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# Electrochemical study of catechol and some 3-substituted catechols in the presence of 4-hydroxy coumarin: application to the electro-organic synthesis of new coumestan derivatives

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**Abstract**

Electrochemical oxidation of catechol (**1d**), 3-methylcatechol (**1a**), 3-methoxycatechol (**1b**) and 2,3-dihydroxybenzoic acid (**1c**) in the presence of 4-hydroxycoumarin as nucleophile in aqueous solution has been studied using cyclic voltammetry and controlled-potential coulometry. The results indicate that (**1a–1d**) participating in a 1,4 (Michael) addition reaction convert to coumestan derivatives (**5a–5d**). The electrochemical synthesis of **5a–5d** has been successfully performed in an undivided cell in good yield and purity.

*Keywords:* Electro-organic synthesis; Catechol; 3-Methylcatechol; 3-Methoxycatechol; 2,3-Dihydroxybenzoic acid; Coumestan derivatives

## 1. Introduction

Many workers have shown that *o*- and *p*-diphenols can be oxidized electrochemically to *o*- and *p*-quinones respectively. The quinones formed are quite reactive and can be attacked by a variety of nucleophiles. Adams and co-workers [1–3] have shown that *o*-benzoquinone can react with nucleophiles such as ammonia, chloride and sulfhydryl compounds to form the addition products. Moreover, Adams and co-workers [4,5] have reported that *p*-benzoquinone, with electron-withdrawing substituents, can be attacked nucleophilically by water to yield a trihydroxy compound which can be oxidized further to the hydroxyquinone. Several other workers [6–9] have investigated the reactions of *o*-quinones from dopa, catechol and 4-methylcatechol in aqueous solutions, but the emphasis has been mostly on acidic solutions at low concentrations which significantly suppress the coupling reactions studied by Stum and Suslov [10] and Ryan et al. [11] in some detail. In this direction, we have recently investigated the electrochemical oxidation of catechol and 4-methylcatechol in methanol and have synthesized electrochemically 4,5-dimethoxy-*o*-benzoquinone and 4-methoxy-5-methyl-*o*-benzoquinone in high yield [12]. Moreover, we have studied the electrochemical oxidation of catechol in the presence of some nucleophiles such as acetylacetone, benzoylacetone, thienoyltrifluoroacetone, diethylmalonate and dimethylmalonate and have suggested that the product of initial oxidation of catechol reacts with these nucleophiles yielding benzofuran derivatives [13]. The importance of compounds known as coumestant [14], 6*H*-benzofuro[3,2-*c*][1]benzopyran-6-one, that have the basic structure of many natural products with interesting physiological activities [15–17], has caused many workers to synthesize a number of coumestan derivatives by chemical [18–20] and electrochemical [21–23] routes, using catechol as a Michael acceptor and a variety of coumarin derivatives as nucleophiles. However, no report has been published until now about the synthesis of coumestans using catechol derivatives. Therefore, we have investigated the electro-oxidation of catechol and some of 3-substituted catechols such as 3-methylcatechol, 3-methoxycatechol, and 2,3-dihydroxybenzoic acid in the presence of 4-hyroxycoumarin as nucleophile and have described a facile electrochemical method for synthesis of some new coumestant derivatives.

## 2. Experimental

Cyclic voltammograms were obtained using a function generator (VA Scanner E 612 from Metrohm) connected to

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a potentiostat (Polarecord E 626, from Metrohm) and were recorded by a Hewlett-Packard 3310 A *X–Y* recorder. Controlled-potential coulometry and preparative electrolysis were performed using an EG&G PAR model 173 potentiostat–galvanostat. The working electrode used in voltammetry was a glassy carbon disc (3 mm diameter) from Metrohm and a platinum wire (from Metrohm) was used as the counter electrode. The working electrode used in controlled-potential macroscale electrolysis was an assembly of five carbon rods (6 mm diameter and 4 cm length, spectrographically pure grade graphite from Johnson Matthey Chemicals Limited) and a large platinum gauze constituted the counter electrode. The working electrode potentials were measured and adjusted vs. a saturated calomel electrode (SCE). All experiments were carried out at a thermostated temperature of 26 ± 1°C by using a jacketed cell. All chemicals (catechols and 4-hydroxycoumarin) were reagent-grade materials from Aldrich and $CH_3COONA$ was of pro-analysis grade from Merck. These chemicals were used without further purification.

### 2.1. Electro-organic synthesis of coumestan derivatives (5a–5d)

In a typical procedure, 100 ml of sodium acetate solution in water (0.15 M) was pre-electrolysed at the chosen potential (see Table 1), in an undivided cell, then 2 mmol of catechol (**1a–1d**) and 4-hydroxycoumarin (2 mmol) were added to the cell. The electrolysis was terminated when the decay of the current became more than 95%. The process was interrupted several times during the electrolysis and the graphite anode was washed in acetone in order to activate it. At the end of electrolysis, a few drops of acetic acid were added to the solution and the cell was placed in a refrigerator overnight. The precipitated solid was collected by filtration and recrystallized from an appropriate solvent (see Table 1). After recrystallization, products were characterized by IR, $^1H$ NMR, $^{13}C$ NMR (with pulse duration of 2 s), MS and elemental analysis (C,H,N).

