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Electrochemical synthesis of 5,6-dihydroxy-2-methyl-1-benzofuran-3-carboxylate derivatives

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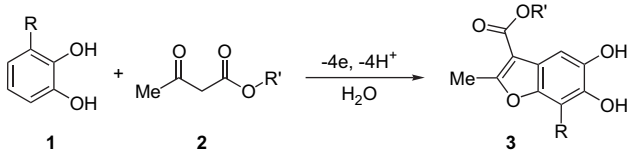
Abstract—Electrochemical oxidation of catechols (**1a–c**) has been studied in the presence of methyl acetoacetate (**2a**) and ethyl acetoacetate (**2b**) as nucleophiles in aqueous solution using cyclic voltammetry and controlled-potential coulometry. The results indicate that the quinones derived from catechols (**1a–c**) participate in Michael addition reactions with **2a** and **2b** to form the corresponding benzofuran derivatives (**3a–f**). The electrochemical synthesis of **3a–f** has been successfully performed in an undivided cell in good yield and purity. The oxidation mechanism was deduced from voltammetric data and by coulometry at controlled potential. The products have been characterized after purification by IR, ^{1}H NMR, ^{13}C NMR, MS, and single crystal X-ray diffraction.

1. Introduction

In nature's collection of biologically active heterocycles benzofuran derivatives[1] constitute a major group. They are usually important constituent of plant extracts used in medicinal chemistry for their various biological activities, including insecticidal, traditional medicine, antimicrobial, and antioxidant properties.[2] The most common synthetic strategy employed for benzofuran synthesis is the annulation of a furan ring onto a preexisting benzene ring through Sonogashira coupling followed by palladium-catalyzed cyclization[3] or through benzannulation onto a preexisting furan ring.[4] Numerous benzofuran-containing natural products have been efficiently synthesized according to these methods. One of the prime principles of green chemistry is to develop an alternative reaction medium, which is the basis for the development of many cleaner chemical technologies and electrochemical synthesis in water. With due attention to our experiences on electrochemical oxidation of catechols in the presence of nucleophiles,[5] we used electrochemical oxidation of catechols in the presence of ethyl acetoacetate and methyl acetoacetate in water medium and synthesis of new benzofurans from β-diketones.

2. Results and discussion

The electrochemical oxidation of catechol (**1**) in the presence of methyl acetoacetate or ethyl acetoacetate (**2**) undergoes a smooth 1:1 addition reaction in water medium at ambient temperature to produce 5,6-dihydroxy-2-methyl-1-benzofuran-3-carboxylate derivatives (**3**) (Scheme 1).



1	R
a	H
b	Me
c	OMe

2	R'
a	Me
b	Et

3	R	R'	%Yield of 3
a	H	Me	60
b	Me	Me	70
c	OMe	Me	55
d	H	Et	65
e	Me	Et	72
f	OMe	Et	60

Scheme 1.

Cyclic voltammetry of 2 mM catechol (**1a**) in phosphate buffer (pH 7.2, C=0.15 M) shows one anodic (A_1) and a corresponding cathodic peak (C_1), which correspond to the transformation of catechol (**1a**) to *o*-benzoquinone (**4a**) and vice versa within a quasi-reversible two-electron process (Fig. 1, curve a). A peak current ratio ($I_P^{C_1}/I_P^{A_1}$) of nearly

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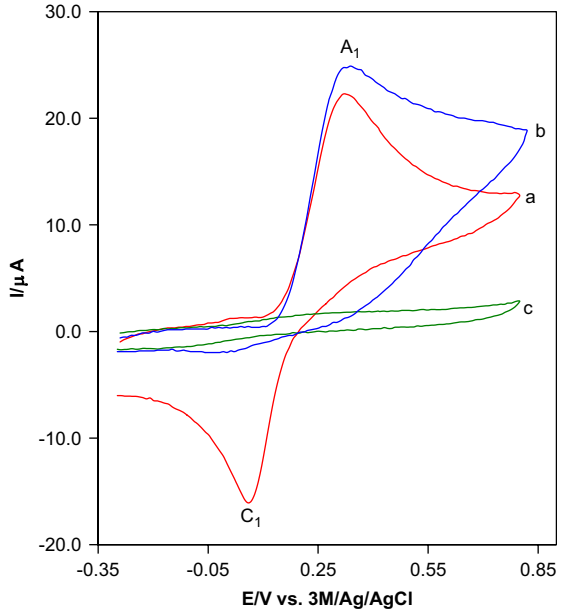


