Hydrocotyle umbellata L. is a groundcover plant that has been used in the folk medicine of Argentina, Brazil, Cuba, and India, mainly to reduce inflammatory processes. The lignan, hibalactone, can be isolated from the roots of the plant. In the anti-inflammatory and antioxidant activity of such natural products, it is believed that the mechanism of action involves the butyrolactone ring, which would act as a free pharmacophore. In this study, electrochemical, spectrometric, and computational chemistry approaches were used to evaluate the lignan antioxidant activity and electro-oxidation pathway. Electrochemical measurements were performed in a 3 mL cell, operated in a three electrode system, consisting of an Ag/AgCl reference electrode, platinum as a counter electrode, and a glassy carbon electrode as a working electrode. Radical scavenging assays were performed with DPPH and ABTS. In the computational chemistry approach geometry optimization was performed with semi-empirical calculations (PM3) and the orbitals/charges calculations were performed with the extended Hückel method. The voltammetry showed a very slight variation with pH alteration, which can be justified by lactone hydrolysis that occurs in acidic and basic pH. In the HOMO and total charge density distribution, it was possible to observe that the higher prevalence was in the benzo[1,3]dioxole rings and in the alkenes/alkanes in proximity with the lactone ring. The hibalactone displayed a single quasi-reversible electro-oxidation. Given the HOMO and charge density distribution in the lignan, more so the single oxidation in the evaluated potential, it is reasonable to infer that the alkene bonded with the lactone ring was a probable site of oxidation.

**Keywords:** electrochemical index, voltammetric profile, redox behavior, natural antioxidants
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