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Green synthesis and study of antioxidant activity of indole derivatives using multicomponent reaction of 2,4-diaminoacetophenone

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Abstract: An efficient procedure for the synthesis of indole derivatives employing 2,4-diamino acetophenone, isopropenylacetylene and activated acetylenic compounds in the presence of KF/CP NPs as a heterogeneous base nanocatalyst in water at 80 ^{o}C is investigated. Also, the antioxidant activity of some synthesized compounds was studied. The workup of reaction is simple and the products can be separated easily from the reaction mixture. KF/CP NPs show a good improvement in the yield of the product. The catalyst displayed significant reusable activity.

Keywords: Water, Isopropenylacetylene, 2,4-diamino acetophenone, Three-component reaction.

Introduction

Employing of green method is to find out procedure for saving resources and decrease prices. Use of ecologically solvents instead of toxic solvents and employing of moderate conditions and cheap reagents are the most attractive methods to expand a simple and green synthesis of organic compounds [1-3]. Water as an available and cheap solvent in large amounts can increase the rate of organic reactions even for compounds that is water-insoluble. Also isolation of product in water is performed by simple filtration. Catalysts have a chief function in green chemistry. It can provide the best yield of the reaction in the low temperatures. Important properties of magnetic nanoparticles (MNPs) for example large surface area to volume ratios, biocompatibility, non-toxicity and easy conversion made them gorgeous for numerous biomedical applications.[3] Simple recovery of MNPs by using of an external magnet because of their superparamagnetic property makes them the best catalyst for green and maintainable chemistry.

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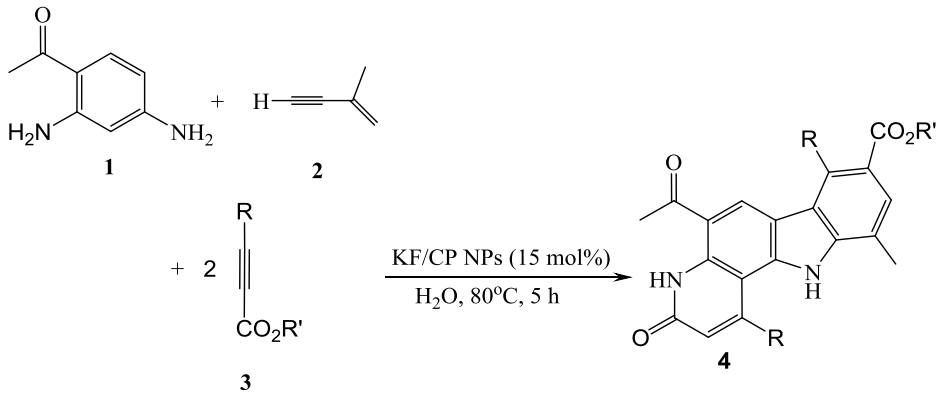
Chromenes are important nucleus in organic and medicinal chemistry due to their power and broad spectrum of biological activities involving antimicrobial [4], antioxidant [5], antimalarial [6], Antibacterial [7] and anticancer [8]. Among different chromenes, benzochromenes are important and considerable compounds due to their biological properties in different subjects [9]. The synthesis of benzochromenes has been investigated in the presence of different catalysts involving lipase[10], Zn(*L*-proline)$_2$ [11], DBU [12], Triethylbenzylammonium Chloride (TEBA) [13], Et_3N [14] and 1-butyl-3-methyl imidazolium hydroxide ([bmim]OH) [15]. However, some of the reported methods have disadvantages involving high reaction times, employing of toxic and non-reusable catalyst and use of specific conditions. Consequently, the study of an efficient and available catalyst with high catalytic activity and short reaction time for the preparation of benzochromenes is still preferred. Certainly, the synthesis of benzochromenes *via* multicomponent reactions (MCR) has much notice due to good synthetic yield and easy separation of product. Lately, there has been an enhanced interest for new applications of

potassium fluoride impregnated on zeolites and clays, as a new natural and inexpensive solid base system [26-34]. Among them Clinoptilolite, a natural zeolite with a high internal surface area, is much more effective because of its high exchange capability for cations particularly for K^+, therefore, more free fluoride anions are capable of functioning as an effective base. On the other hand, the preparation of potassium fluoride impregnated Clinoptilolite (KF/CP) is very simple without the need for any pre-activation [35-36].