Figure 1. Cyclic voltammograms of 2 mM catechol in the absence (a) and presence of 2 mM ethyl acetoacetate (b) and 2 mM ethyl acetoacetate in the absence of catechol (c), at a glassy carbon electrode (1.8 mm diameter) in phosphate buffer (pH 7.2, C=0.15 M); scan rate: 100 mV s^{-1}; t=25±1 °C.

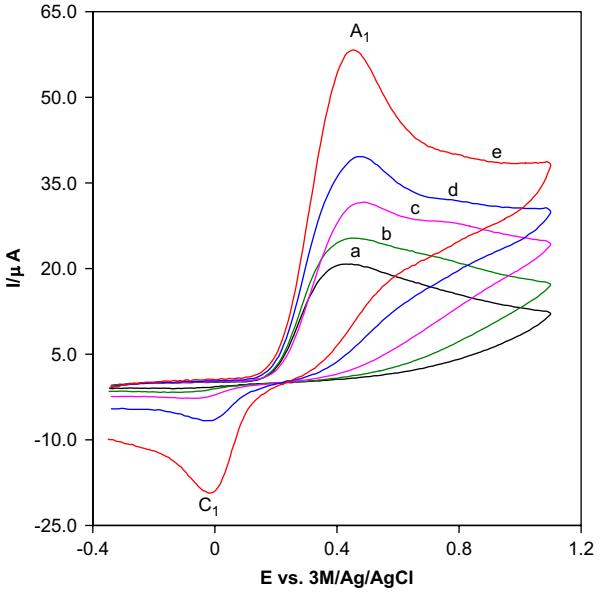


Figure 2. Typical voltammograms of 2 mM catechol in the presence of 2 mM ethyl acetoacetate, at a glassy carbon electrode (1.8 mm diameter) and at various scan rates in phosphate buffer (pH 7.2, C=0.15 M); scan rates from (a) to (e) are: 50, 100, 200, 400, 800 mV s^{-1}, respectively. t=25±1 °C.

unity, particularly during the repetitive recycling of the potential, can be considered as a criterion for the stability of *o*-benzoquinone produced at the surface of electrode under the experimental conditions. In other words, any hydroxylation[6] or dimerization[7] reactions are too slow to be observed on the time scale of the cyclic voltammetry. The oxidation of catechol (**1a**) in the presence of ethyl acetoacetate (**2b**) as a nucleophile was studied in some detail. Figure 1 (curve b) shows the cyclic voltammogram obtained for a 2 mM solution of **1a** in the presence of 2 mM ethyl acetoacetate. The voltammogram exhibits one anodic peak at 0.35 V versus 3 M Ag/AgCl electrode and the cathodic counterpart of anodic peak (C_1) disappears. In this figure, curve c is the voltammogram of 2 mM ethyl acetoacetate (**2b**).

It is seen that, proportional to the augmentation of the potential sweep rate, the height of cathodic peak increases (Fig. 2). A similar situation is observed when the concentration ratio of ethyl acetoacetate (**2b**) to (**1a**) decreased. The current function for the anodic peak, $I_P^{A_1}/v^{1/2}$, changes with increasing scan rate. On the other hand, a plot of the peak current ratio ($I_P^{C_1}/I_P^{A_1}$) versus the scan rate for a mixture of catechol and ethyl acetoacetate (**2b**) shows an increase in the height of the cathodic peak (C_1) at higher scan rates. Such behavior is adopted as indicative of an ECEC mechanism.[8] Controlled-potential coulometry was performed in an aqueous solution containing 0.25 mmol of **1a** and 0.25 mmol of ethyl acetoacetate (**2b**) at 0.40 V versus 3 M Ag/AgCl electrode. The electrolysis progress was monitored by using cyclic voltammetry (Fig. 3). It is shown that, proportional to the advancement of coulometry, the anodic peak (A_1) decreases and disappears when the charge consumption becomes about 4e^- per molecule of **1a**. These observations allowed us to propose the pathway in Scheme 2 for the electrochemical oxidation of **1a** in the presence of ethyl acetoacetate (**2b**).