### 2.2. Characteristics of the products

#### 2.2.1. 3,4-Dihydroxy-2-methyl-6H-benzofuro[3,2,c][1]benzopyran-6-one (5a)

M.p. 304–306°C (dec.). IR (KBr): $\nu_{max}$ 3464, 3260, 2920, 1705, 1629, 1465, 1319, 1288, 1205, 1097, 1032, 1007, 903, 754 $cm^{-1}$. $^1H$ NMR, δ ppm (DMSO-$d_6$): 2.4 (s, 3H methyl protons); 7.2 (s, 1H, aromatic proton C-5); 7.35–8 (m, 4H, aromatic protons C8–C11); 9.4 (broad, 2H hydroxy protons). $^{13}C$ NMR, δ ppm (DMSO-$d_6$) (relative intensity): 9(methyl carbon) (97.5); 102 (59.5), 105 (19), 108 (58.6), 112 (57), 113 (55), 116 (59.5), 121 (60.8), 124 (55), 131 (44), 144 (100), 144.2 (99), 149 (27.5), 152 (63.8), 158 (27.6). MS *m/e* (relative intensity): 282 (100), 281 (17.8), 268 (3), 208 (9.2), 207 (3.5), 152 (12.2), 151 (3), 141 (3.5), 121 (8.6), 115 (10.8), 114 (4.3), 100 (23.5), 99 (17.8), 85 (28.6). Anal. Found: C, 68; 14, H; 3.52. $C_{16}H_{10}O_5$. Calc.: C, 68.09; H; 3.55%.

Table 1
Electroanalytical and preparative data

| Conversion | Peak potentials/V (vs. SCE) [a] | | | Applied potential/V (vs. SCE) | Solvent for crystallization | Product yield/% |
|---|---|---|---|---|---|---|
| | $A_0$ | $A_1$ | $A_2$ | | | |
| **1a–5a** | 0.21 | 0.29 | 1.09 | 0.40 | Ethanol + acetone | 96 |
| **1b–5b** | 0.20 | 0.28 | 1.09 | 0.40 | Ethanol + acetone | 98 |
| **1c–5c** | 0.24 | 0.46 | 1.07 | 0.50 | Water + ethanol | 90 |
| **1d–5d** | 0.26 | 0.40 | 1.08 | 0.45 | Ethanol + acetone | 94 |

[a] Peak potentials were measured from a cyclic voltammogram of each catechol (1 mM) in the presence of 4HC (1 mM) recorded at 100 mV $s^{-1}$.

#### 2.2.2. 3,4-Dihydroxy-2-methoxy-6H-benzofuro[3,2,c][1]benzopyran-6-one (5b)

M.p. 260–261°C (dec.). IR(KBr): $\nu_{max}$ 3371, 2950, 1737, 1630, 1611, 1519, 1369, 1283, 1234, 1092, 758 $cm^{-1}$. $^1H$ NMR, δ ppm (DMSO-$d_6$): 4.14 (s, 3H methoxy protons); 7.1 (s, 1H, aromatic proton C-5); 7.35–8.05 (m, 4H, aromatic protons C8–C11); 9.4 (broad, 2H, hydroxy protons). $^{13}C$ NMR, δ ppm (DMSO-$d_6$) (relative intensity): 60 (methoxy carbon) (100); 99.3 (57), 105.5 (28.5), 112 (63.8), 114 (60), 117 (56), 121 (56.2), 124.8 (54.7), 131.6 (44), 133.7 (42.3), 138 (83.6), 142 (28.5), 146 (96.5), 152.3 (72.9), 158.2 (23.7), 159 (32). MS *m/e* (relative intensity): 298 (100), 297 (76.8), 284 (7.4), 283 (40.2), 255 (13.4), 251 (8.6), 121 (22), 85 (6.2), 83 (12.2), 81 (4.8), 73 (14.6), 71 (13.4), 70 (9.8), 69 (48.7), 64 (48.7). Anal. Found: C, 64.20; H, 3.76. $C_{16}H_{10}O_6$. Calc.: C, 64.43; H, 3.36%.

