J. Iran. Chem. Soc., Vol. 8, No. 1, March 2011, pp. 48-58.

JOURNAL OF THE
Iranian
Chemical Society

A Convergent Paired Electrochemical Synthesis of New Heterocyclic Compounds. Reaction of Benzoquinones with 3-Amino-4-hydroxycoumarin

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(Received 14 January 2010, Accepted 13 February 2010)

Electrochemical oxidation of catechols (**1**) has been studied in the presence of cathodically generated 3-amino-4-hydroxycoumarin (**3a**) as a nucleophile in aqueous solutions, using cyclic voltammetry and controlled-potential coulometry. The results indicate that the *o*-benzoquinones derived from catechols (**1**) participate in Michael addition reaction with 3-amino-4-hydroxycoumarin (**3a**) to form the corresponding new heterocyclic compounds (**7**) (oxidized form of coumestan derivatives). The electrochemical process consists of a multi-step including (a) cathodic reduction of 4-hydroxy-3-nitrocoumarin (**3**) to 3-amino-4-hydroxycoumarin (**3a**), (b) anodic oxidation of catechols (**1**) to related *o*-benzoquinone (**2**), (c) the Michael addition reaction of 3-amino-4-hydroxycoumarin (**3a**) to *o*-benzoquinone (**2**), and (d) anodic oxidation of formed adduct. The paired electrochemical synthesis of compounds **7a** and **7b** has been successfully performed in a one-pot process at carbon rods as working and counter electrodes in an undivided cell.

Keywords: 4-Hydroxy-3-nitrocoumarin, Catechol, Paired electrochemical synthesis, Cyclic voltammetry, 3-Amino-4-hydroxycoumarin

INTRODUCTION

Electrosynthesis offers a powerful tool for the formation of anion and cation radical intermediates and for driving clean synthetic reactions without the need for additional chemical reagents [1]. In electro-organic synthesis, it is known that the number of electrons added at the cathode (for reduction) must simultaneously be removed at the anode (for oxidation). Unfortunately, in most of the processes the product in one of the compartments is undesirable [2]. The strategy of paired electrochemical synthesis for the production of organic chemicals, in which the reactions at both the anode and cathode simultaneously contribute to the formation of the final product(s), could result in as much as a 50% reduction in energy consumption as compared to conventional electro-organic syntheses [3,4]. In commercial electrosynthetic processes, pairing electrode processes has always been important [1]. The most prominent example of a paired electrosynthesis is the production of adiponitrile by electrohydrodimerisation of acrylonitrile, which is an industrially important intermediate used in the manufacture of nylon-6,6 [5]. In paired electrochemical synthesis, processes in which two starting materials upon oxidation and reduction give the same product may be employed in a convergent process [1].

On the other hand, the importance of compounds known as coumestans [6] has led many workers to synthesize a number of coumestan derivatives by chemical [7-10] and electrochemical [11-14] routes. These compounds are derivatives of 6*H*-benzofuro[3,2-c][1]benzopyran-6-one and

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are structural compounds of many natural products such as wedelolactone, medicagol, psoraldin, isopsoraldin, erosnin and the estrogenic coumestrol, which possess interesting physiological activities [15,16].

These objects prompted us to investigate the electrochemical oxidation of catechols in the presence of 4-hydroxy-3-nitrocoumarin and we have discovered an easy and one-pot convergent paired electrochemical method for the synthesis of new oxidized form of coumestan derivatives (**7a**,**b**) in high yield and purity, using this environmentally friendly method with high atom economy.

EXPERIMENTAL

Apparatus and Reagents

Cyclic voltammetry and controlled-potential coulometry were performed using a Behpajoh model BHP-2062 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc (1.8 mm diameter) and platinum wire was used as the counter electrode. The working electrode (cathode) used in controlled-potential coulometry and macroscale electrolysis was an assembly of two graphite rods (6 mm diameter and 6 cm length) and two same graphite rods constituted the counter electrode (anode). The working electrode potentials were measured versus standard calomel electrode (SCE) (all electrodes from AZAR Electrode). All chemicals (4-hydroxy-3-nitrocoumarin, catechol, 3-methylcatechol and 4-methylcatechol) were reagent-grade materials, from Aldrich. Phosphate salts were proanalysis grade from E. Merck. These chemicals were used without further purification.

Electro-organic Synthesis of 3a

An aqueous solution of phosphate buffer (80 ml) (pH 6.0, c = 0.2 M) containing 2 mmol of 4-hydroxy-3-nitrocoumarin (**3**) was electrolyzed at the -0.85 V *vs*. SCE in a divided cell equipped with graphite rods as cathode and anode (an assembly of two rods in each case). The electrolysis was terminated when the cathodic peak that corresponds to the reduction of 4-hydroxy-3-nitrocoumarin (**3**) (C_1 in Fig. 2) in cyclic voltammetry disappears. At the end of the electrolysis, cell was placed in the refrigerator overnight. The precipitated solid was collected by filtration and washed with water.

Isolated yield = 62%. MS: *m/z* (relative intensity); 177 ($M^{+\cdot}$, 23), 121 (100), 92 (29), 65 (44), 39 (45).