In continuation of our attempts to expand new synthetic procedure for chief organic compounds [16-20] herein, we investigated a ‘‘green’’ procedure for the synthesis of some benzofurane derivatives *via* an efficient three component reaction of 2,4-diamino acetophenone **1**, isopropenylacetylene **2**, and activated acetylenic compounds **3** in the presence of a catalytic amount of KF/CP NPs [22-23] in water at 80°C with good yields (Scheme **1**) [24]. Moreover, the antioxidant activities of some derivatives were investigated by DPPH radical scavenging and ferric ion reducing power test.

Result and Discussion

The synthesis of some indole derivatives **4** was performed *via* an efficient three component reaction of 2,4-diamino acetophenone **1**, isopropenylacetylene **2** and activated acetylenic compounds **3** in the presence of a catalytic amount of KF/CP NPs in water at 80°C with good yields (Scheme 1).



4	R	R'	Yield % of **4**
a	CO_2Me	Me	85
b	CO_2Et	Et	80
c	H	Me	78
d	H	Et	75

Scheme 1. Three component reaction for synthesis of indole derivatives of **4** in water.

Catalytic activity of KF/CP NPs in synthesis of indole derivatives

In the starting stage of this work, condensation reaction of 2,4-diamino acetophenone **1**, isopropenylacetylene **2**, and dimethyl acetylenedicarboxylate **3** in water at 80 °C was employed as a sample reaction to achieve the optimum conditions (Table **1**).

These reactions weren’t performed without any catalyst even after 15h (entry 1, Table **1**). By increasing the reaction temperature to 80 °C, a trace amount of **4a** was generated after 15 h (entry 2, Table **1**).

Table 1. Effect of catalyst, its loading and temperature on the condensation reaction of compound **4a**

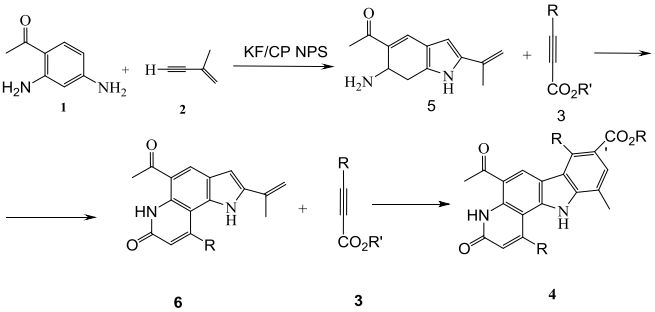
Entry	Catalyst	Temp. (°C)	catalyst (mol%))	Time (h)	Yield%[a]
1	none	-	-	15	-
2	none	80	-	15	10
3	none	90	-	15	10
4	KF/CP NPs	80	10	5	70
5	**KF/CP NPs**	**80**	**15**	**5**	**85**
6	KF/CP NPs	90	15	5	85
7	KF/CP NPs	80	20	5	87
8	Et_3N	80	15	8	65
9	ZnO-NR	80	15	12	70
10	ZnO-NR	90	15	12	70
11	CuO-NPs	80	15	8	60
12	TiO_2-NPs	80	15	10	----

With the purpose of get better this procedure, 10 mol% KF/CP NPs was added to the reaction mixture. After 5 h, 85% yield of **4a** was produced (entry 4, Table 1). Then, the reaction was carried out in the presence of 15 mo% of KF/CP NPs as catalyst. As expected, in these conditions, the yield of product **3a** was achieved in 95% yield after 5 h (entry5, Table **1**). As a result, to discover the optimal catalyst loading, different amounts (10–20 mol%) of KF/CP NPs were employed. The results displayed that 15 mol% of catalyst are enough for produce an excellent yield of **4a** (entry 5, Table **1**). In order to more evaluate the catalytic activity, another catalyst such as ZnO-nanorods, CuO-NPs, TiO_2-NPs and Et_3N were used in this reaction. Consequently, these results showed the main function of KF/CP NPs as catalyst in this reaction. In this research the effects of some solvents was also investigated on the production of **4a** in the presence of 15 mol% of Fe_3O_4-MNPs. The results tabulated in Table **2** display that H_2O is the best solvent for these reaction.