#### 2.2.3. 3,4-Dihydroxy-6-oxo-6H-benzofuro[3,2,c][1]benzopyran-5-carboxylic acid (5c)

M.p. 326–328°C (dec.). IR (KBr): $\nu_{max}$ 3500–2400 (broad), 1707, 1624, 1570, 1500, 1356, 1258, 1200, 1083, 754 $cm^{-1}$. $^1H$ NMR, δ ppm (DMSO-$d_6$): 7.2 (s, 1H, aromatic proton C-2); 7.36–8.10 (m, 4H, aromatic protons, C8–C11): 9.25 (broad, 2H, hydroxy protons); 10.65 (broad, 1H, carboxylic proton). $^{13}C$ NMR, δ ppm (DMSO-$d_6$) (relative intensity): 98.5 (44.3), 111.6 (25.1), 112.2 (71.1), 113.4 (48), 116.4 (55.5), 121.3 (42), 124.5 (38.9), 125.2 (25.2), 131 (47.2), 146.3 (33.6), 147.2 (100), 148 (71), 149 (26.2), 152.1 (79.8), 157.5 (48), 168.2 (63). MS *m/e* (relative intensity): 312 (15.6), 294 (100), 268 (86.3), 238 (17.3), 210 (59.0), 194 (9.6), 138 (13.3), 126 (13.8), 69 (14.3). Anal. Found: C, 61.67; H, 2.56. $C_{16}H_8O_7$. Calc.: C, 61.54; H, 2.56%.

#### 2.2.4. 3,4-Dihydroxy-6H-benofuro[3,2,c][1] benzopyran-6-one (5d)

M.p. 307–309°C (dec.) (Ref. [23] 308–310°C). IR (KBr): $\nu_{max}$ 3350, 3260, 1710, 1630, 1476, 1354, 1280, 1227, 1204, 1086, 1043, 754 $cm^{-1}$. $^1H$ NMR δ ppm

(DMSO-$d_6$): 7.2 (s, 1H, aromatic proton C-2); 7.3 (s, 1H, aromatic proton C-5); 7.45–8.0 (m, 4H, aromatic proton C8–C11); 9.5 (broad, 2H, hydroxy protons). $^{13}$C NMR, $\delta$ ppm (DMSO-$d_6$) (relative intensity): 98.9 (97.4), 104.9 (100), 105.4 (21.4), 112.3 (56), 113.9 (50.8), 116.95 (97.4), 121 (90.3), 124.8 (98.7), 131.2 (80.7), 144.7 (78.1), 146.5 (81.9), 149.4 (40.3), 152.3 (52.3), 157.7 (15.8), 158.1 (22). MS *m/e* (relative intensity): 268 (100), 240 (5.4), 222 (6.8), 212 (3), 194 (7.9), 166 (3), 149 (3), 134 (6.5), 120 (8.2), 97 (12.1), 69 (41.4).

## 3. Results and discussion

### *3.1. Electro-oxidation of 3-methylcatechol (1a) in the presence of 4-hydroxycoumarin (4HC)*

Cyclic voltammetry of 1 mM of **1a** in aqueous solution containing 0.15 M sodium acetate as supporting electrolyte, shows one anodic and a corresponding cathodic peak with a peak separation of about 300 mV, which corresponds to the transformation of 3-methylcatechol (**1a**) to 3-methyl-*o*-quinone (**2a**) and vice versa within a quasi-reversible two-electron process (Fig. 1, curve a). A peak current ratio $I_{pa}/I_{pc}$ of nearly unity, particularly during the repetitive recycling of potential can be considered as a criterion for the stability of *o*-quinone produced at the surface of the electrode under the experimental conditions. In other words, any hydroxylation [4–9] or dimerization [10,11] reactions are too slow to be observed in the time

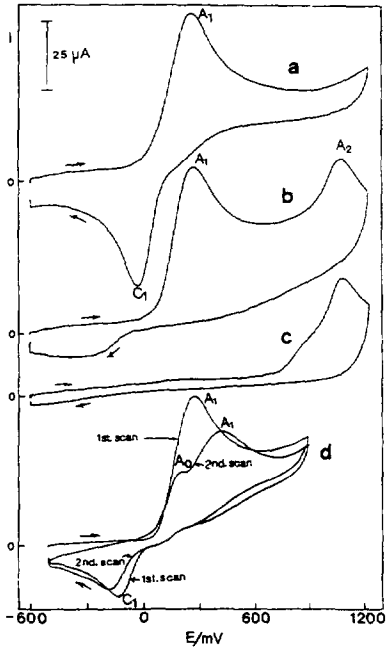



Fig. 1. Cyclic voltammograms of 1 mM 3-methylcatechol: (a) in the absence, (b) and (d) in the presence of 1 mM 4HC and, (c) 1 mM 4HC at a glassy carbon electrode in aqueous solution. Supporting electrolyte 0.15 M $CH_3COONA$; scan rate 100 mV s$^{-1}$; $T = 26 \pm 1$°C.

