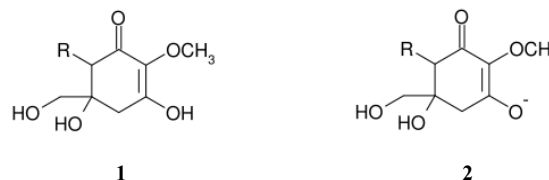
The electrochemical properties of gadusol, a metabolite extracted from fish roes, were determined for the first time by cyclic- and square-wave voltammetries on a glassy carbon electrode in buffered aqueous solutions. The aims of the work were characterization of the redox behavior and assessment of the mechanism underlying the antioxidant capacity of the compound. Anodic waves with peak potentials of  $710 \pm 5$  mV and  $601 \pm 9$  mV vs. Ag/AgCl were obtained for gadusol and its anion gadusolate, respectively. The voltammograms point to the irreversible nature of the oxidation process and reveal better antioxidant properties for the compound under physiological pH, with a moderate reductive power, but improved stability under atmospheric oxidation in comparison with other natural antioxidants such as ascorbic acid. The presence of direct ionic micelles prepared with sodium dodecyl-sulfate or cetyl-trimethyl-ammonium chloride yielded no significant differences regarding homogeneous medium in the cyclic voltammetry of gadusolate. The results provide evidence of the electron transfer mechanism for the quenching reaction of standard-reactive species by gadusolate and support it as a promising candidate to be tested as an antioxidant additive to food, cosmetic and pharmaceutical formulas. The direct analysis of the metabolite in biological systems and natural extracts by electrochemical methods is also envisaged.

**Keywords:** Marine products, Gadusolate, Cyclic voltammetry, Square-wave voltammetry, Direct micelles, ABTS.

Gadusol (3,5,6-trihydroxy-5-hydroxymethyl-2-methoxy-cyclohex-2-en-1-one) (**1**) and deoxygadusol (3,5-dihydroxy-5-hydroxymethyl-2-methoxy-cyclohex-2-en-1-one) are structural- and biosynthetically related to the mycosporine-like amino acids [1a]. This family of metabolites occurs in a variety of marine and terrestrial organisms from the tropics to Antarctica. The compounds have shown sun screening potential and presumed ability to counteracting oxidative stress [1b]. These properties have attracted special attention lately in the search for new ways of protection against direct and indirect harmful effects of the increasing UV-radiation provoked by the stratospheric ozone depletion [1,2]. In addition, the redox interaction of gadusol and ascorbic acid with other endogenous antioxidants in the roe of marine teleosts has been recently insinuated [3]

The high antioxidant capacity of gadusol against hydrosoluble radicals and its reactivity with electronically excited species has been previously determined and led to propose the use of fish roes as a source of this ingredient for human consumption and functional food production [4]. In fact, gadusol deactivates peroxy radicals under physiological conditions with a 6-fold higher efficiency than ascorbic acid, whereas its reactivity against radicals derived from ABTS (2,2'-azinobis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt) is comparable to that of vitamin C [4a]. Thus, distinctive mechanisms of antioxidant action are probably implicated depending on the nature of the antioxidant and reactive species. However, to the best of our knowledge, there are no quantitative reports on the redox properties of gadusols in solution.

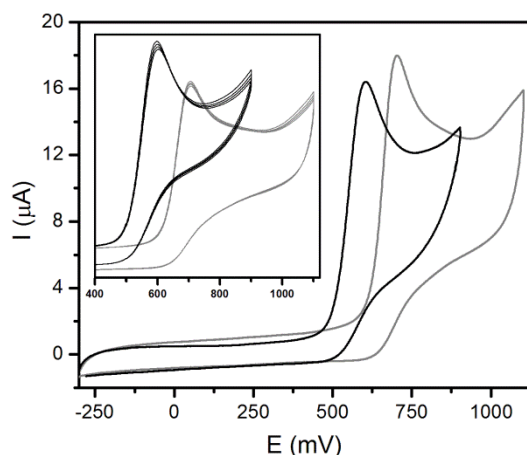
Besides the potential of electrochemical methods as analytical tools for sensing gadusol species in systems that approach the biological matrices, it is worthy to evaluate this compound in the context of



promising applications of an oxidant additive in food, cosmetic and pharmaceutical formulas [5]. Thus, cyclic voltammetry (CV) and the more sensitive square-wave voltammetry (SWV) were carried out on aqueous solutions at pH 2 and 7, in order to assess respectively the electrochemical behavior of the neutral (**1**) and the anionic (**2**) forms of gadusol ( $pK_a = 4.25$ ) [6].

