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ORIGINAL PAPER

Electro-oxidation of rutin in the presence of *p*-toluenesulfinic acid

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Abstract We report the electrochemical oxidation of rutin in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) in the presence of *p*-toluenesulfinic acid. Cyclic voltammetry and controlled potential electrolysis were used to study rutin electro-oxidation and to prepare the sulfone derivatives. Chromatographic methods were employed to separate the products and IR, ^{1}H NMR, ^{13}C NMR, MS and microanalysis to their characterization. Data from cyclic voltammetry allow the identification of three rutin oxidation processes in the presence of *p*-toluenesulfinic acid (E_p^I = 0.56 V, E_p^{II} = 0.81 V and E_p^{III} = 1.32 V). Only the electrode process around peak I was exhaustively studied. The first oxidation step leads to the formation of the corresponding *o*-quinone, which participates in a Michael addition reaction with the *p*-toluenesulfinic acid, forming the 6′(4-methylphenylsulfonyl)rutin and 6′(4-methylphenylsulfonyl)quercetin as majority products.

Keywords Rutin · *p*-Toluenesulfinic acid · Electro-oxidation · Electrochemical reactions · Michael addition reaction

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1 Introduction

The electrochemical approach to organic synthesis is an intrinsically environmentally friendly technique [1]. Some features of electro-synthesis are [1, 2]: (i) the electrode surfaces work as heterogeneous catalysts that are easily separated from the products; (ii) the electrons behave as reagents, drastically reducing the problem of manipulation and disposal of solvents; (iii) the reaction media are usually very mild, using laboratory room temperature and normal pressure, and (iv) usually the supporting electrolyte may be regenerated and recovered. A wide variety of reactions can be performed in all areas of organic chemistry [1–8], but electrochemistry is more adapted to small-scale synthesis of pharmaceutical [9] and other high-value, low-volume specialty products [10].

Sulfones (R–SO_2–R) are synthetic intermediates for pharmaceutical products [11, 12] and are frequently used in the synthesis of biologically active natural compounds. One of the best-known methods of sulfone synthesis uses hydroquinone as a starting material and an appropriate oxidant to transform the hydroquinone to the corresponding quinone [13]. The quinone formed can act as a Michael acceptor towards nucleophiles, resulting in a substituted hydroquinone. The oxidation step can be achieved without complication by electrochemical methods, with the oxidation of hydroquinone at a given controlled potential. Electrochemical synthesis of some organic compounds has been carried out in the presence of benzenesulfinic acids [13–15] as nucleophiles, generating sulfone derivatives. The electrochemical preparation of sulfone derivatives seems to be easier than the analogous chemical synthesis and can be seen as an advantage of

the electrochemical route. Electrochemical synthesis using thio-barbituric acid as a nucleophile has also been carried out in aqueous solution [16].

Rutin (3′,4′5,7-tetrahydroxyflavone-3-O-rutinoside—Fig. 1) is a water low soluble [17] flavonoid present in tomatoes, tobaccos, rue and in numerous vegetables, fruits and grains. Its chemical structure contains the resorcinol group in the ring A (with the *m*-hydroxyls in the positions C5 and C7), the catechol group in the ring B (with the *o*-hydroxyls in the positions C3′ and C4′) and the rutinoside residue (formed by two sugars: rhamnose and glycose) in the position C3 of the ring C, the carbonyl group in the position C4 in the ring C and the C = C bond between the carbons C2 and C3 in the ring C. As can be deduced, rutin presents OH functional groups that can be electrochemically oxidized. The oxidation of the 3′,4′dihydroxy group in the ring B can lead to the formation of the corresponding *o*-quinone. Unlike, the 5,7 dihydroxy group in the ring A cannot lead to the formation of the corresponding *m*-quinone. Additionally, the catechol group in the ring B is oxidized more easily than the resorcinol group in the ring A [18].

It is well known [13–16] that *o*- and *p*-quinones are very reactive and can be easily attacked by nucleophiles. The aim of this work is to electrochemically oxidize rutin in the presence of the *p*-toluenesulfinic acid as nucleophile in view to prepare sulfonyl derivatives via a Michael addition reaction. Cyclic voltammetry and controlled potential electrolysis were used for the electro-oxidation of rutin and to prepare the sulfone derivatives. Chromatographic methods were employed to isolate the formed products; IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry and microanalysis were employed to their characterization.