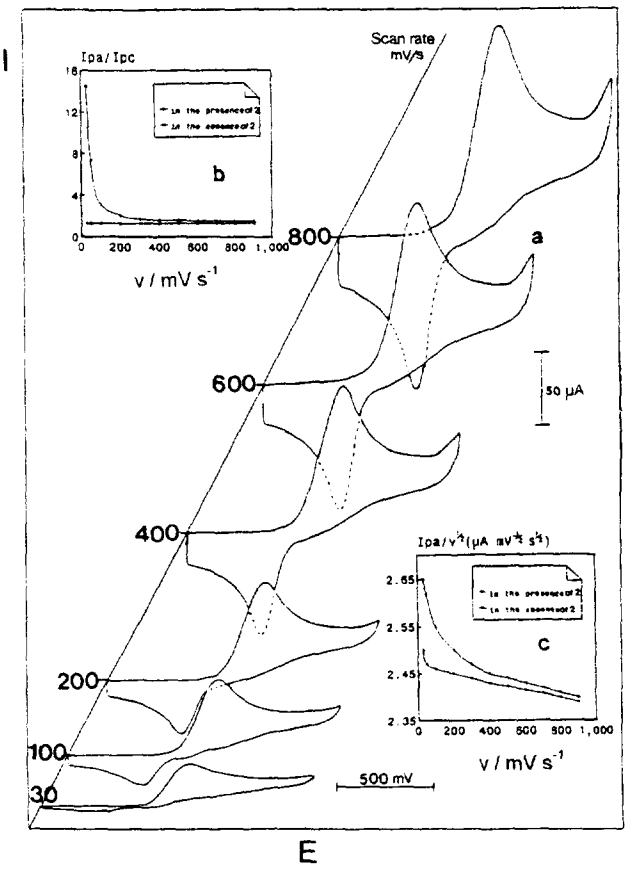



Fig. 2. (a) Typical voltammograms of 1 mM 3-methylcatechol in water in the presence of 1 mM 4HC at a glassy carbon electrode and at various scan rates. Supporting electrolyte 0.15 M $CH_3COONa$; starting potential −500 mV vs. SCE; switching potential +900 mV vs. SCE. (b) Variation of peak current ratio $I_{pa1}/I_{pc1}$ and (c) current function $I_{pa1}/v^{1/2}$) vs. scan rate in the presence and in the absence of 4HC. $T = 26 \pm 1$°C.

scale of cyclic voltammetry. However, when the concentration of **1a** increases, the peak separation and the peak current ratio $I_{pa}/I_{pc}$ increase. This can be related to the dimerization reaction and film formation at the surface of the electrode, enhanced by the excess of **1a** [11,13,24]. The oxidation of **1a** in the presence of 4HC as nucleophile was studied in some detail. Fig. 1 (curve b) shows the cyclic voltammogram obtained for a 1 mM solution of **1a** in the presence of 1 mM 4HC. The voltammogram exhibits two anodic peaks at 0.29 and 1.10 V vs. SCE, and the cathodic counterpart of the anodic peak $A_1$ nearly disappears. The shift of $C_1$ peak in a negative direction in the presence of 4HC (Fig. 1, curve b), is probably due to the formation of a thin film of product at the surface of the electrode [23]. Comparison of the voltammograms b and c in Fig. 1 reveals that the peak $A_2$ (curve b) corresponds to the oxidation of 4HC. This peak decreases dramatically in the second scan of potential because of the consumption of 4HC during its reaction with *o*-quinone (**2a**). The multicyclic voltammetry of **1a** in the presence of 4HC shows that in the second cycle, parallel to the shift of the $A_1$ peak in a positive direction, a new peak $A_0$ appears with an $E_p$