According to our results, it is clear that the 1,4-Michael addition reaction of anion enolate (**5**) to *o*-quinone (**4**) (Eq. 2) is much faster than other secondary reactions, leading presumably to the intermediate (**7**). The oxidation of this compound (**7**) is easier than oxidation of the parent starting molecule (**1**) by virtue of the presence of an electron-donating group. The reaction product (**3**) can also be oxidized at a lower potential than the starting compound **1**. However, overoxidation of **3** was circumvented during the preparative reaction because of the insolubility of the product in the water/phosphate solvent medium (Scheme 2).

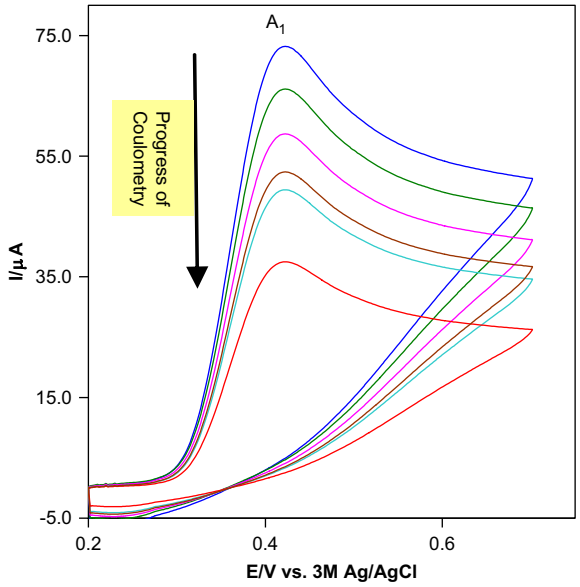
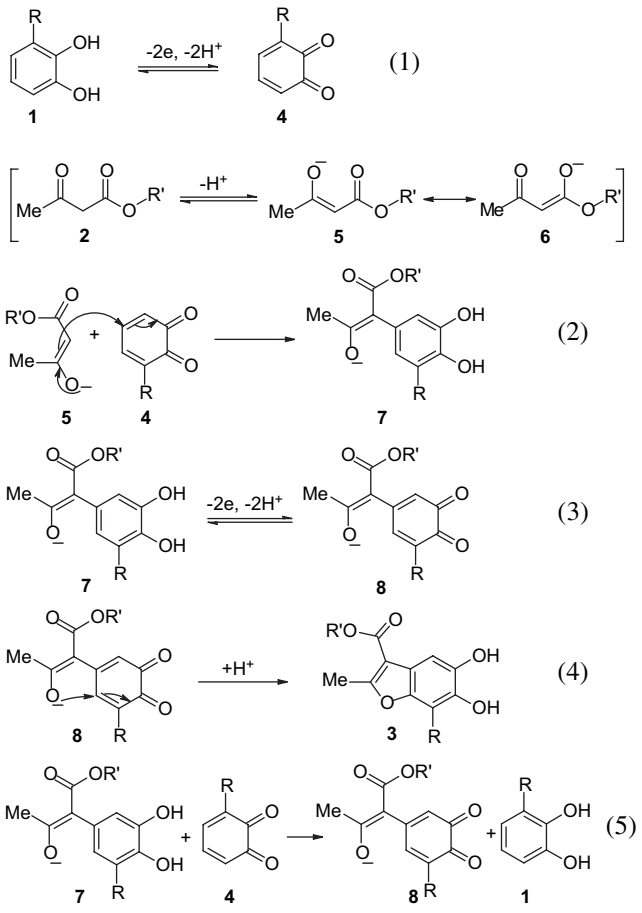
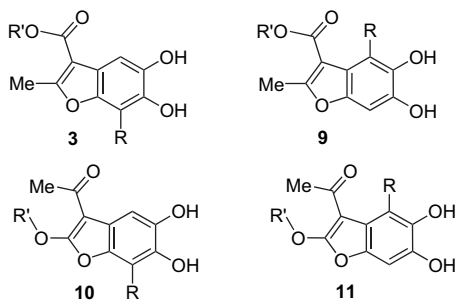