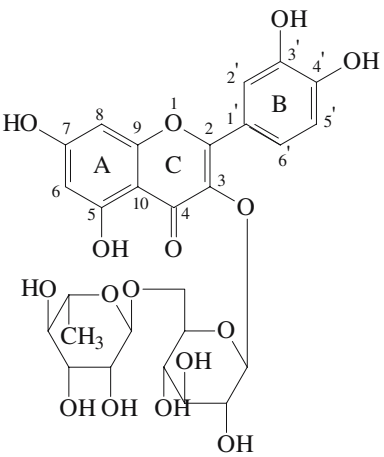

Fig. 1 Chemical structure of rutin

2 Experimental

2.1 Chemicals

Rutin and *p*-toluenesulfinic acid were of analytical grade acquired from Sigma and Acros Organics, respectively. Phosphoric acid, sodium mono and dihydrogen phosphate (from Merck), acetonitrile (from Vetec) and ethyl acetate and ethyl alcohol (from F Maia) were pro-analysis grade and they were used without previous purification. Distilled and deionized water was used for all solution preparations.

2.2 Cyclic voltammetry and controlled potential electrolysis

Cyclic voltammograms were obtained in a 15-mL three-electrode electrochemical cell, using a glassy carbon disk (BAS MF-2012) as working electrode (GCE), a graphite rod as auxiliary electrode and an aqueous saturated calomel electrode (SCE) as reference. All potentials in the text are quoted versus this reference electrode. The working electrode was carefully polished with alumina paste (0.05 μm) and ultrasonically rinsed in deionized water before each voltammogram. A solution of NaH_2PO_4/Na_2HPO_4 (both 0.05 mol L^{-1}) was used as supporting electrolyte. Acetonitrile was added to the supporting electrolyte at the ratio 4:1 (v/v) acetonitrile-sodium phosphate. Following a report [19] that the electrosynthesis of sulfonated hydroquinones via electro-oxidative production of related quinones may be achieved at pH <3.1, the pH was adjusted to 2.0 with H_3PO_4. Rutin (final concentration 1.0 mmol L^{-1}) and *p*-toluenesulfinic acid (final concentration 1.2 mmol L^{-1}) were added directly to the cell after attainment of a cyclic voltammogram of the electrode immersed in the solution free of electro-active species. The solutions were purged with N_2 for 8 min and the experiments were carried out at laboratory room temperature.

Controlled potential electrolysis was carried out in a two-compartment cell. The anodes (an assembly of four spectroscopic graphite rods 10 cm length and 10 mm diameter) and the saturated calomel reference electrode were located in one compartment. The auxiliary electrode (a large graphite rod) was placed in the other. The capacity of each compartment was 80 mL and both were filled with acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution. Electrical contact between the compartments of the anodes and cathode was established with a glass salt bridge filled with 1.5% agar–agar and saturated KCl solution. Rutin (final concentration 1.0 mmol L^{-1})

and *p*-toluenesulfinic acid (final concentration 1.2 mmol L^{-1}) were directly added only to the anode compartment. The applied potential was 0.80 V. Four electrolyses of thirty minutes duration were carried out to synthesize the sulfone derivatives. After each electrolysis the graphite rod working electrodes were ultrasonically washed in water for reactivation and a new voltammogram was obtained in order to evaluate the electrolysis progress. The $i \times t$ curves were obtained under constant stirring and the electrolysis was considered complete when the current was lowered to ca. 90% of its initial value. The consumed charge was obtained by integration of the resulting curves and the number of electrons calculated.

All electrochemical experiments were carried out in an EG & G PAR Model 263A potentiostat/galvanostat with M270 software coupled to a personal computer.