Electro-organic Synthesis of 7a,b

An aqueous solution of phosphate buffer (80 ml) (pH 6.0, c = 0.2 M) containing of catechol {**1a** or **1b** (2 mmol) and **7**, (0.5 mmol)} and 2 mmol of 4-hydroxy-3-nitrocoumarin (**3**) was electrolyzed at the 0.50 V *vs*. SCE in an undivided cell equipped with graphite rods as cathode and anode. The electrolysis was terminated when the cathodic peak that corresponds to the reduction of 4-hydroxy-3-nitrocoumarin (**3**) in cyclic voltammetry disappears. At the end of the electrolysis, cell was placed in the refrigerator overnight. The precipitated solid was collected by filtration and washed with water.

Compound 7a. m.p.: 207-209 °C (dec), isolated yield = 76%. MS: *m/z* (relative intensity); 280 (8.8), 275 (6.9), 180 (4.4), 121 (53.1), 94 (100), 65 (55.5). FT-IR (KBr): ν 3186 (broad), 1728, 1608, 1553, 1490, 1444, 1279, 1209, 1105, 858, 759 cm^{-1}.

Compound 7b. m.p.: 199-201 °C (dec), isolated yield = 81%. MS: *m/z* (relative intensity); 295 (100), 267 (19.7), 238 (32.0), 139 (20.9), 121 (49.2), 91 (36.4), 63 (50.4). IR (KBr): ν 3073 (broad), 1686, 1633, 1611, 1584, 1465, 1433, 1346, 1288, 1212, 1151, 1112, 1040, 904, 774, 724, 669, 605 cm^{-1}.

RESULTS AND DISCUSSION

Electrochemical Study of 4-Hydroxy-3-nitrocoumarin (3)

Cyclic voltammograms of 1 mM solution of 4-hydroxy-3-nitrocoumarin (**3**) in aqueous solutions at various pHs are shown in Fig. 1. Over a pH range from 2.0 to 8.0, cyclic voltammograms show one cathodic (C_1) and anodic (A_1) peak which corresponds to the reduction of 4-hydroxy-3-nitrocoumarin (**3**) to 3-amino-4-hydroxycoumarin (**3a**) and oxidation of 3-amino-4-hydroxycoumarin (**3a**) to 4-hydroxy-3-(hydroxyamino)coumarin (**3b**) (Scheme 1).

As Fig. 1 shows, the peak potentials for peaks C_1, and A_1 shifted to the negative potentials by increasing pH. This is expected because of the participation of protons in the reduction of **3** to **3a** and oxidation of **3a** to **3b**.

Controlled-potential coulometry was performed in aqueous

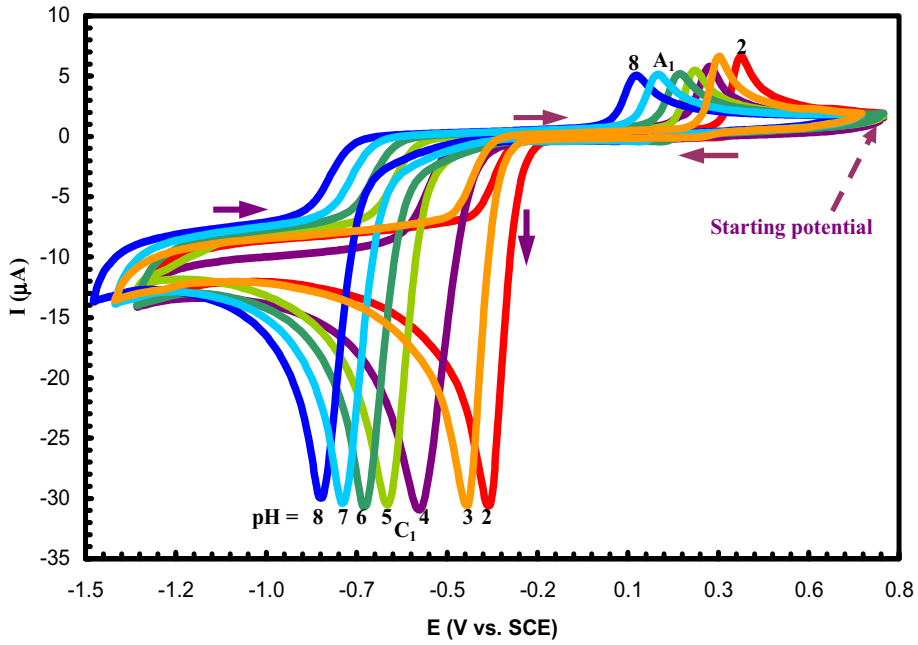
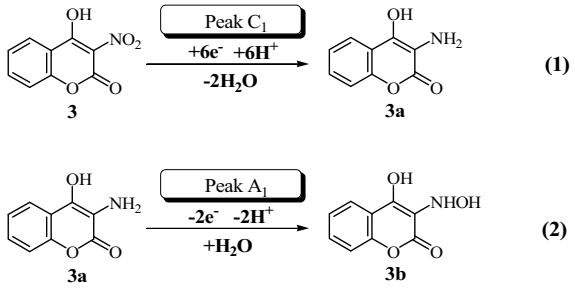


Fig. 1. Cyclic voltammograms of 1 mM 4-hydroxy-3-nitrocoumarin at glassy carbon electrode (1.8 mm diameter), in various pHs (2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0). Scan rate: 100 mV s^{-1}; t = 25 °C.