Figure 3. Cyclic voltammograms of 0.25 mmol catechol in the presence of 0.25 mmol ethyl acetoacetate in phosphate buffer (pH 7.2, C=0.15 M), at a glassy carbon electrode (1.8 mm diameter) during controlled-potential coulometry at 0.40 V versus 3 M Ag/AgCl electrode. Scan rate 100 mV s^{-1}; t=25±1 °C.



Scheme 2.

The presence of a methyl or methoxy group at the C-3 position of catechols (**1b** or **1c**) probably causes the Michael acceptors (**4b** and **4c**) to be attacked by anion enolate ethyl acetoacetate (**2b**) or methyl acetoacetate (**2a**) at the C-4 or C-5 position to yield two types of products in each case. On the other hand, because of asymmetry in structure of ethyl acetoacetate (**2b**), there are two possibilities for enol formation to yield two types of products in each case (Scheme 3). The experimental and calculated[9] ^{13}C NMR results for methyl in the catechol ring and carbonyl of the product and for suggested possible structures (**3**, **9**, **10**, and **11**) are shown in (Table 1). According to the ^{13}C NMR results, we suggested that *o*-quinone **4** is attacked by anion enolate **5** leading to the formation of product **3**. Finally, the structure further confirmed by single crystal X-ray diffraction analyses is shown in Figure 4.



Scheme 3.

Table 1. Experimental and calculated ^{13}C NMR data

Type	^{13}C NMR of methyl group[a]	^{13}C NMR of carbonyl group
Experimental[b]	9.30	164.3
Calculated for **3e**	10.37	161.9
Calculated for **9e**	15.07	162.3
Calculated for **10e**	10.37	189.8
Calculated for **11e**	13.95	188.6

[a] For methyl carbon in catechol ring.
[b] Experimental data obtained for filtrated product after washing with water.

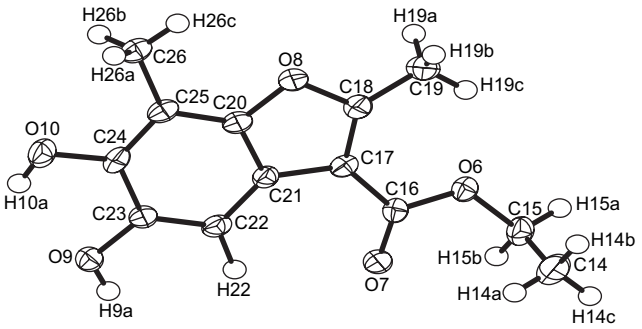


Figure 4.

The same results were obtained in the case of **1c** in the presence of ethyl acetoacetate (**2b**) or **1b** and **1c** in the presence of methyl acetoacetate (**2a**).

3. Conclusions

The results of this work show that catechols are oxidized in water to their respective *o*-quinones. The quinones are then attacked by the enolate anion of ethyl acetoacetate **5b** or methyl acetoacetate **5a** to form benzofuran derivatives **3a–f**. The reaction mechanism for anodic oxidation of catechols in the presence of these nucleophiles is presented in Scheme 1. According to our results, it seems that the 1,4-Michael addition of this nucleophiles to *o*-quinones leads to the formation of new benzofuran derivatives as final products, in good yield and purity.

4. Experimental

4.1. Apparatus and reagents

Cyclic voltammetry was performed using a Metrohm computerized voltammetric analyzer model 747 VA stand. Controlled-potential coulometry and preparative electrolysis were performed using an EG&G PAR model 174 A potentiostat/galvanostat. The working electrode used in the voltammetry experiment was a glassy carbon disc (1.8 mm diameter) and platinum wire was used as the counter electrode. The working electrode used in controlled-potential coulometry and macroscale electrolysis was an assembly of three carbon rods (8 mm diameter and 6 cm length) and a large platinum gauze (2×2 cm^2) constituted as a counter electrode. The working electrode potentials were measured versus the 3 M Ag/AgCl as a reference electrode (all