2.3 Chromatography and characteristics of the formed products

In a typical procedure, 80 mL of a potential-controlled electrolyzed 1.0 mmol L^{-1} rutin + 1.2 mmol L^{-1} *p*-toluenesulfinic acid in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution were evaporated and purified chromatographically on a silica (Merck 70–230 mesh (0.063–0.200 mm)) column using ethyl acetate and ethyl alcohol as eluents. Fractions of 25 mL were obtained and analyzed by thin layer chromatography (Macherey-Nagel Alugram Sil G/UV_{254} plates 0.20 mm thickness). Two majority products were isolated: 3-(α-L-rhamnopyranosyl-1,6-*β*-D-glucopyranosyl)-3′,4′,5,7-tetrahydroxy-6′(4-methylphenylsulfonyl) flavone or 6′(4-methylphenylsulfonyl)-rutin **(1)** and 3,3′,4′,5,7-pentahydroxy-6′(4-methylphenylsulfonyl)flavone or 6′(4-methylphenylsulfonyl)-quercetin **(2)**. The products were characterized by IR (Perkin Elmer FTIR 16PC), ^{1}H NMR (200 MHz, Bruker AC; 400 MHz, Varian Mercury Plus), ^{13}C NMR (100 MHz, Varian Mercury Plus), mass spectrometry (Shimadzu, GCMS-QP5050) and microanalysis (CE Instruments, CHNS-O EA1110).

3-(α-L-rhamnopyranosyl-1,6-*β*-D-glucopyranosyl)-3′,4′,5,7-tetrahydroxy-6′(4-methylphenylsulfonyl)flavone or 6′(4-methylphenylsulfonyl)rutin **(1)** — orange powder obtained with a good purity.

^{1}H NMR (CD_3OD) *δ*/ppm: 1.29 (Me Rha), 3.00–4.00 (H-rutinoside), 4.91 (H-1Glc, masked by the water peak), 4.71 (H-1Rha), 2.42 (s, Met, 4-Met-$PhSO_2$), 5.93 (H-6), 6.24 (H-8), 7.12 (s, H-2′), 7.33 (d, J = 7.20 Hz, H-3 e H-5, 4-Met-$PhSO_2$), 7.61 (d, J = 7.20, H-2 e H-6, 4-Met-$PhSO_2$), 7,80 (s, H-5′). The numbering of the C atoms is shown in Fig. 9.

3,3′,4′,5,7-pentahydroxy-6′(4-methylphenylsulfonyl) flavone or 6′(4-methylphenylsulfonyl)quercetin **(2)** — orange powder obtained with a good purity.

IR (KBr) ν/cm^{-1}: 3399, 1656. ^{1}H NMR (CD_3OD) *δ*/ppm: 2.56 (s, Met, 4-Met-$PhSO_2$), 6.15 (d, J = 1,86 Hz, H-6), 6.38 (d, J = 2,00 Hz, H-8), 7.12 (s, H-2′), 7.41 (d, J = 8,11 Hz, H-2 e H-6, 4-Met-$PhSO_2$), 7.71 (d, J = 8,14, H-3 e H-5, 4-Met-$PhSO_2$), 7.86 (s, H-5′). ^{13}C NMR (CD_3OD) *δ*/ppm: 147.1 (C-2), 137.4 (C-3), 176.5 (C-4), 161.4 (C-5), 98.2 (C-6), 164.4 (C-7), 93.6 (C-8), 157.2 (C-9), 104.2 (C-10), 122.0 (C-1′), 116.7 (C-2′), 146.5 (C-3′), 149.9 (C-4′), 118.9 (C-5′), 139.0 (C-6′), 144.3 (C-1, 4-Met-$PhSO_2$), 129.3 (C-2 e C-6, 4-Met-$PhSO_2$), 127.1 (C-3 e C-5, 4-Met-$PhSO_2$), 130.8 (C-4, 4-Met-$PhSO_2$), 29.5 (Met, 4-Met-$PhSO_2$). Mass: m/z 456 (M^+), 302 (M^+ - 154). Microanalysis for $C_{22}H_{16}O_9S$: C = 57.89, H = 3.50, O = 31.57, S = 7.02; found: C = 59.91, H = 6.31, O = 29.28, S = 4.50. The numbering of the C atoms is shown in Fig. 9.