Only single anodic current waves were observed, the shape and position of them being equivalent for CV (Figure 1), or SWV experiments. The waves are assigned to one-electron oxidation reactions of gadusol and gadusolate, respectively. The similitude of the successive cycles in the inset of Figure 1 suggests that no additional electroactive-oxidation transients or products are involved, nor electrodeposition on the working electrode or passivation effects take place. These results were also independent of the presence of air, ruling out a significant role of  $O_2$  on the oxidation of gadusol species.

The anodic peak potential ( $E_{pa}$ ) for gadusol gradually shifts in the anodic direction on increasing the scan rate ( $v$ ) (Figure 2). The anodic peak current  $I_{pa}$  increases significantly and linearly with  $v^{1/2}$  (inset Figure 2). Analogous results were obtained for gadusolate.

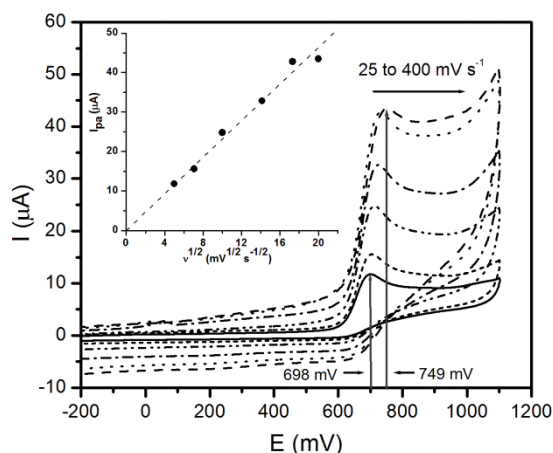


**Figure 1:** Cyclic voltammograms of gadusol (—) and gadusolate (---) in aqueous solution, vs. Ag/AgCl at a scan rate of  $v = 50 \text{ mV s}^{-1}$ . Inset: traces of CV from successive cycles for each species.

The absence of the corresponding cathodic wave of the oxidized species accounts for an irreversible electron lost. A reversible electron transfer followed by an irreversible chemical reaction is discarded since the peak potential is expected to be independent of  $v$  for such a process. The linear dependence of  $I_{pa}$  with  $v^{1/2}$  is rationalized in terms of an irreversible one-electron transfer in a diffusion-controlled process [7]. The lack of reversibility precludes the experimental determination of a formal reduction potential for the oxidized gadusol or gadusolate. However, the formal potential is expected to lie half way between  $E_{pa}$  and the half-peak potential  $E_{p/2}$ , *i.e.* the potential at which the current reaches half its maximum [5b]. This is relevant since the position of the oxidation peaks in the CV for antioxidants is considered as a measure of their reducing power in solution and hence an indication of their effectiveness as antioxidants in biological systems [5c]. The average of five independent determinations at  $10 \text{ mV s}^{-1}$  led to the  $E_{pa}$  values vs. Ag/AgCl of  $710 \pm 5 \text{ mV}$  for gadusol and  $601 \pm 9 \text{ mV}$  for gadusolate anion. Thus, gadusol is a more powerful reducing agent, and therefore a better antioxidant under physiological pH than in acidic medium. This trend is in agreement with that found in the electrochemical behavior as a function of pH of other biological antioxidants with phenolic and enolic functional groups, which are involved in acid-base equilibria [8].