electrodes were obtained from Metrohm). NMR spectra were recorded on a Bruker DRX-300 Avance Instruments. IR spectra were recorded on a Bruker IFS-66 FT-IR Spectrophotometer. MS spectra were obtained using a QP-1100EX Shimadzu GC–MS (EI at 70 eV). Melting points of the products were obtained using an electrothermal melting point model 9200. Chemicals (catechol, 3-methoxycatechol, ethyl acetoacetate, and methyl acetoacetate) were reagent-grade materials and phosphate salts were of pro-analysis grade from E-Merck and 3-methylcatechol was reagent-grade material from Aldrich. These chemicals were used without further purification. All experiments were carried out at room temperature.

4.2. Electrochemical synthesis of 3a–f

In a typical procedure, 100 ml of aqueous solution of phosphate buffer (pH 7.2, C=0.15 M) was pre-electrolyzed at the chosen potential (see Table 2) in an undivided cell. Subsequently, 2 mmol of catechols (**1a–c**) and 2 mmol of nucleophile (**2a** or **2b**) were added to the cell. The electrolysis was terminated when the decay of the current became more than 95%. The process was interrupted during the electrolysis and the carbon anode was washed in acetone in order to reactivate it. At the end of electrolysis, the precipitated solid was collected by filtration and washed with water. Then products were characterized using IR, ^{1}H NMR, ^{13}C NMR, and MS.

Table 2. Electroanalytical and preparative data

Conversion	Applied potential (V) (Ag/AgCl)	Purification	Product yield (%)
1a→3a	0.40	Washing in water	60
1b→3b	0.35	Washing in water	70
1c→3c	0.30	Washing in water	55
1a→3d	0.40	Washing in water	65
1b→3e	0.35	Washing in water	72
1c→3f	0.35	Washing in water	60

4.3. Characteristics of products

4.3.1. Methyl-5,6-dihydroxy-2-methyl-1-benzofuran-3-carboxylate ($C_{11}H_{10}O_5$) (3a). Brown powder, yield: 0.26 g, 60%, mp: 170 °C. IR (KBr) (ν_{max} cm^{-1}): 3414 (OH), 1711 (CO_2Me), 1620 (Ph), 1463 (Ph), 1301 and 1135 (C–O of ester). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.63 (3H, s, CH_3), 3.83 (3H, s, OCH_3), 6.91 (1H, s, CH of Ar), 7.19 (1H, s, CH of Ar), 9.06 (1H, s, OH), 9.12 (1H, s, OH). ^{13}C NMR (75.4 MHz, DMSO-d_6): δ 14.52 (CH_3), 51.73 (OCH_3), 98.28 (C^3 of benzofuran), 106.27 (CH of Ar), 108.47 (C^{3a} of benzofuran), 117.22 (CH of Ar), 143.87 (C–OH), 144.69 (C–OH), 147.52 (C^{7a} of benzofuran), 161.59 (C^2 of benzofuran), 164.66 (CO_2Me). Anal. Calcd for $C_{11}H_{10}O_5$ (222.19): C, 59.5; H, 4.5. Found: C, 59.4; H, 4.5. MS, *m/z* (%): 222 (M^+, 100), 207 (60), 191 (38), 163 (35), 135 (20), 93 (19), 69 (38), 43 (35).

4.3.2. Methyl-5,6-dihydroxy-2,7-dimethyl-1-benzofuran-3-carboxylate ($C_{12}H_{12}O_5$) (3b). Brown powder, yield: 0.33 g, 70%, mp: 163 °C. IR (KBr) (ν_{max} cm^{-1}): 3400 (OH), 1711 (CO_2Me), 1615 (Ph), 1442 (Ph), 1311 and 1133, 1071 (C–O of ester). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.23 (3H, s, CH_3), 2.65 (3H, s, CH_3), 3.83 (3H, s, OCH_3), 7.09 (1H, s, Ar), 8.43 (1H, s, OH), 9.32 (1H, s, OH). ^{13}C NMR (75.4 MHz, DMSO-d_6): δ 9.15 (CH_3), 14.65 (CH_3), 52.46 (OCH_3), 103.19 (C^3 of benzofuran), 107.86 (C^7 of benzofuran), 108.16 (C^{3a} of benzofuran), 116.98 (CH of Ar), 143.76 (C–OH), 144.14 (C^{7a} of benzofuran), 147.18 (C–OH), 162.17 (C^2 of benzofuran), 165.02 (CO_2Me). Anal. Calcd for $C_{12}H_{12}O_5$ (236.22): C, 61.0; H, 5.1. Found: C, 61.2; H, 5.1. MS, *m/z* (%): 236 (M^+, 100), 221 (56), 205 (34), 176 (34), 148 (10), 97 (12), 77 (28), 55 (37), 43 (39).