(1)

(2)

Scheme 1

solution containing 0.29 mmol of 4-hydroxy-3-nitrocoumarin (**3**) in a divided cell at -0.85 V (*vs*. SCE). Monitoring of the progress of the electrolysis was carried out by cyclic voltammetry (Fig. 2). As shown, during coulometry, in parallel with the decrease in height of the cathodic peak C_1, the height of anodic peak A_1 increases. At the end of the coulometry cathodic peak C_1 disappears and only anodic peak A_1 remains. The cathodic peak C_1 disappears when the charge consumption becomes about 6e$^-$ per molecule of **3** (Fig. 2, inset). These voltammetric and coulometric data in addition to mass spectroscopic data (*m/z* = 177) of the final product (see experimental section) in accompany with previous reports on chemical or electrochemical reduction of **3** [17-19], confirm formation of 3-amino-4-hydroxycoumarin (**3a**) in electrochemical reduction of 4-hydroxy-3-nitrocoumarin (**3**) (Scheme 1, Eq. 1).

Electrochemical Study of Catechols (1a and 1b) in the Presence of 4-Hydroxy-3-nitrocoumarin (3)

The electrochemical behavior of catechol (**1a**) in the presence of 4-hydroxy-3-nitrocoumarin (**3**) was studied in some detail. Figure 3 shows the cyclic voltammograms obtained for a 1 mM solution **1a** in the presence of 1 mM **3**, when oxidation of catechol (**1a**) occurs at first stage and reduction of **3** occurs at second stage. At this condition, voltammogram exhibit anodic peak A_2 and two cathodic peaks (C_1 and C_2). These peaks (A_2 and C_2) correspond to the oxidation of catechol (**1a**) to *o*-benzoquinone **2a** and vice versa within a reversible two-electron process [20,21]. Contrary to our previous reports on the electrochemical

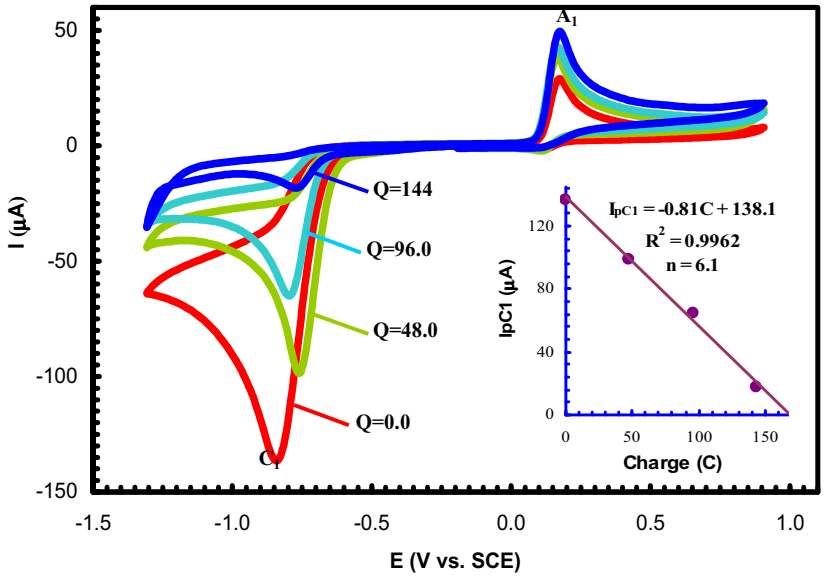


Fig. 2. Cyclic voltammograms of 0.29 mmol 4-hydroxy-3-nitrocoumarin in phosphate buffer solution (c = 0.2 M, pH 6.0), at glassy carbon electrode (1.8 mm diameter) during controlled-potential coulometry at -0.85 V *vs*. SCE. After consumption of: 0.0, 48.0, 96.0 and 144.0 C. Scan rate 100 mV s^{-1}. t = 25 ± 1 °C. Inset: variation of peak current (I_{pC1}) *vs*. charge consumed.

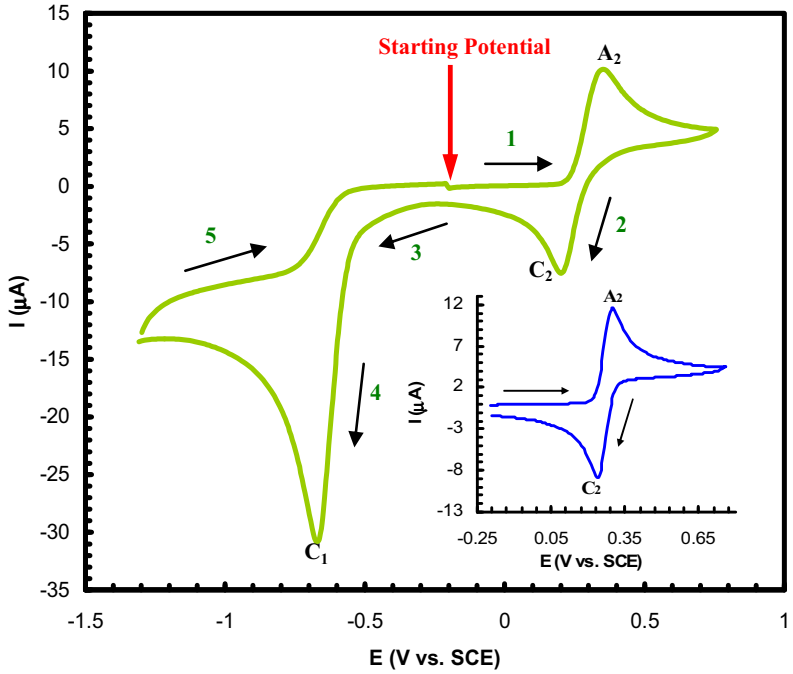


Fig. 3. Cyclic voltammogram of 1 mM catechol in the presence of 1 mM 4-hydroxy-3-nitrocoumarin, in phosphate buffer solution (c = 0.2 M, pH 6.0), at glassy carbon electrode. Sweeping direction: oxidation of catechol at the first stage and reduction of 4-hydroxy-3-nitrocoumarin at the second stage. Scan rate: 50 mV s^{-1}; t = 25 ± 1 °C. Inset; cyclic voltammogram of 1 mM catechol in the absence of 4-hydroxy-3-nitrocoumarin, in same conditions. Arrows 1-5, show sweeping direction.