Table 2. Effects of solvent and temperature on generation of **4a** compound in presence of 15 mol% of KF/CP NPs.

Entry	**Solvent**	**Temperature (°C)**	**Time (h)**	**Yield%[a]**
1	EtOH	80	15	None
2	EtOH	90	15	None
3	CH_2Cl_2	-	8	75
4	CH_2Cl_2	50	8	75
5	H_2O	70	5	85
6	**H_2O**	**80**	**5**	**95**
7	H_2O	90	5	95
8	Solvent-free	80	8	90
10	DMf	80	15	45
11	toluene	80	12	75
12	$CHCl_3$	50	10	75

According to the outcomes of optimization reported in the Tables 1 and 2, KF/CP NPs (15 mol%) as catalyst, water as solvent, and 80 °C were estimated to be the optimum reaction conditions. The reusability of the catalyst was confirmed in the model reaction (the synthesis of compound **3a**). The results showed that the catalyst can be reused five times without loss of activity. After each run, the catalyst was extracted by external magnet and washed with water. It was then dried at ambient temperature for 24 h and employed for the next catalytic cycle. The structures of compounds **5** were confirmed by IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data. For example, the ^{1}H NMR spectrum of **3a** revealed two singlets at $\delta = 2.15$ and 2.52 ppm for methyl protons, four singlets at 4.58, 5.37, 6.14 and 7.75 ppm for methin proton along with signals for aromatic moiety. In the ^{13}C NMR spectrum, the signals corresponding to the carbonyl group of **3a** were observed at δ 160.2 and 197.6 ppm. The IR spectrum of **3a** was displayed characteristic C=O bands. Although there is no information about the mechanistic details, the reaction can be described by the mechanism proposed in Scheme **2**.



Scheme 2. Proposed mechanism for the formation of **4**.

First, 2,4-diamino acetophenone **1**, and isopropenylacetylene **2** is reacted in the presence of KF/CP NPs that is generated intermediate **5**. Intermediate **5** is attacked to compound **3** in the presence of KF/CP NPs and produced Diels-Alder production **6**. The chief benefits of our method are high atom economy, green reaction conditions, use a small amount nanocatalyst, higher yield, shorter reaction times, and easy work-up, which are in good agreement with some principles of green chemistry.

Investigation of antioxidant activity using DPPH

Diphenyl-2-picrylhydrazyl (DPPH) radical scavenging test is broadly employed to estimate the ability of compounds to capture free radicals and their antioxidant activity in foods and biological systems [25-26]. The DPPH analyze donating activity of the hydrogen atom (or one electron) and gives an evaluation of antioxidant activity because of free radical scavenging. The antioxidant activity of **4a-4d** was investigated by testing their ability to the DPPH radical. DPPH radical shows the absorption in area 517 nm but its absorption decreases when is reduced by an antioxidant or a radical species. In this study, the antioxidant activity of **4a-4d** was compared to BHT and TBHQ at different concentrations from 200 mmol/L to 1000 mmol/L (Figure **1**).

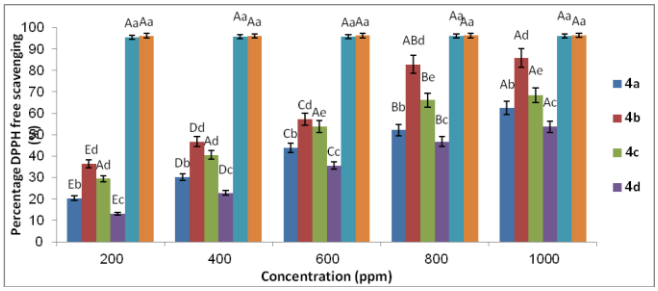


Figure 1. Radical scavenging activity (RSA) of **4a-4d**

At all concentrations, the new synthesized compounds had significant differences compared to BHT and TBHQ (Figure **1**). Overall, the all compounds were shown excellent free radical scavenging performance compared to BHT and TBHQ at 1000 ppm concentration (Figure **1**).

Ferric ions (Fe^{3+}) reducing potential (FRAP)

The ability of the synthesized compounds to reduce Ferric ions (Fe^{3+}) was studied by measuring the amount of exchange of Fe^{3+}/ferricyanide complex to the Fe^{2+}/ ferrous shape at 700 nm. The ability of compound to reducing may act as a important indicator of its potential antioxidant activity. Compound **4b** was displayed good reducing activity compared to standards (BHT and TBHQ).