4.3.3. Methyl-5,6-dihydroxy-7-methoxy-2-methyl-1-benzofuran-3-carboxylate ($C_{12}H_{12}O_6$) (3c). Brown powder, yield: 0.27 g, 55%, mp: 167 °C. IR (KBr) (ν_{max} cm^{-1}): 3442 (OH), 1715 (CO_2Me), 1609 (Ph), 1511 (Ph), 1224 and 1091 (C–O of ester). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.66 (3H, s, CH_3), 3.95 (OCH_3), 4.25 (OCH_3), 6.87 (1H, s, Ar), 8.72 (1H, s, OH), 9.2 (1H, s, OH). ^{13}C NMR (75.4 MHz, DMSO-d_6): δ 14.62 (CH_3), 56.25 (OCH_3), 66.80 (OCH_3), 106.12 (C^3 of benzofuran), 108.75 (C^{3a} of benzofuran), 122.12 (CH of Ar), 127.25 (C–OH), 138.12 (C–OH), 138.95 (C–OCH_3), 141.15 (C^{7a} of benzofuran), 148.18 (C^2 of benzofuran), 150.12 (CO_2Me). Anal. Calcd for $C_{12}H_{12}O_6$ (252.22): C, 57.1; H, 4.8. Found: C, 57.3; H, 4.8. MS, *m/z* (%): 252 (M^+, 100), 237 (30), 221 (48), 205 (30), 140 (25), 109 (50), 81 (87), 43 (40).

4.3.4. Ethyl-5,6-dihydroxy-2-methyl-1-benzofuran-3-carboxylate ($C_{12}H_{12}O_5$) (3d). Brown powder, yield: 0.30 g, 65%, mp: 180 °C. IR (KBr) (ν_{max} cm^{-1}): 3439 (OH), 1659 (CO_2Et), 1634 (Ph), 1503 (Ph), 1314, 1255, and 1182 (C–O of ester). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.35 (3H, t, $^3J_{HH}$=6.6 Hz, OCH_2CH_3), 2.63 (3H, s, CH_3), 4.29 (2H, q, $^3J_{HH}$=6.6 Hz, OCH_2CH_3), 6.91 (1H, s, CH of Ar), 7.22 (1H, s, CH of Ar), 8.99 (1H, s, OH), 9.08 (1H, s, OH). ^{13}C NMR (300 MHz, DMSO-d_6): δ 14.52 (CH_3), 14.69 (OCH_2CH_3), 60.28 (OCH_2CH_3), 98.25 (C^3 of benzofuran), 106.32 (CH of Ar), 108.55 (C^{3a} of benzofuran), 117.26 (CH of Ar), 143.83 (C–OH), 144.65 (C–OH), 147.51 (C^{7a} of benzofuran), 161.54 (C^2 of benzofuran), 164.23 (CO_2Et). Anal. Calcd for $C_{12}H_{12}O_5$ (236.22): C, 61.0; H, 5.1. Found: C, 61.2; H, 5.2. MS, *m/z* (%): 236 (M^+, 54), 207 (100), 191 (28), 162 (12.5), 69 (12), 43 (20).