oxidation of catechols in the presence of 4-hydroxycoumarin [13,14], in this condition, the peak current ratio (I_p^{C2}/I_p^{A2}) is near unity. This indicates that, 4-hydroxy-3-nitrocoumarin (**3**) doesn't have any nucleophilisity. This is related to the presence of nitro substituent, which has electron-withdrawing property in the structure of the 4-hydroxy-3-nitrocoumarin.

Figure 4 shows the cyclic voltammograms obtained for a 1 mM solution **1a** in the presence of 1 mM 4-hydroxy-3-nitrocoumarin (**3**), when reduction of **3** occurs at first stage and oxidation of **1a** occurs at second stage. The reactivity of anodically generated *o*-benzoquinone (**2a**) toward cathodically generated 3-amino-4-hydroxycoumarin (**3a**) is supported by the following evidence: (a) Decreasing of peak C_2 during the reverse scan. This indicates that *o*-benzoquinone **2a** is partially removed from the surface of electrode by chemical reaction with 3-amino-4-hydroxycoumarin (**3a**). (b) Increasing of peak A_2 current. This could be indicative of increasing of apparent number of electron (n_{app}) and (c) appearing of new anodic and cathodic peaks A_3 and C_0. In this case, the peak current ratio (I_p^{C2}/I_p^{A2}) is less than unity and depends on the sweep rate. It reaches to nearly unity in higher sweep rates. Also, disappearance of peak A_3 in higher sweep rates is another aspect of increasing of sweep rate. This peak (A_3) can be related to the oxidation of intermediate **6a** (see Scheme 2). Peak C_0 is independent to the peak A_1 and has dependency to peak A_2 (Fig. 5).

Furthermore, in the second cycle, a new anodic peak (A_0) which is counterpart of peak C_0, appears with an *E*p value of 0.01 V *vs*. SCE (Fig. 6). These peaks (C_0 and A_0) correspond to the oxidation of catechol **4a** to *o*-benzoquinone **5a** and vice versa (see Scheme 2). The oxidation of intermediate **4a** is easier than the oxidation of catechol **1a** by virtue of the presence of an electron-donating amine group. Diagnostic criteria of cyclic voltammetry and the mass spectrum of

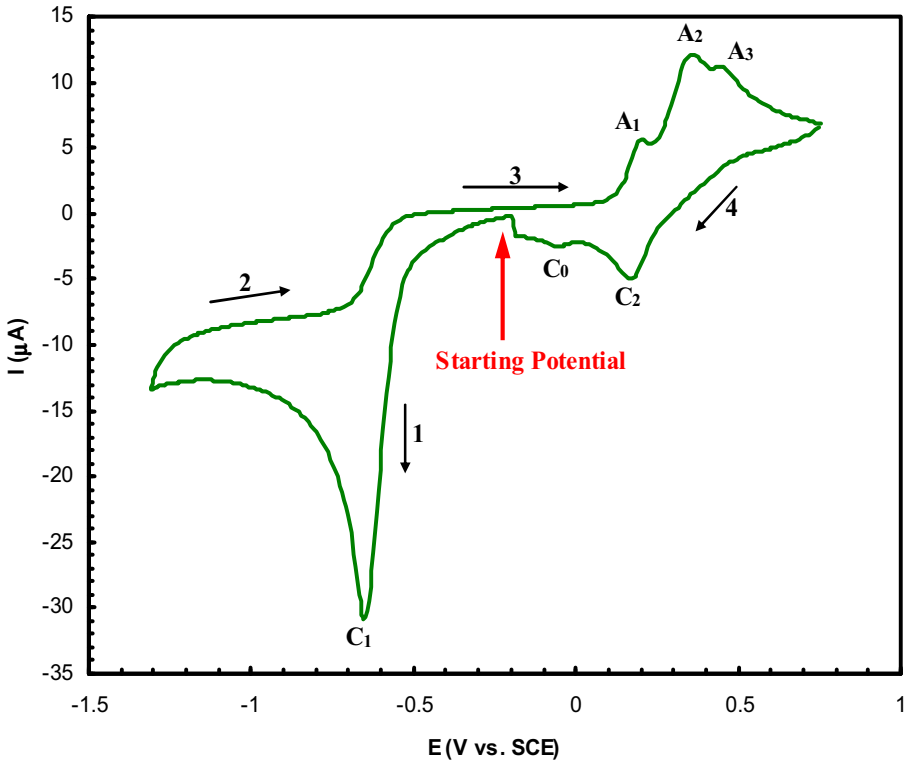


Fig. 4. Cyclic voltammogram of 1 mM catechol in the presence of 1 mM 4-hydroxy-3-nitrocoumarin, in phosphate buffer solution (c = 0.2 M, pH 6.0), at glassy carbon electrode. Sweeping direction: reduction of 4-hydroxy-3-nitrocoumarin at the first stage and oxidation of catechol at the second stage. Scan rate: 50 mV s^{-1}; t = 25 ± 1 °C. Arrows 1-4, show sweeping direction.

