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A Green Approach for the Electroorganic Synthesis of New Dihydroxyphenyl-indolin-2-one Derivatives

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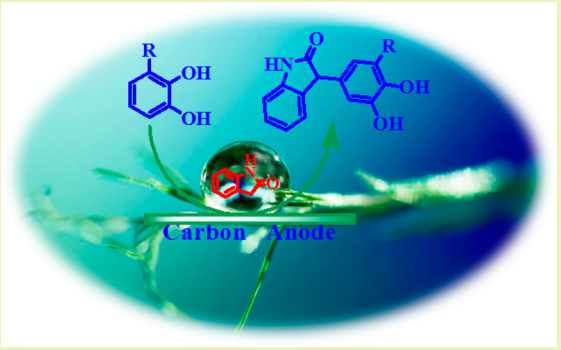
ABSTRACT: In an aqueous solution containing oxindole as a nucleophile, electrochemical oxidation of 2,3-dimethylhydroquinone and some catechols have been studied using cyclic voltammetry and controlled potential coulometry. The voltammetric data show that electrochemically generated *para*- and *ortho*-benzoquinones participate in Michael addition reactions with oxindole to form the corresponding dihydroxyphenyl-indolin-2-one derivatives. In this work, we have proposed a mechanism for the electrode process, and we report an efficient and one-pot green method for the synthesis of dihydroxyphenyl-indolin-2-one derivatives based on the Michael reaction of electrochemically generated *ortho*- and *para*-benzoquinones with oxindole in an undivided cell using an environmentally friendly reagentless method in ambient conditions.



KEYWORDS: *Green synthesis, Oxindole, Catechol, Cyclic voltammetry, Michael addition reaction*

INTRODUCTION

Electroorganic synthesis has become recognized as a powerful tool to develop environmentally compatible processes.[1] It is characterized by high selectivity, readily available starting materials, good atom economy, low-energy consumption and temperature, low costs for reagents, and material failure. In addition, electrons are considered to be clean reagents,[2] and electrodes may be regarded as heterogeneous catalysts that are easily separated from the products. So, it can be concluded that electrosynthesis is a green tool for organic synthesis. Oxindole derivatives are valuable building blocks for indole chemistry.[3] These natural products show potent antioxidant, anticancer, anti-HIV, neuroprotective and other biological properties[4] because of their ability to increase the breakdown of estrogen in the human body.[5,6] These compounds are also known to possess a variety of biological activities, such as potent inhibition of monoamine oxidase in human urine and rat tissues[7] and inhibition of several enzymes such as acetylcholinestrease,[8] and are potent antagonists of in vitro receptor binding by atrial natriuretic peptide.[9] On the other hand, many catechols such as catecholamines are biologically active compounds. Caffeic acid is inhibitory to soil bacteria and fungi, but species differences exist, while its methyl ester has more pronounced activity against *Bacillus* and *Pseudomonas* species. Hydroxychavicol inhibits a greater number of microorganisms including *Pseudomonas*, *Cladosporium*, and *Pythium* species. Many of flavonoids and catechol derivatives turned out to be antimicrobial agents.[10] Because of the medicinal properties of oxindole and catechol derivatives, we thought that synthesis of new organic compounds with both catechol and oxindole moieties may be useful from the point of view of pharmaceutical properties. In this direction, we and other researchers have shown that catechols and hydroquinones can be oxidized electrochemically to *ortho*- or *para*-benzoquinones, respectively. These compounds are very reactive and can be attacked by a variety of nucleophiles.[11−25] Adams and coworkers have reported that *o*-benzoquinone can react with nucleophiles such as ammonia, chloride, and sulfhydryl compounds to form the addition products.[11−13] They have also shown that *p*-benzoquinone, containing electron-withdrawing substituents, can be attacked by water.[14,15] Tabakovic and co-workers have also reported the electrochemical synthesis of a number of coumestan derivatives using the reaction of electrogenerated *o*-benzoquinone with some coumarin derivatives.[16,17] We and several other researchers have investigated the reactions of anodically generated benzoquinones in the presence of some nucleophiles.[18−25] This idea prompted us to investigate the electrochemical oxidation of 2,3-dimethylhydroquinone and some catechol derivatives in the presence of oxindole as a nucleophile and represent a green and one-pot electrochemical method for the synthesis of some new dihydroxyphenyl-indolin-2-one derivatives in high yield using an environmentally friendly method.