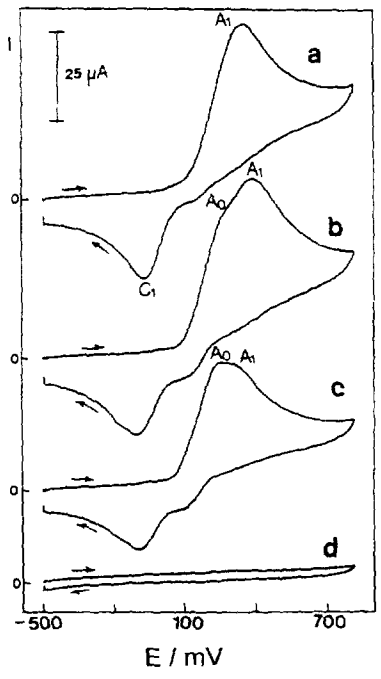
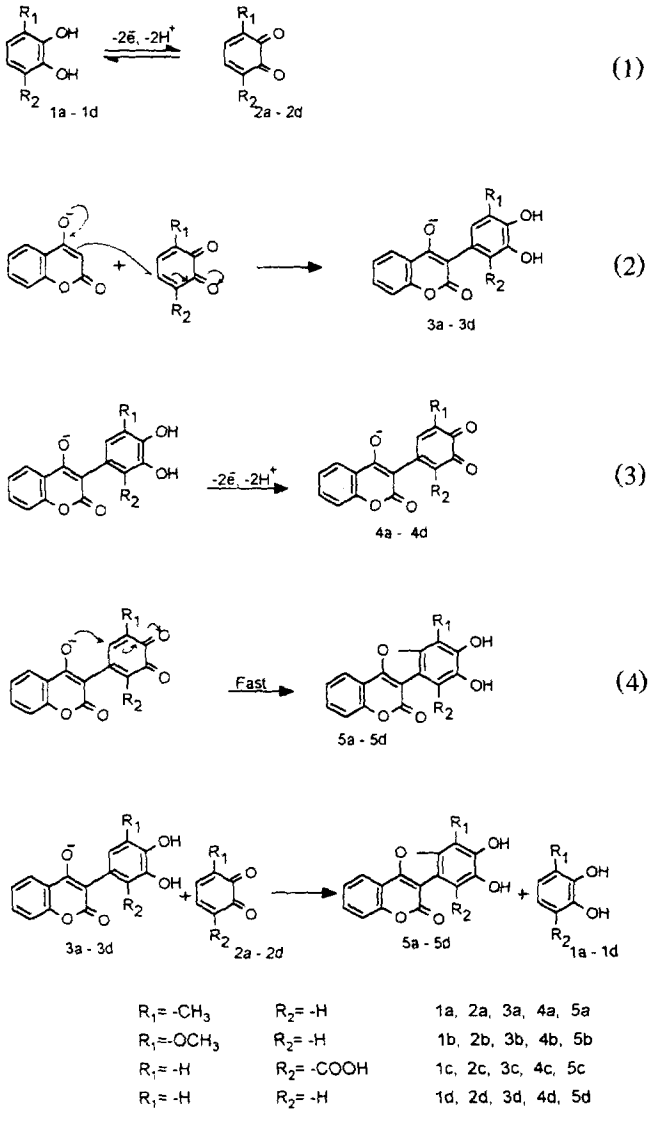



Fig. 3. Cyclic voltammograms of 1 mM 3-methylcatechol in water in the presence of 1 mM 4HC, at a glassy carbon electrode during controlled-potential coulometry at 0.40 V vs. SCE. (a) at the beginning of, (b) and (c) in the course of, and (d) at the end of coulometry. Scan rate $100\,mV\,s^{-1}$; $T = 26 \pm 1$°C.

value of 0.21 V vs. SCE (Fig. 1, curve d). This new peak $A_0$ is related to the electro-oxidation of intermediate **3a**, and the shift of peak $A_1$ is due to the deposition of product on the surface of the electrode, inhibiting to a certain extent the performance of the electrode process. Furthermore, a comparison of voltammograms b and d shows that the peak current ratio $I_{pa1}/I_{pc1}$ is dependent on the switching potential. In addition, it is seen that proportional to the augmentation of potential sweep rate, the height of the $C_1$ peak of **1a** increases (Fig. 2 curves a). A similar situation is observed when the 4HC to **1a** concentration ratio is decreased. A plot of peak current ratio vs. scan rate for a mixture of **1a** and 4HC confirms the reactivity of **2a** towards 4HC, appearing as an increase in the height of the cathodic peak $C_1$ at higher scan rates (Fig. 2, curve b). In contrast, the current function for the $A_1$ peak ($I_{pa1}/v^{1/2}$) changes only slightly with increasing scan rate (Fig. 2, curve c) and such behaviour is taken to be indicative of an EC mechanism [25]. Controlled-potential coulometry was performed in aqueous solution containing 1 mM of **1a** and 1 mM of 4HC at 0.40 V vs. SCE. The monitoring of electrolysis progress was carried out by cyclic voltammetry (Fig. 3). It is shown that, proportional to the advancement of coulometry, anodic peak $A_1$ (as well as $A_2$) decreases and a new anodic peak $A_0$ appears at less positive potentials (Fig. 3 curves b and c) which is related to the oxidation of the intermediate (**3a**). The cyclic voltammogram reduces to curve d (Fig. 3) when the charge consumption becomes about $4e^-$ per molecule of **1a**.

These observations allow us to propose the reaction scheme pathway for the electro-oxidation of **1a** in the presence of 4HC shown in Eqs. (1)–(5).




(1) (2) (3) (4) (5)