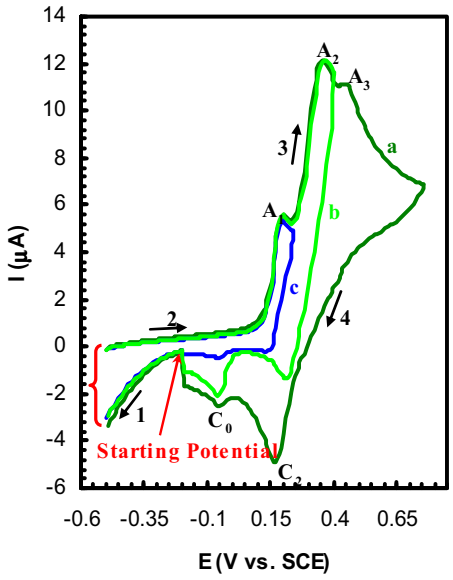


Fig. 5. Cyclic voltammograms of 1 mM catechol in the presence of 1 mM 4-hydroxy-3-nitrocoumarin, in phosphate buffer solution (c = 0.2 M, pH 6.0), at glassy carbon electrode with various switching potentials. Sweeping direction: reduction of 4-hydroxy-3-nitrocoumarin at the first stage and oxidation of catechol at the second stage. Scan rate: 50 mV s^{-1}; t = 25 ± 1 °C. Arrows 1-4, show sweeping direction. The reduction peak of 4-hydroxy-3-nitrocoumarin didn't show.

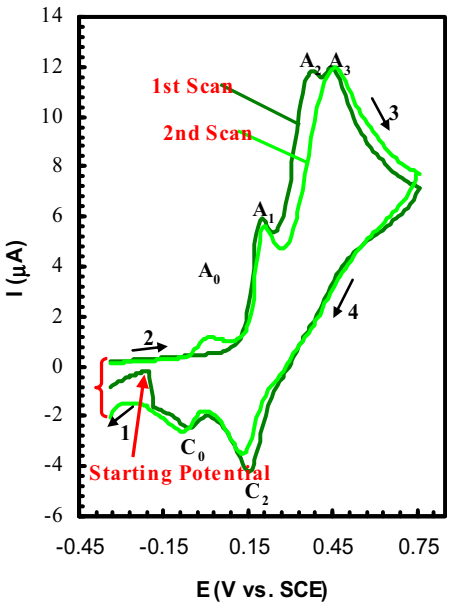


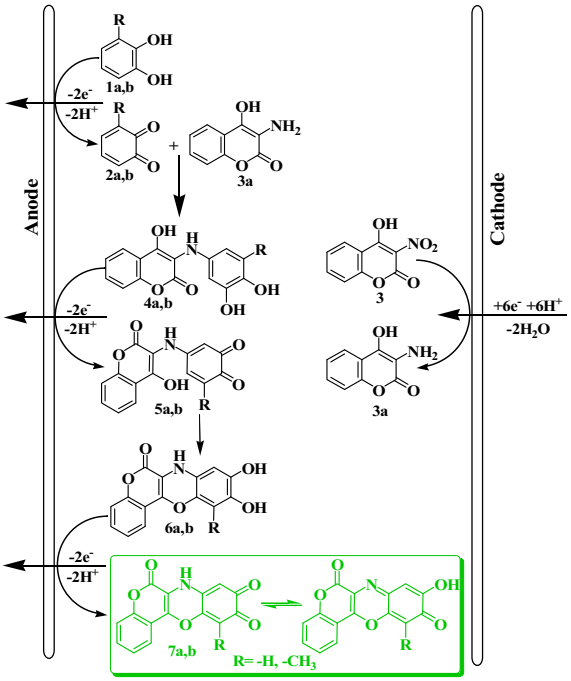
Fig. 6. First and second cycles of cyclic voltammograms of 1 mM catechol in the presence of 1 mM 4-hydroxy-3-nitrocoumarin, in phosphate buffer solution (c = 0.2 M, pH 6.0), at glassy carbon electrode. Sweeping direction; reduction of 4-hydroxy-3-nitrocoumarin at the first stage and oxidation of catechol at the second stage. Scan rate: 50 mVs^{-1}; t = 25 ± 1 °C. Arrows 1-4, show sweeping direction. The reduction peak of 4-hydroxy-3-nitrocoumarin didn't show.

isolated product indicate that the reaction mechanism of electrooxidation of catechols (**1a,b**) in the presence of 4-hydroxy-3-nitrocoumarin (**3**) is *ECECE* (Scheme 2).