3 Results and discussion

Figure 2 shows a cyclic voltammogram at a glassy carbon working electrode in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution for 1.0 mmol L^{-1} rutin in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid for a scan rate of 100 mV s^{-1}. In the positive potential scan three oxidation peaks are visible (E_p^I = 0.56 V, E_p^{II} = 0.81 V e E_p^{III} = 1.32 V). In the negative potential scan only some fluctuations in the current are perceptible and the accurate localization of potential peaks is

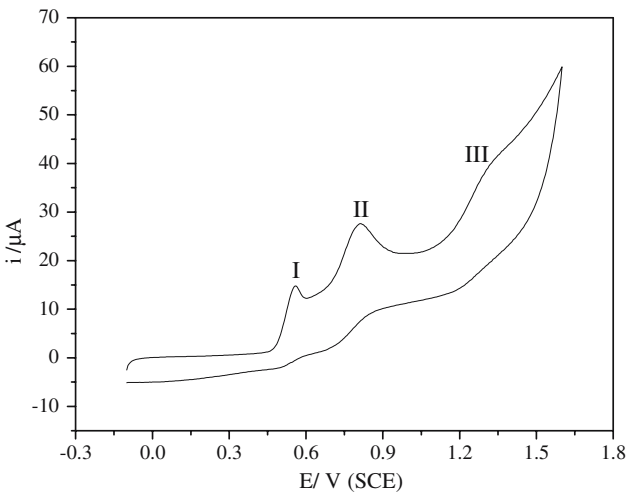

Fig. 2 Cyclic voltammogram for 1.0 mmol L^{-1} rutin in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid. Conditions: acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution (GCE, 100 mV s^{-1})

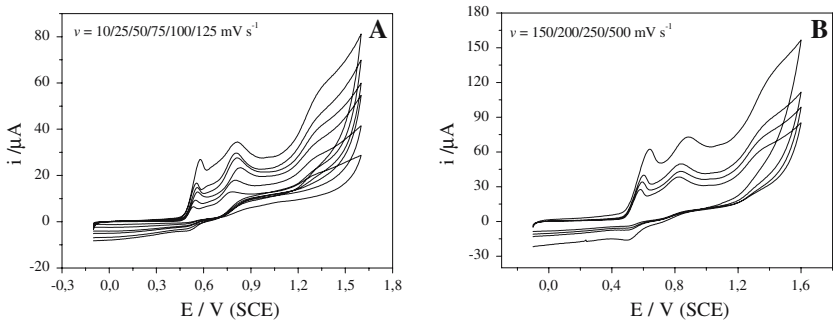

Fig. 3 Cyclic voltammogram for 1.0 mmol L^{-1} rutin in acetonitrile- sodium phosphate (4:1 (v/v); pH 2.0) solution in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid (GCE, 10–500 mV s^{-1})

not evident. As in the electrochemical oxidation of the quercetin [20], we believe that the first peak (E_p^I) is associated with the oxidation of the catechol moiety 3′,4′-dihydroxyl group at ring B. It will be shown later in the paper that the resulting *o*-quinone, as a consequence of its high reactivity, reacts with the *p*-toluenesulfinic acid nucleophile in a homogenous chemical reaction. The resulting electrochemically active sulfone derivatives can be oxidized at more positive potentials (E_p^{II} and E_p^{III}). The same behavior was recently found for the electrochemical oxidation of quercetin, rutin and morin in aqueous media in the absence of nucleophiles [20–22]. For purposes of electro-synthesis however, only the first heterogeneous oxidation reaction is relevant.

The electrodic processes at planar electrodes surfaces can be characterized by changes in the scan rate of the cyclic voltammetric experiments [23–26]. The results and discussion below are based on the Refs. [23–26]. Figure 3 shows cyclic voltammograms at a glassy carbon working electrode in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution for 1.0 mmol L^{-1} rutin in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid for scan rates from 10 to 500 mV s^{-1}. Increasing the scan rate displaced the oxidation peaks towards more positive potentials, describing irreversible electrochemical reactions. Figure 4 depicts the E_p^I and $E_p^{II} \times v$ behavior for the electro-oxidation of rutin in the presence of *p*-toluenesulfinic acid under the same conditions as shown in Fig. 3. For a reversible electrochemical reaction, a potential peak is independent of *v*. So, we can conclude that the heterogeneous electronic transfer at peaks I and II are irreversible or there is a homogeneous chemical reaction following each electrochemical reaction at the electrode surface. Owing to the difficulty of precisely localizing the potential, no data were obtained for the third oxidation process as a function of scan rate.

