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5. THE THEORETICAL DESCRIPTION FOR AESCULETIN AND QUERCETIN CATHODIC ELECTROCHEMICAL DETERMINATION IN JUICE

Douro juice is one of the symbols of Portugal. Douro wine region was the first demarked in XVIII century. Juice has its own characteristic scent and flavor, due to the presence of some aromatic lactones. But the main alimentary value to the juice is given by its polyphenolic composition [1].

On the other hand, the chestnut *C. Sativa* is one of the most important product and ingredient for the cuisine of Trás-os-Montes [2]. The districts of Vila Real and Bragança produce 25% of Portuguese chestnut. Chestnuts have played an essential role in human nutrition since ancient times. Studies conducted on chestnuts' chemical and nutritional composition confirm that this fruit is low in fat, cholesterol-free, and glutenfree. On the other hand, it is a rich source of starch (carbohydrates), protein, dietary fiber, vitamins, minerals (such as potassium, phosphorous, and magnesium), lipids, and nutrients.

Its pulp and flowers possess high concentrations of flavonoid (for example, quercetin) and coumarinic (for example, aesculetin) polyphenols, mainly those with hydroquinonic moiteies (Fig. 1), which, in quinonic forms, act as antioxidants and conservants.





Quercetin is an antioxidant flavonol belonging to the flavonoid group and generally present as Que glycoside. It is chemically composed of three benzene rings and five hydroxyl groups. The Que aglycone is able to conjugate with glucose, xylose, or rutinose attaching to one of the Que's hydroxyl groups with the consequent creation of various Que glycoside forms. The hydroxyl groups at the A and B rings' 3, 5, 7, 3', and 4', the double bond between the second and third carbons, and the carbonyl group on the fourth carbon were verified to have a major part in the antioxidant capabilities of quercetin [3].

Quercetin-3-O-glycoside mostly serves as a pigment in flowers, vegetables, and fruits. Quercetin are even more powerful antioxidants than vitamins C and E. Many studies had shown that Que is a promising drug target for treating diabetes [4].

Esculetin (6,7-dihydroxychromen-2-one) is a coumarin derivative that structurally contains the two hydroxyl groups at the 6th and 7th carbon atoms, which belongs to the class of benzopyrone. The bioactivities and therapeutic applications of coumarin compounds and their derivatives depend on their structural arrangement. Free radicals act as a potent source for the pathogenesis of many diseases, whereas the presence of hydroxyl groups on esculetin makes this compound more efficient to act as an antioxidant by inhibiting the oxidative stress in disease conditions.

It has been found that the attachment of the hydroxyl group to phenolic compounds can effectively connect with free radicals. These hydroxyl groups in phenolic compounds can also exhibit chelation with transient metals such as copper and iron. Esculetin exhibits dual modulation of apoptosis, as well as anti-diabetic and anti-inflammatory action that may be partly attributed to its antioxidant characteristic [5].

Recent advances in electrochemical methods such as voltammetry, amperometry, impedance spectroscopy have made it possible to develop methods for detection of a broad range of substances using uniquely designed electrodes and microelectrode arrays.

In this aspect, the electrochemical determination of both aesculerin and quercetin in juice becomes actual, and the anodic determination is the most viable in this case, although cathodic one is also possible. If cobalt oxyhydroxide is used for this purpose, the electrooxidation will be given by quinone-hydroquinonic mechanism, manifesting specific oxidation peaks. For this reason, the qualitative determination is viable. The mathematical model, like also its analysis, confirms the efficiency of quantitative CoO(OH)-assisted aesculetin and quercetin determination in juice.

Conclusion. The mathematical model and its analysis confirm the effectiveness of the quantification of esculetin and quercetin in juices using CoO(OH).

Therefore, the determination of polyphenolic antioxidants is necessary for predicting the stability of beverages and their antioxidant properties.

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