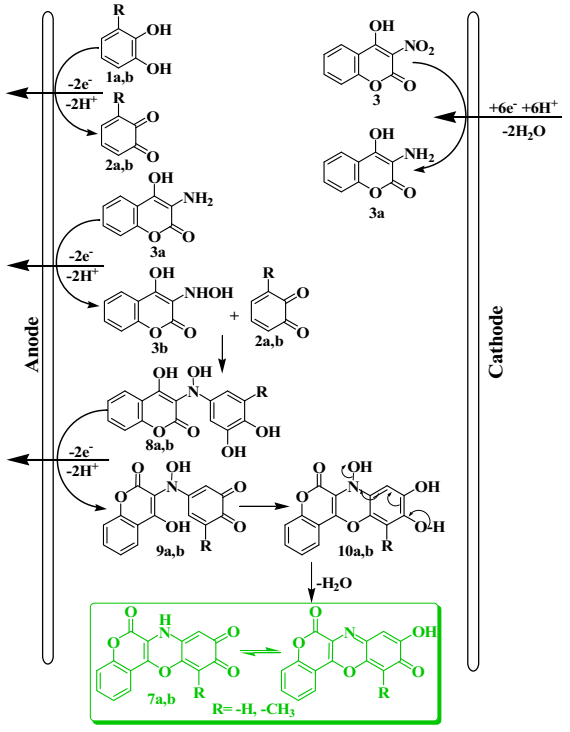
According to our results, it seems that the intermolecular Michael addition reaction of the cathodically generated 3-amino-4-hydroxycoumarin (**3a**) to *o*-bezoquinone **2a** leads to the intermediate **4a**. The oxidation of this compound (**4a**) is easier than the oxidation of the parent-starting molecule (catechol) by virtue of the presence of an electron-donating amine group in the structure of **4a**. The intramolecular Michael addition reaction in next stage converts *o*-bezoquinone **5a** to compound **6a** and in final stage and during the preparative reaction, the over-oxidation of product **6a** converts it to its oxidized form as final product (**7a**). The same results were obtained in the case of 3-methylcatechol (**1b**).

Since, oxidation potential of **3a** is less than E_{pA} of **1a** ($E_{pA1} < E_{pA2}$), oxidation of **3a** during the oxidation of **1a** is possible. So, presentation of a new Scheme according to oxidation of **3a** in anode is also probable (Scheme 3).

According to our results, it seems that the Michael addition reaction of **3b** to *o*-benzoquinone **2a**, leads to the intermediate **8a**. Oxidation of intermediate **8a** is easier than the oxidation of catechol **1a** by virtue of the presence of an electron-donating hydroxylamine group in structure of **8a**. In continuation, the intramolecular Michael addition reaction converts *o*-bezoquinone **9a** to compound **10a** which in the next step with removal of H_2O is converted to **7a**.



Scheme 2



Scheme 3

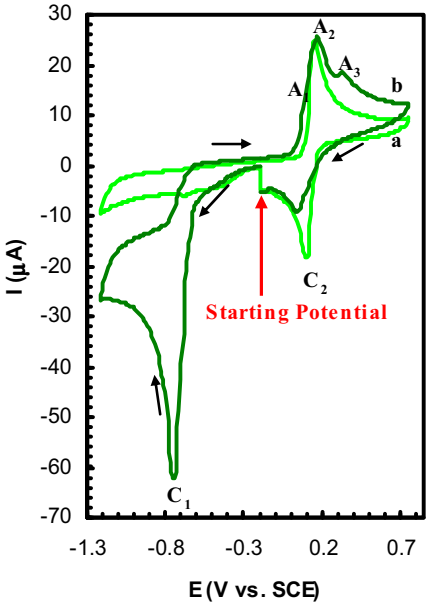


Fig. 7. Cyclic voltammograms of 1 mM 4-methylcatechol (a) in the absence and (b) in the presence of 1 mM 4-hydroxy-3-nitrocoumarin, in phosphate buffer solution (c = 0.2 M, pH 6.0), at glassy carbon electrode in various scan rates. Scan rate: 100 mV s^{-1}; t = 25 ± 1 °C. Arrows show sweeping direction.

Electrochemical Study of 4-Methylcatechol (1c) in the Presence of 4-Hydroxy-3-nitrocoumarin (3)

Among catechols, 4-alkylcatechols have special properties. *o*-Benzoquinone, formed from oxidation of 4-alkylcatechols can be converted to their tautomeric *p*-quinone methides form [22]. 4-Methylcatechol is a sample of 4-alkylcatechols, and also a model for biological molecules with biologic and therapeutic effects [23-25]. So we chose it with the aim of investigation of electrooxidation of 4-alkylcatechols in the presence of 3-amino-4-hydroxycoumarin (**3a**).

The cyclic voltammogram of a 1 mM solution of 4-methylcatechol (**1c**) in aqueous solution containing 0.2 M phosphate buffer (pH 6.0) is shown in Fig. 7 (curve a). The voltammogram shows one anodic (A_2) and a corresponding cathodic peak (C_2), which corresponds to the transformation of 4-methylcatechol (**1c**) to *o*-benzoquinone **2c** and vice versa within a quasi-reversible two-electron process [26]. Figure 7 (curve b) shows the cyclic voltammogram obtained for a 1

mM solution of **1c** in the presence of 1 mM 4-hydroxy-3-nitrocoumarin (**3**) in same condition. Decreasing of peak C_2 current during the reverse scan and appearing of a new anodic peak A_3 are evidences for reactivity of anodically generated *o*-benzoquinone (**2c**) or its tautomer form toward cathodically generated 3-amino-4-hydroxycoumarin (**3a**). Also, it is seen that proportional to the increasing of the potential sweep rate, parallel to the increase in current of the C_2 the height of A_3 decreases (Fig. 8). This peak (A_3) disappears in high scan rates (Fig. 8, curves e and f). These evidences reconfirm reactivity of **2c** toward **3a**. After exhaustive electrolysis, the formed product was compound **7a**. Therefore, it can be suggested that the formation of the unexpected product **7a** arises from an oxidative cleavage of the methyl group [27].

It is probable that this abnormal process was accomplished *via* enolization of the methyl group followed by chemical reactions on the tautomeric quinone methide [22,28,29] (see Scheme 4). We saw previously this unexpected type of product in electrochemical oxidation of 4-methylcatechol (**1c**) in methanol [30]. According to diagnostic criteria of cyclic voltammetry and the mass spectrum of isolated product, we proposed a mechanism including the generation of quinone methide and formation of a carbocation-leaving group in convergent paired electrochemical synthesis of **7a** (Scheme 4).

