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KF/Clinoptilolite promoted synthesis of quinolines in water using multicomponent reactions

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Abstract: The preparation of functionalized quinolines were performed by using one-pot three-component reactions aniline, diethyl oxalate, activated acetylenic compounds, and amines in the presence of KF/CP (NPs) as a heterogeneous base nanocatalyst, at room temperature in water**.** Due to having NH protones, we investigate antioxidant property of some synthesized compounds by diphenyl-picrylhydrazine (DPPH) radical trapping and power of ferric reduction experiment. Short time of reaction, high yields of product, easy separation of catalyst and products are some benefits of this process.

Keywords: Quinolines, Heterogeneous nanocatalyst, KF/Clinoptilolite nanoparticles, Analine, Activated acetylenic compounds.

Introduction

Multicomponent reactions (MCRs) are significant method for preparation of complex molecules from simple starting materials [1]. The molecules that were generated by this procedure is attracting for medicinal and synthetic chemists [2]. Also, producing many of substance by expand environmentally gentle paths is the important point in chemistry [3]. Green chemistry move towards procedure that decreases byproducts, waste and energy costs [4]. Of all the trends in chemistry, medicinal and pharmaceutical chemistry with their conventionally big volume of waste/product ratio, are ready for greening [5]. In addition, the removal of explosive organic solvents in organic synthesis is the most important purpose in green chemistry [6-8].

Heterocycles with nitrogen group are a main piece of natural and unnatural compounds with significant biological activity [9].

Quinolines are important groups of *N*-based heterocyclic compounds and are generally known to have a broad range of applications in medicinal, bioorganic, and industrial chemistry as well as in the field of synthetic organic chemistry [10]. Some key biological activities of quinoline derivatives include antimalarial, antibacterial, anti-asthmatic, antihypertensive, anti-staphylococcal, antiplatelet and anti-inflammatory [11-18]. 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 [19-27]. 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 [28, 29]. Frequently compounds with antioxidant ability, eliminate the negative property of free radicals and

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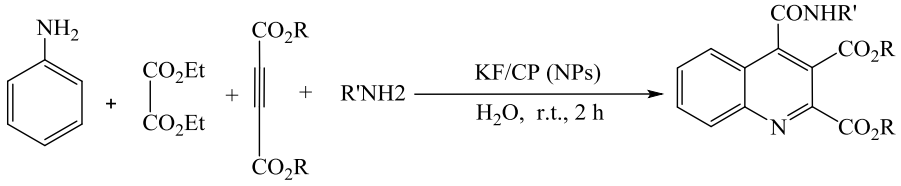
utilize as transitional metals chelators. This result is due to their reducing properties and chemical structure. Also, these compounds could be avoid or decrease many sicknesses such as cardiovascular, inflammatory bowel syndrome, cancer, ageing, and alzheimer [30-32]. Herein, in continuing research of my study for finding out new process for generation of valuable organic compounds [33-43], we report an efficient and green synthesis of functionalized quinolines **5a-e** through the reaction of aniline **1**, diethyloxalate **2**, activated acetylenic compounds **3** and primary amines **4** in the presence of catalytic amount of KF/CP (NPs) in water as the solvent at room temperature (Scheme **1**).



5	R	R/	Yield (%) of 5
a	Me	Me	85
b	Me	Et	87
c	Et	Me	85
d	Me	^{n}Pr	85
e	Et	Et	87

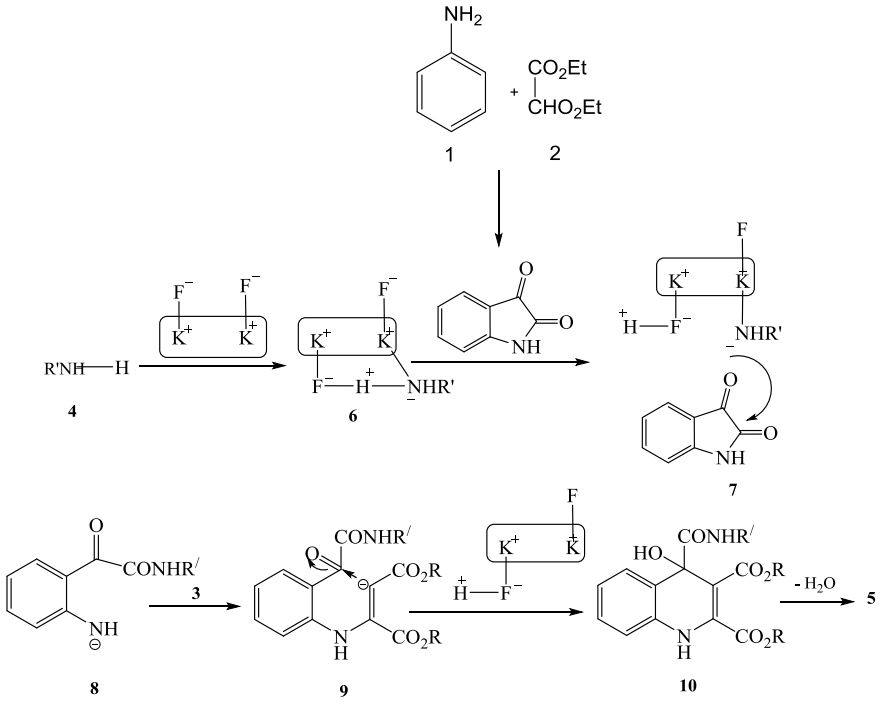
Scheme 1: Synthesis of functionalized quinolines.