Conclusion

In summary, we investigate an useful, green, and environmentally procedure including 1-(6-hydroxy-2-isopropenyl-1-benzofuran-yl)-1-ethanone, aldehydes, alkyl bromides and triphenylphosphin in the presence of Fe_3O_4-MNPs at 80°C in water which provides a new path to the synthesis of benzochromens. The present method has many advantages such as high atom economy and yield, mild and clean reaction condition, low catalyst loading, and short reaction time. Also, the antioxidant activities of **3a-3d** compounds were evaluated by DPPH radical scavenging and ferric reducing power analyzes. The compounds **3a-3d** exhibit good DPPH radical scavenging activity, but

showed moderate FRAP compared to synthetic antioxidants BHT and TBHQ.

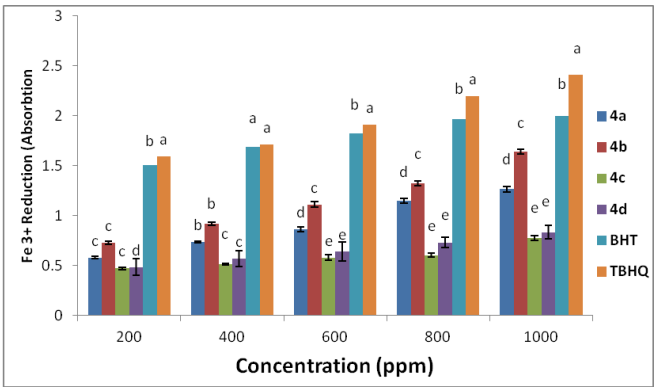


Figure 2. Ferric ions (Fe^{3+}) reducing antioxidant power (FRAP) of compounds **4a-4d.**

Experimental

All chemicals employed in this work were prepared from Fluka (Buchs, Switzerland), Merck, Lolitech, and Aldrich Chemical Companies and employed without further purification. KF/CP NPs were produced according to a reported method. The morphology of Fe_3O_4-MNPs was confirmed by scanning electron microscopy (SEM) employing a Holland Philips XL30 microscope. Crystalline structure of KF/CP NPs was discovered by Xray diffraction (XRD) analysis at room temperature employing a Holland Philips Xpert X-ray powder diffractometer, with CuKa radiation (l = 0.15406 nm), with 2θ ranging from 20 to 80°. The elemental analyses for the determination of C, H, and N were performed employing a Heraeus CHNO-Rapid analyzer. The mass spectra were recorded on a FINNIGAN-MAT 8430 spectrometer operating at an ionization potential of 70 eV. IR spectra were measured on a Shimadzu IR-460 spectrometer. The ^1H and ^{13}C NMR spectra were measured employing a Bruker DRX-500 advance spectrometer at 500.1 MHz and 125.8 MHz, respectively. The ^1H and ^{13}C spectra were achieved for $CDCl_3$ solutions emploing TMS as the internal standard or 85 mass % H_3PO_4 as external standard; chemical shifts (d) are given as parts per million (ppm).

General procedure for preparation of compounds 4a–d:

A mixture of 2,4-diamino acetophenone **1** (2 mmol), and isopropenylacetylene **2** (2 mmol), activated acetylenic compounds **3** (2 mmol) and KF/CP NPs (0.02 g) in water (3 mL) was at 80°C for an appropriate time showed in Table 1. After completion the reaction, the KF/CP NPs were separated by filteration. The organic and aqueous layers were separated by filtration and washed with Et_2O to afforded pure title compound **5**.