According to our results, it seems that the Michael addition reaction of 3-amino-4-hydroxycoumarin (**3a**) to *p*-quinone methide **2d** leads to intermediate **11**. The oxidation of this compound (**11**) is easier than the oxidation of the parent-starting molecule (4-methylcatechol) by virtue of the presence of an electron-donating group in structure of **11**. Therefore, in applied potential for oxidation of **1c**, this intermediate converts to *o*-benzoquinone **11a** which then under tautomerization reaction changes to *p*-quinone methide **11b**. In next step, intermolecular Michael addition reaction of **3a** to *p*-quinone methide **11b** converts **11b** to catechol **12**. Such as intermediate **11**, the oxidation of **12** is easier than oxidation of **1c** by virtue of the presence of two electron-donating groups in structure of it. Oxidation, tautomerization and subsequent intramolecular Michael addition reaction converts **12** to catechol **13**. As same as catechols **11** and **12**, under oxidation conditions, catechol **13** changes to related *o*-benzoquinone (**13a**). Intrermolecular Michael addition reaction, oxidation and then intramolecular Michael addition reaction together

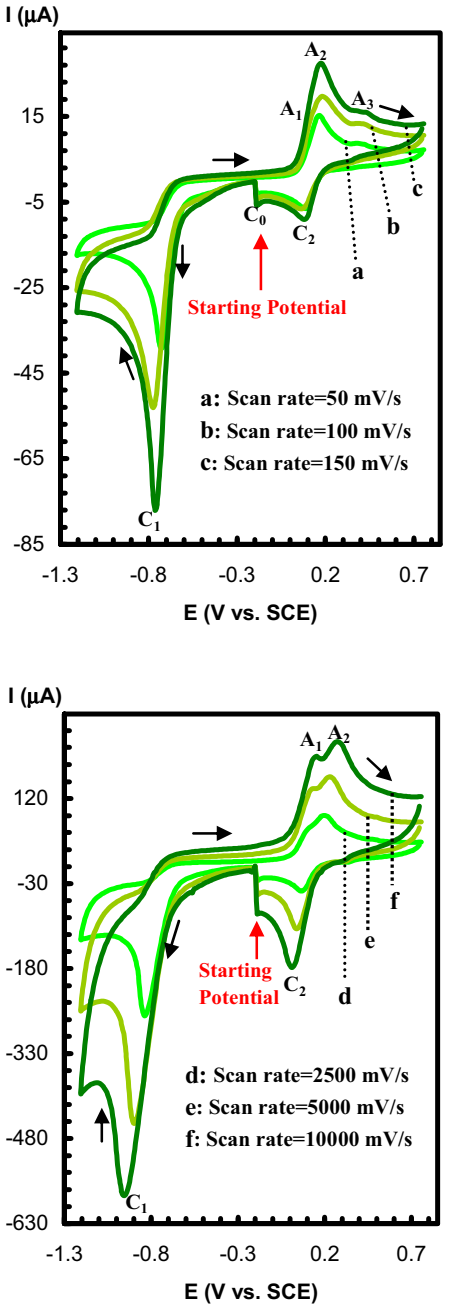
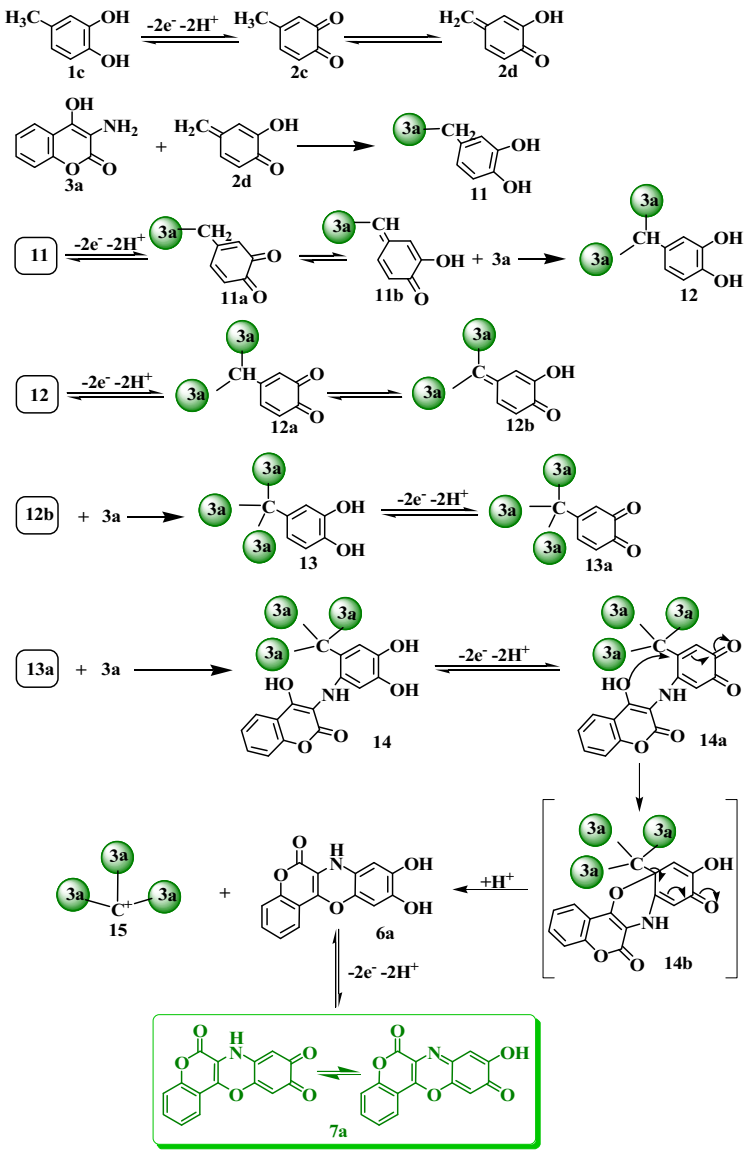