The existence of a methyl group with electron-donating character at the C-3 position of the *o*-quinone ring (**2a**) probably causes the Michael acceptor (**2a**) to be attacked by enolate anion (**2**) from the C-4 and C-5 positions to yield two types of product. However, $^1H$ NMR [26] and $^{13}C$ NMR results indicate that 3-methyl-*o*-quinone (**2a**) formed from the oxidation of **1a** is selectively attacked at the C-5 position by enolate anion (**2**) leading to the production of the selective product (**5a**). According to our results, it seems that the intermolecular (Eq. (2)) and intramolecular (Eq. (4)) 1,4-(Michael) addition of anion enolate of 4HC (**2**) to *o*-quinone (**2a**) is faster than other secondary reactions, leading presumably to the intermediate (**3a**). The oxidation of this compound (**3a**) is easier than the oxidation of parent starting molecule (**1a**) by

virtue of the presence of the electron-donating group. It can be seen from the mechanism of Eqs. (1)–(5), that as the chemical reaction (Eq. (2)) occurs, **1a** is regenerated through homogeneous oxidation (Eq. (5)) and hence can be reoxidized at the electrode surface. Thus, as the chemical reaction takes place, the apparent number of electrons transferred increases from the limit of $n = 2$ to $n = 4$ electrons per molecule. The reaction product (**5a**) can also be oxidized at a lower potential than the starting **1a** compound. However, overoxidation of **5a** was circumvented during the preparative reaction because of the insolubility of the product in water + sodium acetate media.

### 3.2. Electro-oxidation of 3-methoxycatechol (1b) in the presence of 4HC (2)

Cyclic voltammetry of 1 mM **1b** in aqueous solution containing 0.15 M sodium acetate as supporting electrolyte exhibits an anodic and cathodic peak corresponding to the quasi-reversible two-electron transformation of 3-methoxycatechol (**1b**) to 3-methoxy-*o*-benzoquinone (**2b**) and vice versa. The peak current ratio $I_{pa}/I_{pc}$ is nearly unity, particularly during the repetitive recycling of potential, suggesting stability of the electrode oxidation product and no occurrence of hydroxylation or dimerization reactions [4–11] under the experimental conditions. The electro-oxidation of 1 mM of **1b** in the presence of 1 mM of 4HC proceeds in a way similar to that of **1a**. However, in this case, the presence of the methoxy group as an electron-donating substituent on the molecular ring causes a diminution in the activity of 3-methoxy-*o*-quinone (**2b**) as a Michael acceptor towards the 1,4-(Michael) addition reaction. Consequently, contrary to other catechol cases, the peak current ratio increases moderately in the presence of 4HC and the new anodic peak $A_0$ is not observed during the repetitive scans, mainly because of the low concentration of intermediate **3b** at the surface of the electrode. However, the plot of peak current ratio vs. scan rate confirms the reaction between the oxidation product of **1b** and 4HC, appearing as a decrease in the peak current ratio $I_{pa1}/I_{pc1}$ with increasing scan rate. The variation of current function $I_{pa1}/v^{1/2}$ with scan rate also agrees with the above-mentioned results. Controlled-potential coulometry was performed in aqueous solution containing 1 mM of **1b** and 1 mM of 4HC at 0.40 V vs. SCE (Fig. 4). The monitoring of the electrolysis progress by cyclic voltammetry shows that, parallel to the advancement of coulometry, both anodic peaks $A_1$, and $A_2$ decrease and a new anodic peak $A_0$ appears at less positive potentials (Fig. 4 curve b). On warming the electrolysed solution for some time (at 35°C for 10 min), the shape of the cyclic voltammogram changes (Fig. 4, curve d) and a decrease in the peak current of $A_0$ is observed together with the reappearance of peak $A_1$ (Eq. (5)). This relates to the relative stability of the intermediate **3b** arising from the presence

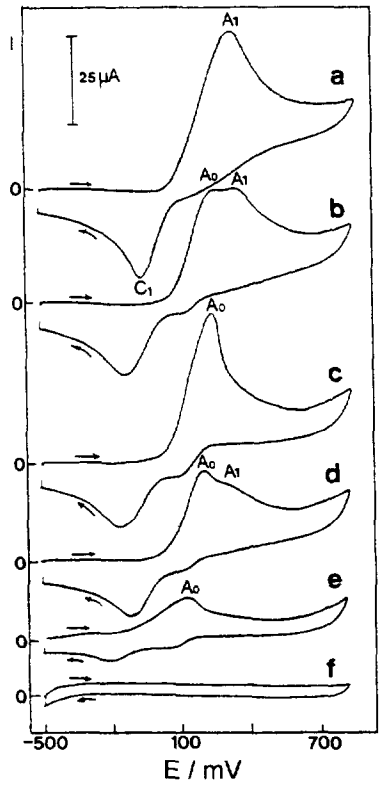
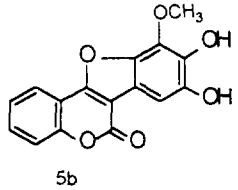



Fig. 4. Cyclic voltammograms of 1 mM 3-methoxycatechol in the presence of 1 mM 4HC in water at a glassy carbon electrode during controlled-potential coulometry at 0.40 V vs. SCE. (a) At the beginning of, (b)–(e) in the course of, and (f) at the end of coulometry. Scan rate 100 mV $s^{-1}$; $T = 26 \pm 1$°C.

of the electron-donating methoxy group in the molecule and the occurrence of solution electron transfer (SET) between **3b** and 3-methoxy-*o*-benzoquinone. All anodic and cathodic peaks disappear when the charge consumption becomes about 4 $e^-$ per molecule of **1b** (Fig. 4, curve e). The reaction mechanism is similar to that of the previous case and, according to these results, it seems that the chemical reaction between 4HC and 3-methoxy-*o*-benzoquinone is fast enough and leads presumably to the formation of product (**5b**).