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MATERIALS AND METHODS

Apparatus and Reagents. Cyclic voltammetry and preparative electrolysis were performed using a μAutolab potentiostat/galvanostat type III. The working electrode that is used in the voltammetry experiment was a glassy carbon disk (1.8 mm diameter), and a Pt wire was used as a counter electrode. The working electrode potentials were measured versus the Ag/AgCl (3 M) as a reference electrode (all electrodes were obtained from Metrohm). The working electrode used in controlled potential coulometry was a carbon rod (6 mm diameter and 4 cm length), and macroscale electrolysis was carried out with an assembly of three carbon rods (8 mm diameter and 6 cm length). The pH was measured using a Metrohm pH meter 744 with a combined glass electrode. All chemicals (catechols, 2,3-dimethylhydroquinone, and oxindole) were reagent-grade materials from Aldrich, and phosphate salts were of pro-analysis grade from E. Merck These chemicals were used without further purification. All experiments were carried out at room temperature. The peak current ratios (I_{pC1}/I_{pA1}) were determined using the following equation given in ref 26.

$$I_{pc}/I_{pa} = (I_{pc})_0/I_{pa} + 0.485(I_{sp})_0/I_{pa} + 0.086$$

where $(I_{pc})_0$ and $(I_{sp})_0$ are cathodic peak current and "switching potential" current with respect to the zero current, respectively. I_{pc} and I_{pa} have their usual meanings.

Electroorganic Synthesis. In a typical procedure, 100 mL of phosphate buffer aqueous solution (c = 0.2 M, pH 7.2) was pre-electrolyzed at 0.35 V vs Ag/AgCl (3 M) in an undivided cell; then, 1.0 mmol of catechols (**1a**–**1c**) or 2,3-dimethylhydroquinone (**1d**) and oxindole (**3**) were added to the cell. Electrolysis was terminated when the decay of the current became more than 95%. The process was interrupted during electrolysis, and the carbon anode was washed in acetone to reactivate it. The precipitated solid was collected by filtration and washed several times with water. After drying, the products were characterized by IR, ^{1}H NMR, ^{13}C NMR, and MS.

Characteristics of 3,4-Dihydroxy-5-methylphenylindolin-2-one (5a). Yield: 74.8%. Mp: 256–258 °C. IR (KBr) ν/cm^{-1}: 3271, 1708, 1620, 1471, 1304, 1203, 1112, 1045, 835, 754, 676. ^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 2.07 (s, 3H, methyl), 4.46 (s, 1H, CH), 6.00 (d, 1H, J = 7.0, aromatic in oxindole ring), 6.12 (d, 1H, J = 7.0, aromatic in oxindole ring), 6.50–7.16 (m, 4H, aromatic in catechol and oxindole rings), 9.00 (broad, NH), 10.15 (s, 1H, OH), 10.35 (s, 1H, OH). MS (EI); m/z (relative intensity): 255 [M]$^+$ (35), 226 (20), 210 (25), 133 (90), 104 (100), 78 (85), 63 (35), 51 (70).

Characteristics of 3,4-Dihydroxyphenylindolin-2-one (5b). Yield: 71.4%. Mp: 250–252 (dec.) °C. IR (KBr) ν/cm^{-1}: 3249, 3000, 1708, 1620, 1471, 1330, 1207, 1110, 887, 754, 671, 500. ^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 4.45 (s, 1H, CH), 5.98 (d, 1H, J = 9.0 Hz, aromatic in oxindole ring), 6.05 (d, 1H, J = 9.0, aromatic in oxindole ring), 6.7–7.2 (m, 5H, aromatic in catechol and oxindole rings), 9.03 (s, 1H, NH), 10.16 (s, 1H, OH), 10.37 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 55.8 (−CH−), 109.5 (aromatic), 110.2 (aromatic), 115.2 (aromatic), 121.6 (aromatic), 124.8 (aromatic), 126.2 (aromatic), 127.9 (aromatic), 128.7 (aromatic), 129.1 (aromatic), 129.8 (aromatic), 144.1 (aromatic), 145.4 (aromatic), 176.7 (C═O). MS (EI); m/z (relative intensity): 241 [M]$^+$ (60), 212 (55), 196 (45), 133 (90), 104 (100), 78 (70), 63 (60), 51(45).