Fig. 8. Cyclic voltammograms of 1 mM 4-methylcatechol in the presence of 1 mM 4-hydroxy-3-nitrocoumarin, in phosphate buffer solution (c = 0.2 M, pH 6.0), at glassy carbon electrode in various scan rates. t = 25 ± 1 °C. Arrows show sweeping direction.

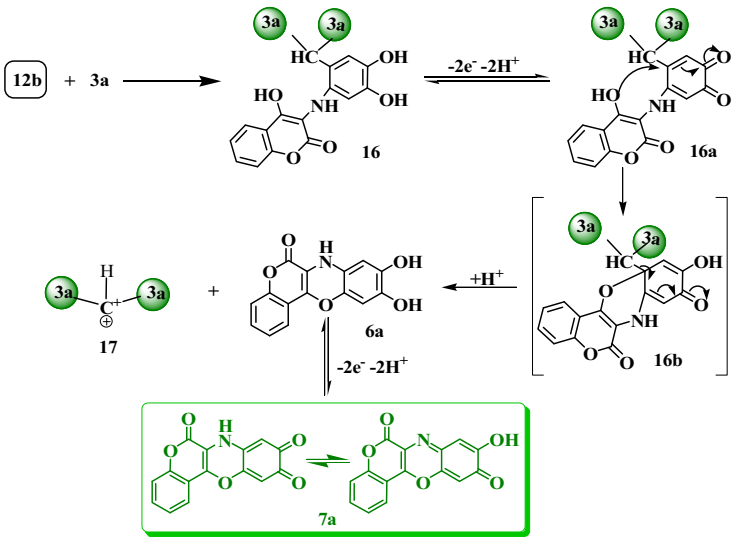


Scheme 4

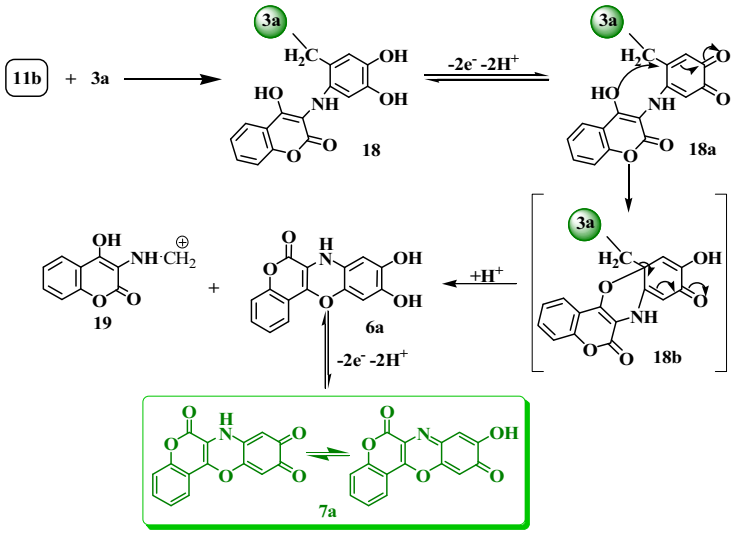
with removal of carbocation-leaving group **15** converts **13a** to compound **6a**. The over-oxidation of product **6a** during the preparative reaction, converts compound **6a** to its oxidized form as final product (**7a**).

Methyl group as a carbocation can not leave the molecule. The elimination of methyl group was performed when it converts to carbocation-leaving group **15**. Also, the elimination of methyl group can be carried out after formation of *p*-quinone methides **12b** or **11b** (Schems 5 and 6, respectively).

Controlled-potential coulometry of 4-methylcatechol (**1c**) in the presence of 4-hydroxy-3-nitrocoumarin (**3**) in aqueous solution containing 0.2 M phosphate buffer (pH 6.0) shows the consumption of about 10e$^-$ (n = 10.3) per molecule of **1c**.



Scheme 5



Scheme 6

According to this data we think that the elimination of methyl group can be carried out after formation of *p*-quinone methides **12b** (Schems 5). Also, as shown in Scheme 3, it is possible that instead of nucleophile **3a**, compound **3b** as a nucleophile participates in Michael addition reactions.

CONCLUSIONS

The results of this work show a convergent paired electrochemical synthesis of new heterocyclic compounds **7a** and **7b**. These products, which are oxidized form of

coumestan derivatives, were obtained after two successive intermolecular and intramolecular Michael addition reactions of 3-amino-4-hydroxycoumarin with quinones. The reaction mechanism for the synthesis of compounds **7a** and **7b** is presented in Schemes 2-6. In this work, a simple and efficient paired method for synthesis of compounds **7a** and **7b** is described. Furthermore, the results of this work introduce electrochemistry as a powerful and green tool in organic synthesis and mechanistic investigations.

ACKNOWLEDGMENTS

The authors acknowledge to Bu-Ali Sina University Research Council and Center of Excellence in Development of chemical Methods (CEDCM) for supporting this work.

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