4.3.5. Ethyl-5,6-dihydroxy-2,7-dimethyl-1-benzofuran-3-carboxylate ($C_{13}H_{14}O_5$) (3e). Brown powder, yield: 0.36 g, 72%, mp: 157 °C. IR (KBr) (ν_{max} cm^{-1}): 3422 (OH), 1669 (CO_2Et), 1620 (Ph), 1460 (Ph), 1378, 1307, and 1134 (C–O of ester). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.35 (3H, t, $^3J_{HH}$=6.6 Hz, OCH_2CH_3), 2.24 (3H, s, CH_3), 2.66 (3H, s, CH_3), 4.29 (2H, q, $^3J_{HH}$=6.6 Hz, OCH_2CH_3), 7.12 (1H, s, CH of Ar), 8.37 (1H, s, OH), 9.26 (1H, s, OH). ^{13}C NMR (75.4 MHz, DMSO-d_6): δ 9.30 (CH_3), 14.62 (CH_3), 14.69 (OCH_2CH_3), 60.32 (OCH_2CH_3), 103.26 (C^3 of benzofuran), 107.63 (C^7 of benzofuran), 108.75 (C^{3a} of benzofuran), 116.39 (CH of Ar), 142.33 (C–OH), 143.46 (C^{7a} of benzofuran), 147.13 (C–OH), 161.42 (C^2 of benzofuran), 164.35 (CO_2Et). Anal. Calcd for $C_{13}H_{14}O_5$ (250.25): C, 62.4; H, 5.6. Found: C, 62.6; H, 5.6. MS, *m/z* (%): 250 (M^+, 62), 221 (100), 205 (25), 176 (18), 67 (16), 43 (20).

Crystal data for $C_{13}H_{14}O_5$ (**3e**) (CCDC 608893): M_w=250.24, triclinic, space group $P\bar{1}$, a=5.691(5) Å, b=9.624(9) Å, c=21.796(15) Å, α=89.91(7)°, β=90.42(6)°, γ=89.81(7)°, V=1193.8(16) Å^3, Z=4, D_C=1.392 mg/m^3, F(000)=528, crystal dimension 0.25×0.15×0.05 mm^3, radiation Mo Kα (λ=0.71073 Å), $4.24<2\theta<49.52$, intensity data were collected at 293 K with a STOE IPDS II two-circle diffractometer and employing ω-scanning technique, in the range of $-5\leq h\leq 6$, $-11\leq k\leq 11$, $-25\leq l\leq 25$. The structure was solved by a direct method, all nonhydrogen atoms were positioned, and anisotropic thermal parameters refined with R(int)=0.1143 by a full-matrix least squares technique converged to R_1=0.0698 and wR_2=0.2047.

4.3.6. Ethyl-5,6-dihydroxy-7-methoxy-2-methyl-1-benzofuran-3-carboxylate ($C_{13}H_{14}O_6$) (3f). Brown powder, yield: 0.32 g, 60%, mp: 170 °C. IR (KBr) (ν_{max} cm^{-1}): 3501 (OH), 3326 (OH), 1666 (CO_2Et), 1619 (Ph), 1516 (Ph), 1458 (Ph), 1364, 1311, and 1208 (C–O of ester). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.35 (3H, t, $^3J_{HH}$=6.8 Hz, OCH_2CH_3), 2.66 (3H, s, CH_3), 3.93 (3H, s, OCH_3), 4.3 (2H, q, $^3J_{HH}$=6.8 Hz, OCH_2CH_3), 6.99 (1H, s, CH of Ar), 8.60 (1H, s, OH), 9.12 (1H, s, OH). ^{13}C NMR, (75.4 MHz, DMSO-d_6): δ 14.62 (CH_3), 14.72 (OCH_2CH_3), 56.38 (OCH_2CH_3), 67.30 (OCH_3), 104.43 (C^3 of benzofuran), 110.17 (C^{3a} of benzofuran), 124.51 (CH of Ar), 127.20 (C–OH), 137.61 (C–OH), 138.74 (*C*–OCH_3), 141.31 (C^{7a} of benzofuran), 146.25 (C^2 of benzofuran), 148.78 (CO_2Et). Anal. Calcd for $C_{13}H_{14}O_6$ (266.25): C, 58.6; H, 5.3. Found: C, 58.7; H, 5.3. MS *m*/*z* (%): 266 (M^+, 100), 237 (50), 221 (25), 180 (18), 43 (25).

Acknowledgements

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