3-Ethyl 7,8-dimethyl-5-acetyl-1-(4-methoxyphenyl)-10-methyl-1H-[1]-benzofuro[2,3-f]chromene-3,7,8-tri carboxylate (4a):

Yellow powder, mp 173-175˚C, Yield: 1.08 g (95%). IR (KBr) (ν_{max}/cm^{-1}): 1742, 1735, 1683, 1585, 1462, 1274 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 1.32 (3 H, t, ^3J = 7.4 Hz, CH_3), 2.15 (3 H, s, Me), 2.52 (3 H, s, Me), 3.75 (3 H, s, MeO), 3.85 (3 H, s, MeO), 4.03 (3 H, s, MeO), 4.26 (2 H, q, ^3J = 7.3 Hz, CH_2O), 4.47 (1 H, d, ^2J = 4.5 Hz, CH), 5.87 (1 H, d, ^2J = 4.5 Hz, CH), 7.12 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.63 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.75 (1 H, s, CH), 8.13 (1 H, s, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): 14.2 (Me), 22.6 (Me), 30.2 (Me), 41.2 (CH), 51.2 (MeO), 52.3 (MeO), 55.7 (MeO), 61.4 (CH_2O), 109.3 (2 CH), 113.2 (C), 114.3 (C), 115.6 (CH), 123.4 (C), 124.2 (C), 124.8 (CH), 127.2 (C), 127.3 (2 CH), 127.6 (CH), 128.2 (C), 130.5 (C), 135.4 (C), 145.2 (C), 153.7 (C), 159.2 (C), 159.8 (C), 160.3 (C), 161.2 (C=O), 165.3 (C=O), 166.4 (C=O), 197.6 (C=O) ppm.

3-Ethyl 7,8-dimethyl-5-acetyl-1-(4-methylphenyl)-10-methyl-1H-[1]-benzofuro[2,3-f]chromene-3,7,8-tri carboxylate (4b):

Yellow powder, mp 162-164˚C, Yield: 1.03 g (93%). IR (KBr) (ν_{max}/cm^{-1}): 1740, 1735, 1726, 1683, 1575, 1472, 1295 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 1.34 (3 H, t, ^3J = 7.4 Hz, CH_3), 2.16 (3 H, s, Me), 2.23 (3 H, s, Me), 2.53 (3 H, s, Me), 3.87 (3 H, s, MeO), 4.05 (3 H, s, MeO), 4.25 (2 H, q, ^3J = 7.4 Hz, CH_2O), 4.65 (1 H, d, ^2J = 4.5 Hz, CH), 6.12 (1 H, d, ^2J = 4.5 Hz, CH), 7.32 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.58 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.78 (1 H, s, CH), 8.25 (1 H, s, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): 13.5 (Me), 22.0 (Me), 22.7 (Me), 30.4 (Me), 40.8 (CH), 51.4 (MeO), 52.6 (MeO), 61.6 (CH_2O), 112.3 (C), 114.2 (C), 115.8 (C), 124.2 (2 CH), 124.8 (C), 125.2 (CH), 126.3 (2 CH), 127.2 (C), 127.8 (CH), 128.2 (C), 128.6 (C), 130.2 (C), 134.3 (C), 136.2 (C), 145.5 (C), 153.2 (C), 158.4 (C), 159.6 (C), 160.7 (C=O), 166.3 (C=O), 167.2 (C=O), 197.4 (C=O) ppm.

Dimethyl-5-acetyl-10-methyl-3-(4-methylphenyl)-1-phenyl-1H-[1]-benzofuro[2,3-f]chromene-7,8-dicarboxylate (4c):

Yellow powder, mp 175-177˚C, Yield: 0.76 g (90%). IR (KBr) (ν_{max}/cm^{-1}): 1742, 1738, 1725, 1692, 1563, 1485, 1274 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 2.15 (3 H, s, Me), 2.35 (3 H, s, Me), 2.54 (3 H, s, Me), 3.83 (3 H, s, MeO), 3.96 (3 H, s, MeO), 4.74 (1 H, d, ^2J = 4.5

Hz, CH), 6.12 (1 H, d, ^2J = 4.5 Hz, CH), 6.75 (1 H, t, ^3J = 7.5 Hz, CH), 7.12 (2 H, t, ^3J = 7.5 Hz, 2 CH), 7.35 (2 H, d, ^3J = 7.8 Hz, 2 CH), 7.46 (2 H, d, ^3J = 7.5 Hz, 2 CH), 7.73 (2 H, d, ^3J = 7.8 Hz, 2 CH), 7.82 (1 H, s, CH), 8.32 (1 H, s, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): 16.7 (Me), 21.6 (Me), 30.5 (Me), 42.3 (CH), 51.5 (MeO), 52.7 (MeO), 102.4 (CH), 112.3 (C), 114.4 (C), 115.3 (CH), 124.2 (2 CH), 124.6 (CH), 125.2 (2 CH), 125.6 (C), 126.5 (2 CH), 127.2 (CH), 127.6 (C), 128.4 (2 CH), 128.8 (C), 130.2 (C), 131.3 (C), 131.8 (C), 134.2 (C), 136.5 (C), 153.3 (C), 153.8 (C), 159.3 (C), 160.3 (C), 166.3 (C=O), 167.2 (C=O), 197.5 (C=O) ppm.