Characteristics of 3,4-Dihydroxy-5-methoxyphenylindolin-2-one (5c). Yield: 78.8%. Mp: 247–249 °C. IR (KBr) ν/cm^{-1}: 3369, 2965, 1708, 1619, 1517, 1471, 1829, 1205, 1093, 754, 678. ^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 3.70 (s, 3H, OCH_3), 4.57 (s, 1H, CH), 6.01 (d, 1H, J = 7.4, aromatic in oxindole ring), 6.08 (d, 1H, J = 7.4, aromatic in oxindole ring), 6.7–7.2 (m, 4H, aromatic in catechol and oxindole rings), 8.42 (s,1H, aromatic in catechol ring), 8.96 (s, 1H, NH), 10.17 (s, 1H, OH), 10.41(s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 52.0 (CH_3O), 56.5 (−CH−), 104.2 (aromatic), 109.5 (aromatic), 109.7 (aromatic), 121.1 (aromatic), 121.3 (aromatic), 125.3 (aromatic), 126.8 (aromatic), 128.3 (aromatic), 128.6 (aromatic), 128.9 (aromatic), 133.8 (aromatic), 143.4 (aromatic), 178.1 (C═O). MS (EI); m/z (relative intensity): 271 [M]$^+$ (60), 212 (25), 182 (20), 154 (20), 133 (90), 104 (100),78 (70), 51 (65).

Characteristics of 2,5-Dihydroxy-3,4-dimethyphenylindolin-2-one (5d). Yield: 68.1%. Mp: 187–189 °C. IR (KBr) ν/cm^{-1}: 3256, 1691, 1618, 1471, 1328, 1229, 1080, 751. ^{1}H NMR (300 MHz, DMSO-d_6) δ/ppm: 1.96 (s, 1H, CH_3), 2.11 (s, 3H, CH_3), 3.46 (s, 1H, CH), 6.73–7.73 (m, 4H, aromatic in hydroquinone and oxindole rings), 7.72 (s, 1H, aromatic in hydroquinone ring), 8.62 (s, 1H, NH), 10.36 (s, 1H, OH), 10.80 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6) δ/ppm: 12.6 (CH_3), 13.5 (CH_3), 60.5 (−CH−), 110.3 (aromatic), 121.6 (aromatic), 125.4 (aromatic), 127.0 (aromatic), 127.9 (aromatic), 128.2 (aromatic), 133.2 (aromatic), 140.7 (aromatic), 142.0 (aromatic), 144.1 (aromatic), 144.7 (aromatic), 145.0 (aromatic), 184.5 (C═O). MS (EI); m/z (relative intensity): 269 [M]$^+$ (60), 224 (80), 194 (20), 165 (23), 104 (30), 77 (40), 39 (45).

RESULTS AND DISCUSSION

A cyclic voltammogram (first cycle) of 3-methylcatechol (**1a**) (1.0 mM) in an aqueous phosphate buffer solution (pH 7.2, c = 0.2 M), shows one anodic peak (A_1) at 0.35 V and a corresponding cathodic peak at −0.08 V (C_1), which represent the transformation of **1a** to 3-methylcyclohexa-3,5-dien-1,2-dione (**2a**) and vice versa within a quasi-reversible two-electron process[18–21] (Figure 1, curve a). A peak current ratio (I_{pC1}/I_{pA1}) of nearly unity can be considered as a criterion for the stability of **2a** under the experimental conditions. This implies that some possible side reaction including, hydroxylation,[15] dimerization,[27–29] and oxidative ring cleavage[30] reactions are too slow to be observed at the time scale of the cyclic voltammetry. Figure 1, curves b and c, shows the cyclic voltammograms obtained for **1a** in the presence of oxindole (**3**). Comparison of these voltammograms with cyclic voltammogram of **1a** in the absence of **3** shows that the cathodic peak C_1 decreased. In this figure, curve d is related to the cyclic voltammogram of oxindole (**3**) in the absence of **1a**. This figure also shows that the peak current ratio (I_{pC1}/I_{pA1}) is dependent on the concentration of **3** and decreases with increasing it.