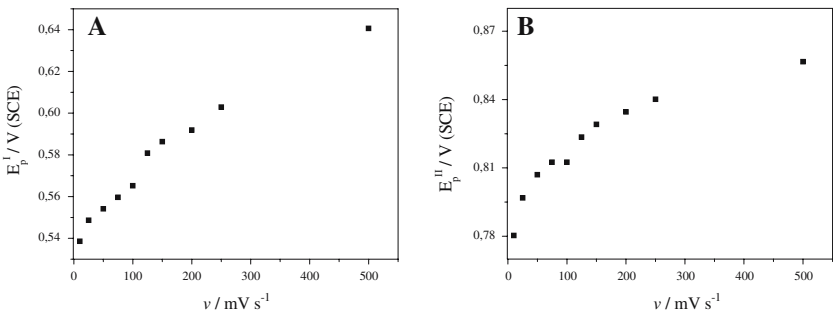

Fig. 4 $E_p^I \times v$ (**A**) and $E_p^{II} \times v$ (**B**) curves for 1.0 mmol L^{-1} rutin in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid

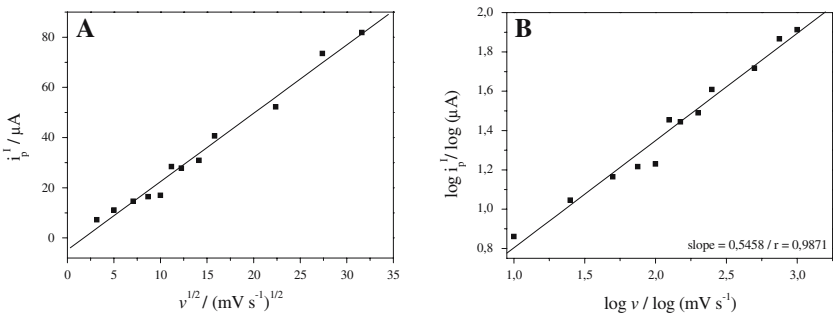

Fig. 5 $i_p^I \times v^{1/2}$ (**A**) and log $i_p^I \times \log v$ (**B**) curves for 1.0 mmol L^{-1} rutin in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid

Two approaches widely used to study the reversibility of reactions and to determine whether a reaction rate is adsorption or diffusion controlled are the analyses of the $i_p \times v^{1/2}$ and log $i_p \times$ log v curves. Figure 5 shows these plots for the first oxidation peak of rutin in the presence of *p*-toluenesulfinic acid in the same conditions as described above. For reversible or irreversible systems without kinetic complications, i_p varies linearly with $v^{1/2}$, intercepting the origin. However, the plot $i_p \times v^{1/2}$ deviate from linearity and present a value different to zero for the linear coefficient if the electrodic process is preceded or followed by a homogeneous chemical reaction. In Fig. 5A it can be seen that the graph of i_p^I vs. $v^{1/2}$ is linear, but it does not intercept the origin. This suggests that the electrode reaction at peak I is diffusion-controlled and also that there is a chemical reaction coupled to the electron transfer. Figure 5B shows the log $i_p^I \times$ log v curve with slope of ~0.5. A slope close to 0.5 is expected for controlled-diffusion electrodic processes and close to 1.0 for adsorption-controlled processes. Therefore, it is clear that mass transfer controls the oxidation of rutin in the presence of *p*-toluenesulfinic acid.

A criterion widely used to determine if the non-reversibility of the electrode process is due to a sluggish heterogeneous electron transfer kinetic or to a homogeneous coupled chemical reaction is the analysis of the $i_p v^{-1/2} \times v$ curve. The current function ($i_p v^{-1/2}$) is independent of v for reversible and irreversible processes. However, if the non-reversibility is due to a coupled chemical reaction, the current function varies with v and an increase or a decrease can be observed depending of the nature of the chemical reaction. Figure 6 shows the $i_p^I v^{-1/2} \times v$ for the electro-oxidation of the 1.0 mmol L^{-1} rutin in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid at glassy carbon working electrode in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution. Accordingly, the decrease of the current function with v indicates that a chemical reaction is coupled to the electrode process.

Figure 7 shows cyclic voltammograms obtained in the same conditions as for Fig. 3, except that the potential was switched at E_p^I + 0.1 V/SCE. The voltammograms are characteristic of an irreversible process, showing only one oxidation peak whose potential is dependent on the scan rate, suggesting that the product formed at E_p^I is quickly consumed in the bulk solution. This type of behavior was observed for small potential scan rates of 10–125 mV s^{-1}.