***Diethyl-5-acetyl-10-methyl-3-(4-methoxyphenyl)-1-(4-methylphenyl)-1H-[1]-benzofuro[2,3-f]chromene-7,8-dicarboxylate (4d)**:*

Yellow powder, mp 187-189˚C, Yield: 0.78 g (87%). IR (KBr) (ν_{max}/cm^{-1}): 1738, 1735, 1725, 1692, 1578, 1487, 1295 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 1.12 (3 H, t, ^3J = 7.4 Hz, CH_3), 1.28 (3 H, t, ^3J = 7.4 Hz, CH_3), 2.12 (3 H, s, Me), 2.17 (3 H, s, Me), 2.56 (3 H, s, Me), 3.87 (3 H, s, MeO), 4.26 (2 H, q, ^3J = 7.4 Hz, CH_2O), 4.32 (2 H, q, ^3J = 7.4 Hz, CH_2O), 4.82 (1 H, d, ^2J = 4.7 Hz, CH), 5.24 (1 H, d, ^2J = 4.7 Hz, CH), 7.32 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.38 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.62 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.75 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.85 (1 H, s, CH), 8.35 (1 H, s, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): 13.8 (Me), 14.2 (Me), 16.8 (Me), 21.8 (Me), 30.6 (Me), 42.4 (CH), 55.6 (MeO), 61.3 (CH_2O), 62.4 (CH_2O), 102.3 (CH), 112.3 (C), 114.5 (2 CH), 114.9 (C), 115.3 (CH), 124.2 (2 CH), 124.7 (CH), 125.2 (C), 125.8 (2 CH), 126.3 (C), 127.2 (C), 128.2 (2 CH), 128.7 (C), 129.3 (C), 129.8 (C), 134.2 (C), 135.8 (C), 153.6 (C), 154.2 (C), 158.3 (C), 159.2 (C), 159.8 (C), 160.2 (C=O), 164.3 (C=O), 198.2 (C=O) ppm.

1,1-Diphenyl-2-picrylhydrazyl (DPPH) radical scavenging test

Radical scavenging activity of **4a-4d** was measured by DPPH radical scavenging test according to the reported method by Shimada et al.[38]. Different concentrations of **4a-4d** (200–1000 ppm) were added to an equal volume of methanolic solution of DPPH (1 mmol/L). The mixtures were well shaken and then placed in a dark room. After 30 min at room temperature, the absorbance was recorded at 517 nm. In the control sample, **4a-4d** were replaced with 3 mL methanol. Butylated hydroxytoluene (BHT) and 2-tertbutylhydroquinone (TBHQ) were used as standard controls. The percentage inhibition of the DPPH radical was calculated according to the formula of Yen and Duh [39].

Reducing power test

The ability of compounds **4a-4d** to reduce iron (III) was evaluated by the method of Yildirim et al. [40] Samples (1 mL) were mixed with 2.5 mL of phosphate buffer (0.2 mol/L, pH 6.6) and 2.5 mL of potassium ferricyanide (K3Fe(CN)6; 10g/L) and showed for 30 min at 50 8C. Then, 2.5 mL of trichloroacetic acid (10% w/v) were added to the solution and centrifuged for 10 min. Finally, 2.5 mL of supernatant was combined with 2.5 mL of distilled water and 0.5 mL $FeCl_3$ (1 g/L). The absorbance of samples was measured at 700 nm. Higher absorbance means higher reducing power.

Each measurement was carried out in triplicate. The data were analyzed by running one way analysis of variance (ANOVA) using SPSS software version 18.0. A one way ANOVA was employed to evaluate difference in the mean value of samples and control. All mean separations were performed by Duncan multiple range test using the significance level of 95% ($P < 0.05$).

Acknowledgments

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