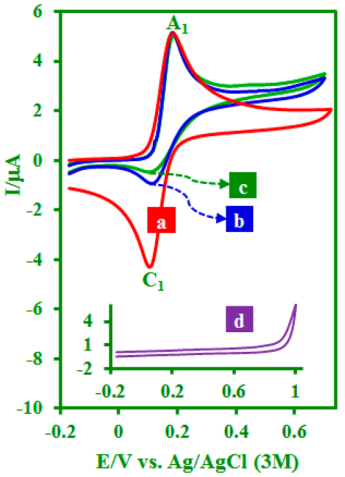

Figure 1. (a): Cyclic voltammograms of 3-methylcatechol (**1a**) (1.0 mM) in the absence of oxindole (**3**). (b): 3-Methylcatechol (**1a**) in the presence of **3** (2.0 mM). (c): 3-Methylcatechol (**1a**) in the presence of **3** (5.0 mM). Scan rate: 10 mV s^{-1}. (d) Oxindole (**3**) (1.0 mM) in the absence of **1a** at a glassy carbon electrode in aqueous phosphate solution (pH 7.2, c = 0.2 M). Scan rate: 100 mV s^{-1}; t = 25 ± 1 °C.

More studies were performed by varying the potential scan rate of **1a** in the presence of **3** (Figure 2). The results indicate

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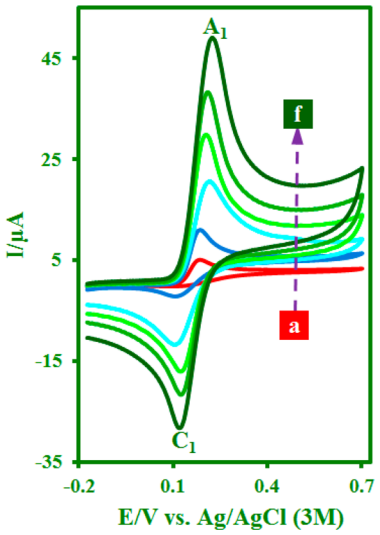


Figure 2. Typical cyclic voltammograms of 3-methylcatechol (**1a**) (1.0 mM) in the presence of oxindole (**3**) (1.0 mM) in aqueous phosphate solution (pH 7.2, c = 0.2 M) at a glassy carbon electrode and at various scan rates. Scan rates from (a) to (f) are 50, 100, 200, 400, 600, and 800 mV s^{-1}, respectively; t = 25 ± 1 °C.

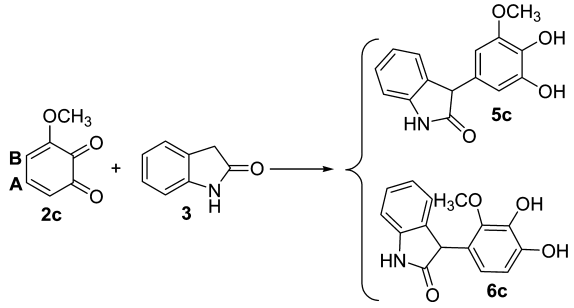
that the peak current ratio (I_{pC1}/I_{pA1}) is dependent on the potential scan rate and increases with increasing it. The occurrence of a chemical reaction after the electron-transfer process is supported by the decreasing of peak C_1 during the reverse scan, which could indicate that the **2a** formed at the surface of the electrode is consumed by a chemical reaction with **3**. On the other hand, with increasing the potential scan rate, the time required for the reaction of **3** with **2a** is not enough, and consequently, the peak current ratio (I_{pC1}/I_{pA1}) increases with increasing scan rate.[26]

Controlled potential coulometry was performed in a cell containing 0.25 mmol of **1a** and 0.25 mmol of **3**. Cyclic voltammetric analysis was carried out during the coulometry. Our data show that proportional to the advancement of coulometry the anodic peak A_1 decreases. This peak disappears when 2F/mol of electricity was consumed. Coulometry, cyclic voltammetry, and spectroscopic data of the final product obtained from exhaustive oxidation of **1a** in the presence of **3** allow us to propose the following mechanism for the electrochemical oxidation of **1a** in the presence of **3** (Scheme 1). Similar results were observed for the oxidation of **1b**−**1d** in the presence of **3**.