Controlled potential coulometry was performed in acetonitrile sodium phosphate (4:1 (v/v); pH 2.0) solution for 1.0 mmol L^{-1} rutin in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid at 0.80 V/SCE in

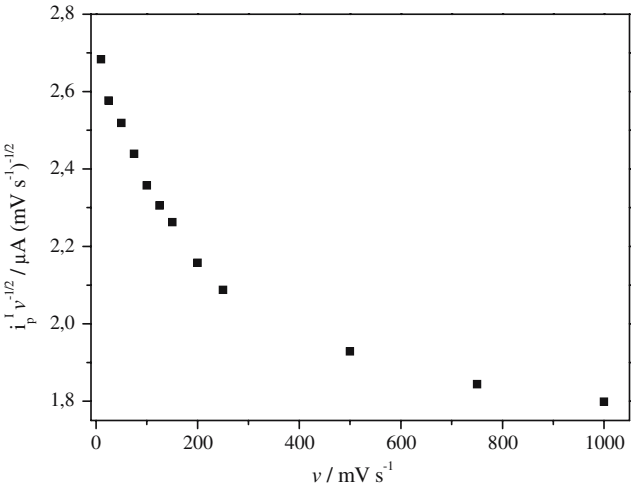

Fig. 6 $i_p^I v^{-1/2} \times v$ curve for 1.0 mmol L^{-1} rutin in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid

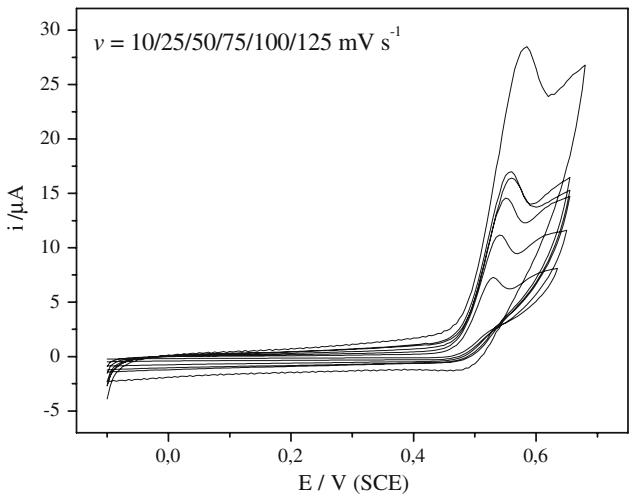

Fig. 7 Cyclic voltammograms for 1.0 mmol L^{-1} rutin in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid (GCE, 10–125 mV s^{-1}, $E_{\lambda,c}$ = –0,10 mV, $E_{\lambda,a}$ = (E_p^I + 0,10) V/SCE)

order to determine the number of electrons and to prepare the sulfone derivatives. The electrolysis progress was monitored by cyclic voltammetry and the resulting electrolyzed solution was carefully handled in order to isolate and identify the product. The charge consumption amounted to about 2 electrons per molecule of rutin. During the electro-synthesis, principally in the initial minutes, the solution changed color from yellow to brown, the characteristic color of *o*-quinones solutions. The calculated number of electrons and the color of the solution are evidence that the rutin is initially oxidized to a corresponding *o*-quinone. The presence of the *p*-toluenesulfinic acid in solution

favors the formation of a product more stable than *o*-quinone, i.e., the sulfone derivatives.

The crude product was subjected to column chromatography on silica gel to give two main organic compounds. The structure of these compounds was determined by IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry and microanalysis as being 6′(4-methylphenylsulfonyl)rutin **(1)** and 6′(4-methylphenyl sulfonyl)quercetin **(2)**. The localization of the 4-methylphenylsulfonyl group in the position C6′ in both products was deduced through of the hydrogen H2′ and H5′ resonance as singleto at δ 7,12 and 7,80 ppm, respectively. Compound **(2)** was firstly obtained by Nematollahi and Malakzadeh [15]. Our results from spectroscopic and elemental analyses agree well with those published. The main difference between **(1)** and **(2)** is the presence of sugars in **(1)**. The sugars were characterized by ^{1}H NMR, as well as the localization of the 4-methylphenylsulfonyl group in the position C6′.