5b

Similar to **1a**, $^1H$ NMR [26] and $^{13}C$ NMR results indicate that 3-methoxy-*o*-benzoquinone (**2b**), produced from the oxidation of **1b**, is selectively attacked from C-5 by enolate anion **2**, to produce the product **5b**.

### 3.3. Electro-oxidation of 2,3-dihydroxybenzoic acid (1c) in the presence of 4HC

Fig. 5 (curve a) shows the cyclic voltammogram of a 1 mM solution of **1c** in water, containing 0.15 M of sodium acetate. In this condition, the cyclic voltammogram exhibits a quasi-reversible two-electron process corresponding to the 2,3-dihydroxy-benzoic acid (**1c**)/*o*-quinone-3-carboxylic acid (**2c**) couple. The cathodic counterpart of the anodic peak decreases when 1 mM of 4HC is added, and a second irreversible peak $A_2$ appears at more positive potentials (Fig. 5, curve b). This peak $A_2$ is related to the oxidation of 4HC. The multicyclic voltammogram of this solution shows a new anodic peak $A_0$ at 0.24 V vs. SCE, which can be attributed to the oxidation of intermediate **3c**, followed by a decrease in the height of peak $A_2$ (Fig. 5, curve c). Under these conditions, the peak current ratio $I_{pa1}/I_{pc1}$ and the current function $I_{pa1}/v^{1/2}$ decrease with increasing scan rate. As in the previous cases, controlled-potential coulometry for determination of the number of transferred electrons was performed at 0.50 V vs. SCE, and cyclic voltammetric analysis carried out during the electrolysis in order to elucidate the formation of intermediate(s) and other products, shows the formation of the new anodic peak $A_0$. All anodic and cathodic peaks disappear when the consumed charge reaches a limit of $4e^-$ per molecule (Fig. 6). The presence of an electron-withdrawing group at the C-3 position of the *o*-quinone ring (**2c**), causes a difference in the reactivity between the C-4 and C-5 positions. However, $^1$H NMR [26] and $^{13}$C NMR results indicate that *o*-quinone-3-carboxylic acid (**2c**) formed from the oxidation of **1c** is selectively attacked from the C-4 position by enolate anion **2** leading to the formation of product (**5c**).

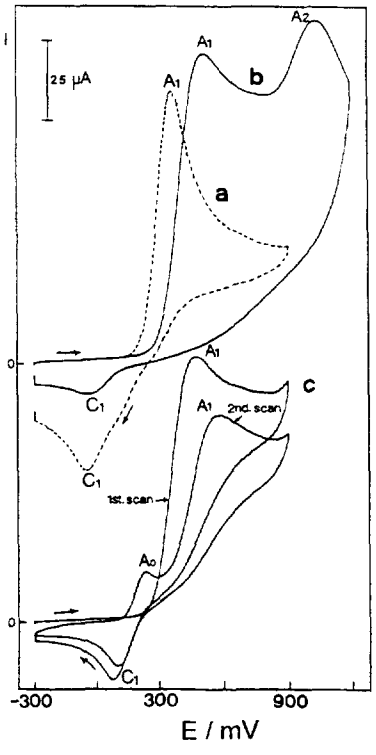



Fig. 5. Cyclic voltammograms of 1 mM 2,3-dihydroxybenzoic acid, (a) in the absence of, (b) in the presence of 1 mM 4HC at a glassy carbon electrode and at a scan rate of 200 mV s$^{-1}$; (c) as (b) at a scan rate of 100 mV s$^{-1}$. Supporting electrolyte 0.15 M $CH_3COONa$; $T = 26 \pm 1$°C.

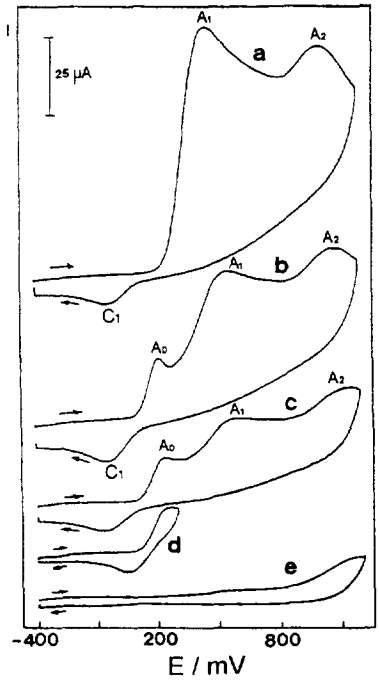
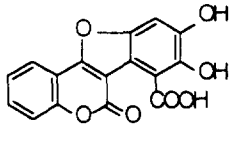



Fig. 6. Cyclic voltammograms of 1 mM 2,3-dihydroxybenzoic acid in the presence of 1 mM 4HC in water at a glassy carbon electrode during controlled-potential coulometry at 0.50 V vs. SCE. (a) At the beginning of, (b)–(d) in the course of, and (e) at the end of coulometry. Scan rate 100 mV s$^{-1}$; $T = 26 \pm 1$°C.