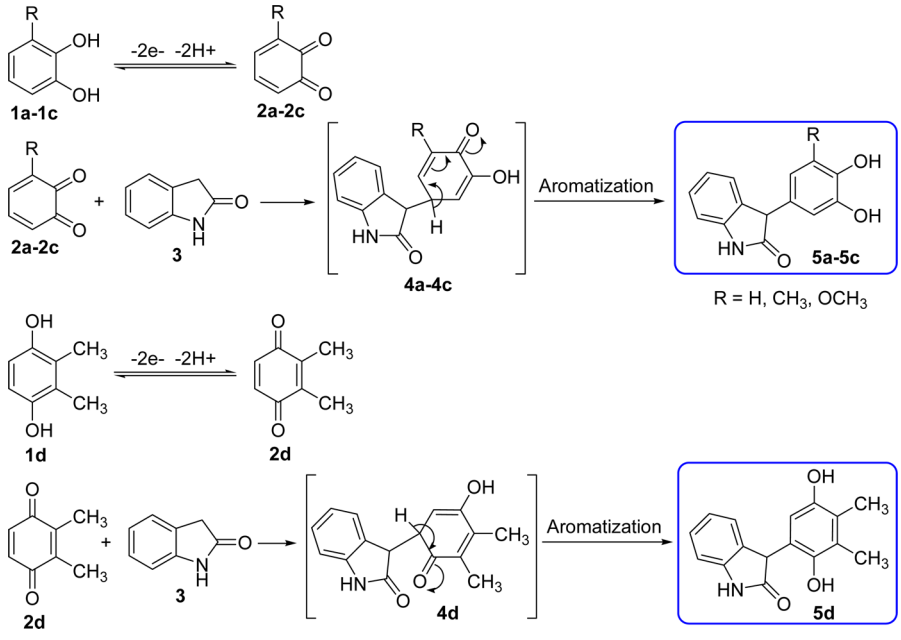
According to this scheme, the generation of *o*- and *p*-benzoquinones **2a**−**2d** is followed by a Michael addition reaction of **3** producing the dihydroxybenzenes **5a**−**5d** as the final products. In this work, the oxidation of dihydroxybenzenes **5a**−**5d** was circumvented during the reaction because of the insolubility of the final products **5a**−**5d** in the aqueous phosphate buffer solution (pH 7.2). To determine faradaic efficiency, controlled potential coulometry of **1a**−**1d** in the presence of **3** was performed at 0.35 V vs Ag/AgCl. On the basis of the obtained results, the calculated faradaic efficiency for the synthesis of **5a**−**5d** is 65%, 67%, 62%, and 59%, respectively.

o-Benzoquinone **2c** can be attacked by **3** from sites A or B to yield two types of products (**5c** and **6c**) (Scheme 2). The ^{1}H

Scheme 2. Possible Structures in the Electrochemical Synthesis Using 3-Methoxycatechol (1c)



Scheme 1. Electrochemical Oxidation of Catechols (1a−1c) and 2,3-Dimethylhydroquinone (1d) in the Presence of Oxindole (3)



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NMR data of the isolated product shows a singlet peak at δ = 8.42 consistent with the preferential addition at site A. The addition to the site B would result in the generation of *ortho* protons, which would result in a doublet with a coupling constant, *J*, of about 10 Hz. These results are consistent with the existence of two protons in the catechol ring of isolated product in a *meta* position.[31] Therefore, according to ^{1}H NMR results, we suggest that 3-methoxy-*o*-benzoquinone **2c** is attacked from the site A selectively by **3**, leading to the formation of the product **5c**. The same results obtained in the case of 3-methylcatechol (**1a**).

CONCLUSIONS

The medicinal properties of oxindole, catechols, and hydroquinones prompted us to synthesize a number of compounds containing either catechol (or hydroquinone) and oxindole moieties. The prominent features of this paper, the synthesis of valuable compounds in aqueous solution instead of toxic solvents, high energy efficiency, room-temperature conditions, and using the electrode as an electron source instead of toxic reagents, are in accord with the principle of green chemistry.[32,33] The results of this work show that electrogenerated *o*- and *p*-benzoquinones **2a−2d** are attacked by oxindole (**3**). Final products are obtained via an *EC* mechanism after consumption of 2F/mol of **1a−1d**. This work affords a product of high quality such that no further purification is necessary.

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Notes

The authors declare no competing financial interest.

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