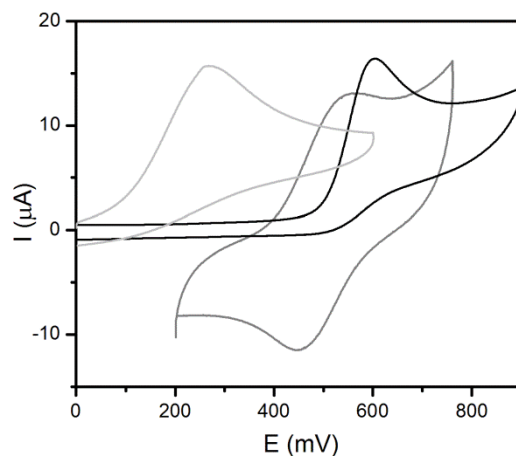
The CV parameters are expected to be related to the antioxidant capacity [9]. The ABTS assay is one of the usual tests for evaluation of this property by sensing the ability of a molecule to deactivate the hydrosoluble ABTS<sup>•+</sup> radical [10]. Thus, solutions of gadusolate and ABTS<sup>•+</sup> were separately analyzed by CV with the purpose of searching for mechanistic evidence on the previously studied capacity of the metabolite to reduce the radical species. For comparative purposes, voltammograms of ascorbic acid solutions were also recorded under equivalent experimental conditions (Figure 3).

The ABTS<sup>•+</sup>/ABTS couple yields the typical reversible wave, differing from those recorded for ascorbate and gadusolate anions. The maximal anodic current for ABTS species appears at higher potential than that of the ascorbate anion. On this basis, ascorbate is thermodynamically able to reduce the ABTS<sup>•+</sup> radical under our experimental conditions. On the contrary, the maximum anodic current for gadusolate anion emerges at a higher potential than that for the ABTS species.



**Figure 2:** Cyclic voltammograms for gadusol at different scan rates  $v$ , from 25 to  $400 \text{ mV s}^{-1}$ . Inset: Linear dependence of the anodic peak current,  $I_{pa}$ , on  $v^{1/2}$

However, the difference between both anodic potentials is small enough to make the voltammograms overlap from *ca.* 480 to 550 mV, *i.e.* in a range that includes the anodic peak for ABTS. Thus, gadusolate begins to oxidize in a potential domain where ABTS<sup>•+</sup> radical has already been formed. In this sense, our CV experiments reflect the ability of gadusolate to reduce ABTS<sup>•+</sup> although the complex characteristics of antioxidant processes should be considered. In fact, since gadusolate oxidation is an irreversible process, the oxidized-formed species might continue reacting through several mechanisms, supplying the driving force of the overall reaction. Such secondary steps might account for the similar reactivity of gadusolate and ascorbate towards ABTS<sup>•+</sup> radicals [4a], despite vitamin C being a more powerful reducing agent.



**Figure 3:** Cyclic voltammograms of aqueous solutions of gadusolate (—), ABTS<sup>•+</sup> (---) and ascorbate anion (---), *ca.*  $10^{-3} \text{ M}$  and pH 7.4 vs. Ag/AgCl,  $v = 25 \text{ mV s}^{-1}$

The electrochemical behavior of gadusolate in simple organized systems that model biological microenvironments was explored by CV and SWV analysis in the presence of aqueous sodium dodecyl-sulfate (SDS) and cetyl-trimethyl-ammonium chloride (CTAC) direct micelles at pH 7. The shape of the voltammograms was rather similar to those obtained in homogeneous solution. The data in Table 1 reveal that the electrode processes of gadusolate anion are not remarkably affected in the presence of the direct micelles.