5c

According to the voltammetric results, it seems that the chemical reaction between 4HC and *o*-quinone-3-carboxylic acid is fast enough and favours the progress of the subsequent reactions.

### 3.4. Electro-oxidation of catechol (1d) in the presence of 4HC

The oxidation of catechol (**1a**) in the presence of 4HC as a nucleophile in water was studied by cyclic voltammetry. Fig. 7 (curve a) shows the cyclic voltammogram of 1 mM catechol in aqueous solution containing 0.15 M

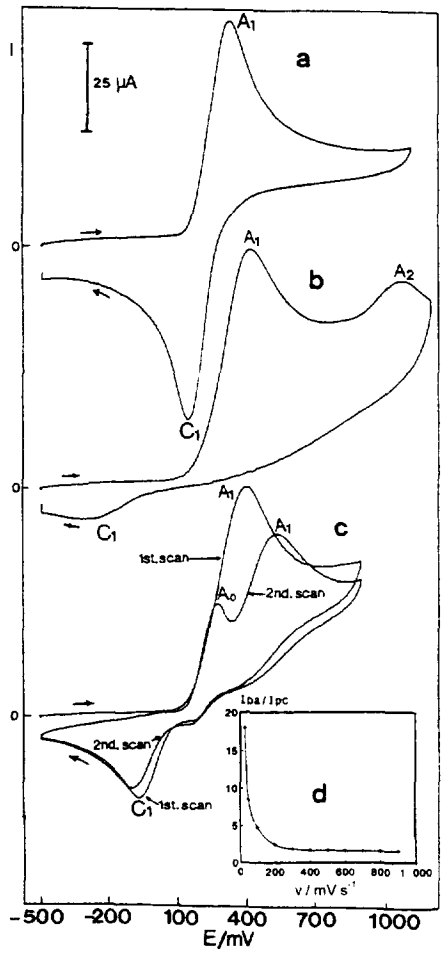
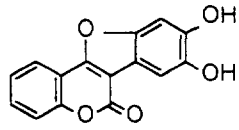



Fig. 7. Cyclic voltammograms of 1 mM catechol in water, (a) in the absence of, (b) and (c) in the presence of 1 mM 4HC at a glassy carbon electrode electrode. (d) Variation of peak current ratio $I_{pa1}/I_{pc1}$) vs. scan rate. Supporting electrolyte 0.15 M $CH_3COONa$; scan rate 100 mV $s^{-1}$; $T = 26 \pm 1$°C.

sodium acetate. Similar to the previous cases, in the presence of 4HC, the peak current ratio $I_{pa1}/I_{pc1}$ increases proportionally to the augmentation in 4HC concentration, as well as by decreasing the potential sweep rate, and a second irreversible peak appears at 1.10 V vs. SCE (Fig. 7, curve b). Contrary to the report of Tabacovic et al. [23], this peak $A_2$ can be attributed to the oxidation of 4HC (see Fig. 1, curve c). Moreover, the multicyclic voltammogram of catechol in the presence of 4HC shows a new anodic peak $A_0$ at 0.26 V vs. SCE (Fig. 7, curve c). For this solution, the effect of increasing potential scan rate on the peak current ratio is shown in Fig. 7, curve d. Controlled-potential coulometry was performed at 0.45 V vs. SCE, and cyclic voltammetric analysis carried out during the electrolysis shows the formation of a new anodic peak $A_0$ at less positive potentials. All anodic and cathodic peaks decrease and disappear at a rate corresponding to the consumption of $4e^-$ per molecule. The reaction mechanism is similar to that of previous cases, and according to our results it seems that the chemical reaction between 4HC and *o*-quinone (**2d**) is fast enough and favours the progress of the subsequent reactions leading to the formation of product (**5d**).




5d

## 4. Conclusions

The present results complete the previous report on the anodic oxidation of some catechols in aqueous solutions. The results of this work show that catechols are oxidized in water to their respective quinones. The quinones are then attacked by enolate anion of 4-hydroxycoumarin to form coumestans. The overall reaction mechanism for anodic oxidation of catechols in the presence of 4-hydroxycoumarin as nucleophile is presented in Eqs. (1)–(5). According to our results, it seems that the intermolecular and intramolecular 1,4-(Michael) addition of this nucleophile to the *o*-quinones formed (Eqs. (2) and (4)) leads to the formation of new coumestan derivatives as final products, in good yields and purity.

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