Figure 8A shows cyclic voltammograms at a glassy carbon working electrode in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution for 1.0 mmol L^{-1} rutin in absence of *p*-toluenesulfinic acid for scan rate from 10 to 125 mV s^{-1}. The potential was switched at E_{p}^{I} + 0.10 V/SCE. Two peaks are observed: one for the positive and one for the negative potential scan. Both peaks are scan rate dependent, indicating the instability of the oxidation product. Figure 8B depicts cyclic voltammograms obtained for 1.0 mmol L^{-1} rutin in the presence of 1.2 mmol L^{-1} *p*-toluenesulfinic acid for a scan rate of 50 mV s^{-1} (a) before and (b) after the electrolysis. Other experimental conditions are the same as for Fig. 8A. In the cyclic voltammogram obtained before the electrolysis only one oxidation peak was observed, similar to those observed in Fig. 7. After the electrolysis the voltammogram was similar to those shown in the Fig. 8A.

According to our findings, the rutin electro-oxidation in the presence of *p*-toluenesulfinic acid can be described as in Fig. 9. Initially, the rutin is oxidized, forming the corresponding *o*-quinone in a two-electron two-proton heterogeneous process. The generated *o*-quinone is unstable and can generate other more stable products in solution. However, *o*-quinone is electrochemically active and can be reduced to its starting compound (rutin). This electrochemical step is compatible with the voltammograms shown in the Fig. 8A, which show one oxidation and one reduction peak dependent on the scan rate. In the presence of the *p*-toluenesulfinic acid (nucleophile), the rutin is electrochemically oxidized at the electrode surface forming the corresponding *o*-quinone, which then reacts in the bulk solution with the nucleophile to form the 6′(4-methylphenylsulfonyl)rutin **(1)**. The voltammograms (Fig. 8B (a) before; (b) after electrolysis) are compatible with this proposition. Before the electrolysis, rutin oxidizes forming the corresponding *o*-quinone, which quickly reacts with the *p*-toluenesulfinic acid in the solution forming the sulfone derivative. In this homogeneous chemical reaction, the catechol group present in the ring B is regenerated (Fig. 9). The positive potential scan shows one oxidation peak, but the negative one does not show a reduction peak, because there is no *o*-quinone available to be reduced. After electrolysis the major product in the solution is the 6′(4-methylphenylsulfonyl)rutin **(1)**. The cyclic voltammetry of this solution (Fig. 8B(b)) shows the electro-oxidation of **(1)** in the positive potential scan, also generating the corresponding *o*-quinone, which is very stable and can be reduced in the negative potential scan.

The presence of the 6′(4-methylphenylsulfonyl)-quercetin **(2)** in the electrolyzed solution does not alter the cyclic voltammogram (Fig. 8B(b)). The main difference between **(1)** and **(2)** are the sugars present in **(1)**. As the sugars do not participate in the electrochemical step, the profile and the interpretation of the voltammogram are unchanged. For the formation of **(2)**, the reaction scheme is similar to that

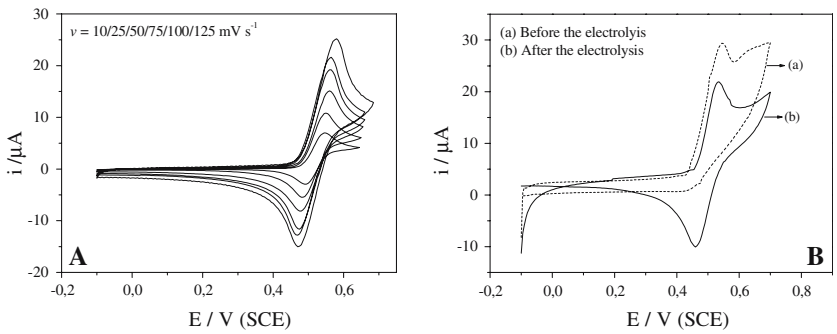

Fig. 8 Cyclic voltammograms for 1.0 mmol L^{-1} rutin in acetonitrile-sodium phosphate (4:1 (v/v); pH 2.0) solution in absence (**A**—10–125 mV s^{-1}) and in the presence (**B**—50 mV s^{-1}) of 1.2 mmol L^{-1} *p*-toluenesulfinic acid (a) before and (b) after the electrolysis (GCE, $E_{\lambda,c}$ = –0,10 mV, $E_{\lambda,a}$ = (E_{p}^{I} + 0,10) V/SCE)