**Table 1:** Cyclic voltammogram parameters, anodic peak potential  $E_{pa}$  vs. Ag/AgCl, and anodic peak current  $I_{pa}$ , for gadusolate in different environments

Medium	$E_{pa}$ , mV <sup>a</sup>	$I_{pa}$ , $\mu\text{A}^a$
Aqueous	601	42
Aqueous/ $1.2 \times 10^{-2}$ M SDS	630	33
Aqueous/ $1.8 \times 10^{-3}$ M CTAC	615	39

<sup>a</sup> Estimated maximal uncertainty in peak parameters is ca. 2%

$E_{pa}$  and  $I_{pa}$  vary in the same direction in both micellar solutions, thus electrostatic interactions *per se* between gadusolate and the head groups of the surfactants (anionic SDS and cationic CTAC) do not explain the results. However, the formation of micelles may modify the mass transport of electroactive species to the electrode [11]. The micelle-water interfaces seem to be the most probable location of gadusolate, and thus the effects on the voltammograms are probably due to the masking of the electroactive site of the molecule located in the vicinity of the micellar surfaces, which may turn the oxidation harder [12].

Finally, the CV parameters here reported are relevant for the analytical determination of gadusol species in complex mixtures such as biological samples and natural extracts.

## Experimental

**Extraction of gadusol:** Gadusol was obtained by solvent extraction of the mature gonads of female *Pseudoperca semifasciata* and purified by ion-exchange chromatography, as described elsewhere [4a].

**Sample preparation:** Aqueous solutions of gadusol were prepared in buffers at 0.04 M final concentration:  $\text{H}_3\text{PO}_4$  (Cicarelli, P.A.)/ $\text{KH}_2\text{PO}_4$  (Sigma,  $\geq 99.0\%$ ) at pH 2, and  $\text{K}_2\text{HPO}_4$  (Fluka,  $>99.0\%$ )/ $\text{KH}_2\text{PO}_4$  (Sigma,  $\geq 99.0\%$ ) at pH 7; 0.5 M KCl (Cicarelli P.A.) was utilized as supporting electrolyte. Tensioactive reagents SDS (Sigma-Aldrich,  $>99\%$ ) and CTAC (Fluka, 25% solution) were used for preparing the direct micelles. CTAC was purified by evaporation to dryness and recrystallization from a 50% ethanol-acetone mixture. Either solid SDS or CTAC was dissolved in tridistilled water and buffered. The critical micelle concentration (CMC) of the surfactants was verified by conductimetry and the

results were SDS:  $8.0 \times 10^{-3}$  M and CTAC:  $1.4 \times 10^{-3}$  M; these values are in full agreement with previous report [13]. In the micelles solutions, the pH was regulated within the neutral range by means of a *tris* [hydroxymethyl] amino-methane (Trizma® base, Sigma, reagent grade)/HCl (Cicarelli, P.A.) buffer. The experiments were carried out in air and with 0.2 M NaCl (Cicarelli, P.A.) as supporting electrolyte.

ABTS<sup>•+</sup> and ascorbic acid (Sigma,  $>99\%$ ) solutions ca.  $1 \times 10^{-3}$  M at pH 7.4 and under air atmosphere were used in the CV and SWV experiments. ABTS<sup>•+</sup> radical was prepared as previously reported [4a], by oxidation of 2,2'-azinobis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS, Fluka) with potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ , Aldrich).

**Electrochemical analysis:** The CV experiments were carried out in a hermetically-sealed conventional three-electrode cell. The working electrode was a 3-mm diameter glassy-carbon disk (BASi), thoroughly cleaned before each measurement by polishing with a soft cloth soaked in an aqueous suspension of 1% alumina (0.05  $\mu\text{m}$ , Merck), sonication in 50% v/v water/acetone and subsequent rinsing with distilled water. A Pt wire (1  $\text{cm}^2$ ) was used as the auxiliary electrode, and cleaned by immersion in sulfonitic solution. All measurements were registered vs. Ag/AgCl/3 M KCl ( $E^\circ = 196$  mV vs. NHE, Radiometer Analytical<sup>TM</sup>).

Voltammograms were registered on ca.  $1 \times 10^{-3}$  M buffered gadusol solution prepared by dilution from aqueous concentrated metabolite solutions. The potential was swept between  $-300$  and  $1200$  mV, and the scan rate was increased from 25 to  $1000$   $\text{mV s}^{-1}$  using a potentiostat (Teq-02). Runs on air-saturated solutions or under nitrogen atmosphere (99,998 %) were alternatively carried out for comparative purposes.

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