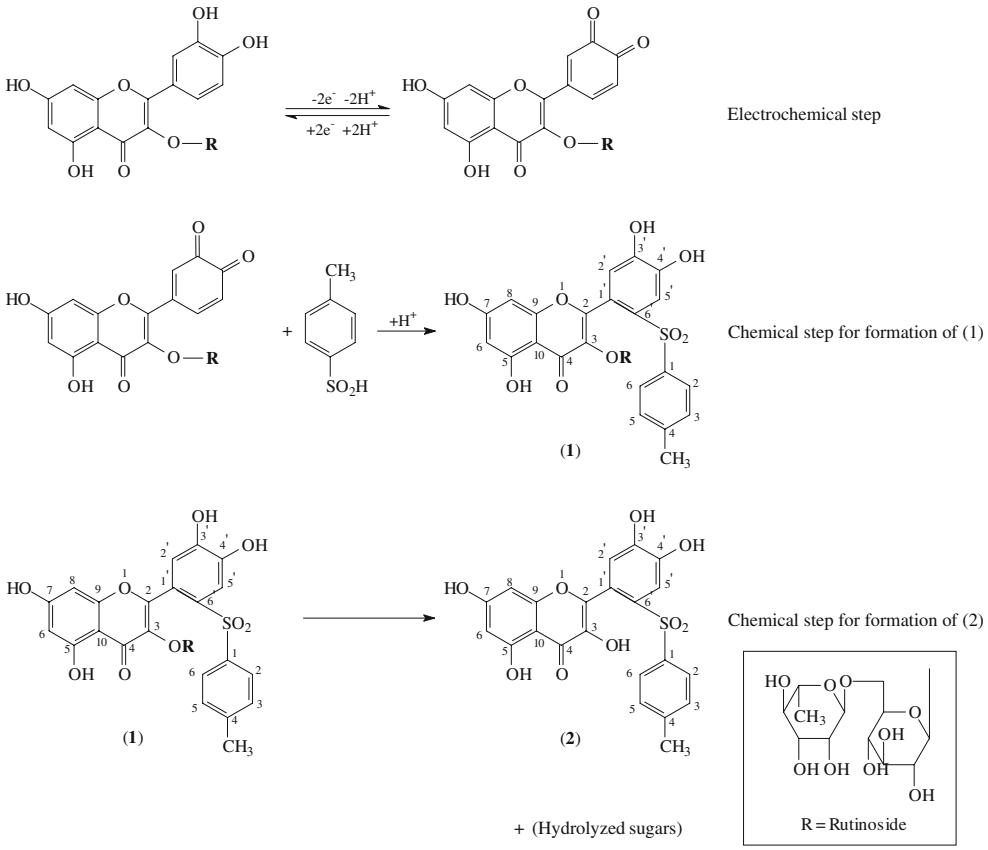

Fig. 9 Reactions scheme for the electro-synthesis of 6′(4-methylphenylsulfonyl) rutin **(1)** and 6′(4-methylphenylsulfonyl) quercetin **(2)**

proposed for **(1)**, but in the formation of **(1)** the sugars are not hydrolyzed during electrolysis.

4 Conclusions

The results demonstrate the formation of 6′(4-methylphenylsulfonyl)rutin and of 6′(4-methylphenylsulfonyl)quercetin in a simple electrochemical procedure. The starting reagent rutin is electrochemically oxidized at a glassy carbon electrode in a two-electron, two-proton process. In this electrochemical step the generated resultant *o*-quinone reacts in the bulk solution with the *p*-toluenesulfinic acid to form the sulfone derivatives. The resulting mechanism is EC (Electrochemical-Chemical). In the electrochemical reaction the diffusion of the rutin towards the electrode surface is the rate determining reaction step. In the chemical reaction the *o*-quinone participates in a Michael addition reaction with the *p*-toluenesulfinic acid forming the sulfone derivatives with good purity. An overall reaction scheme is proposed to illustrate the EC mechanism for both products.

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