Results and discussion

To achieve the optimum conditions the condensation reaction of aniline **1**, diethyloxalate **2**, dimethyl acetylenedicarboxylate **3a** and methyl amine **4a** was performed by varying the catalyst, solvent and temperature for preparation of the product **5a**. Et_3N, pyridine, piperidine, K_2CO_3, KF/CP (NPs), and ZnO (NPs) were used as catalyst. According to the outcomes of optimization, 10% (w/w) KF/CP (NPs) as catalyst, water as solvent and room temperature were estimated to be the optimum reaction conditions.

Having established the optimal reaction conditions, the scope of the reaction was examined using aniline **1**, diethyloxalate **2**, activated acetylenic compounds **3** and amines **4** in the presence of catalytic amount of KF/CP (NPs) in water as the solvent at room temperature (Scheme **1**). The structures of compounds **5a-5e** were apparent from the ^{1}H NMR, ^{13}C NMR, IR and mass spectra which were in agreement with the proposed structures. The ^{1}H NMR spectrum of **5a** showed three singlet for methoxy protons at δ = 3.89 and 3.98 ppm along with characteristic signals for the aromatic moiety. The resonances of carbonyl groups of ester in the ^{13}C NMR spectra of **5a** found at δ = 165.5, 165.6 and 165.7 ppm. The mass spectrum of **5a** displayed the molecular ion peak at *m/z* = 303.

The reaction can be described as occurring by the mechanism proposed in Scheme **2**. It is conceivable that the reaction starts with the formation of hydrogen bonding between fluoride ion and proton of the amine giving rise to the intermediate **6**, followed by nucleophilic substitution at position C-2 of the isatin **7**, leading to the opening of the heterocyclic ring enabling the formation of anion intermediate **8**. The nucleophilic attack of ring-opened intermediate **8** to **3** leads to the formation of anionic intermediate **9** which undergoes intramolecular exo-trig cyclization to generate functionalized quinolines **5** after elimination of H_2O**.**



Scheme 2: Plausible mechanism for the generation of **5**.

Evalution of antioxidant ability employing diphenyl-2-picrylhydrazyl (DPPH)

For the confirmation of antioxidant ability or power of compounds to take free radicals of some synthezied compounds and antioxidant property of them in foods and biological structures [44, 47]DPPH radical trapping experiment is widely used. In these evaluation, antioxidant capacity of synthesized quinolines was determined by taking the hydrogen atom or one electron by DPPH radical and order of antioxidant ability of synthesized quinolines are basis of percentage of DPPH radical free trapping. The electron or hydrogen donating power of quinolines **5a-5d** to the radical of DPPH determined the antioxidant ability of them.The radical of DPPH absorption was decreased from 517 nm when give one electron or hydrogen from antioxidant or a radical typs. In this research, the antioxidant ability or power of quinolines **5a-5d** for taking free radicals was compared to synthesized antioxidant such as BHT and TBHQ at different concentrations. Overall, the power of DPPH trapping was obtained TBHQ≈BHT>**5c**>**5a**>**5d**>**5b** (Figure **1**).

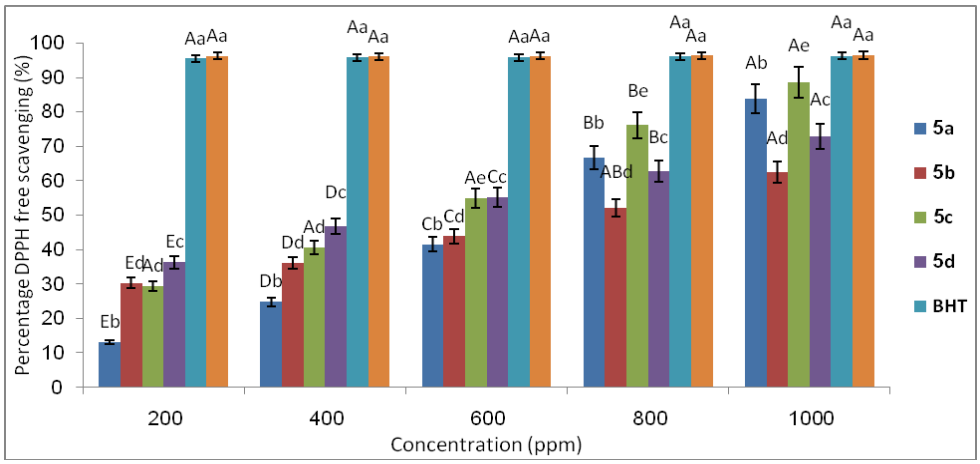


Figure 1: Radical scavenging activity (RSA) of **5a-5d.**

As seen in Figure **1**, in all concentrations of the new prepared naphthyridine derivatives existed good difference relative to BHT and TBHQ. Compound **5c** in among experimented compounds displayed good activity for trapping of radical relative to BHT and TBHQ as standard antioxidant.

The potential of synthesized quinoline *via* Ferric ions (Fe^{3+}) reducing

The reducing ferric ions (Fe^{3+}) ability of some synthesized quinolines such as **5a-5d** are calculated based on the quantity reducing of Fe^{3+}/ferricyanide to the Fe^{2+}/ ferrous at 700 nm. As seen in Figure **1**, compound**5c** was shown good ability of reducing than to BHT and TBHQ as standard antioxidants. The reducing activity trend of the samples was as follows: TBHQ>BHT>**5c**>**5a**>**5d**>**5b**. The outcomes are displayed in Figure **2**.

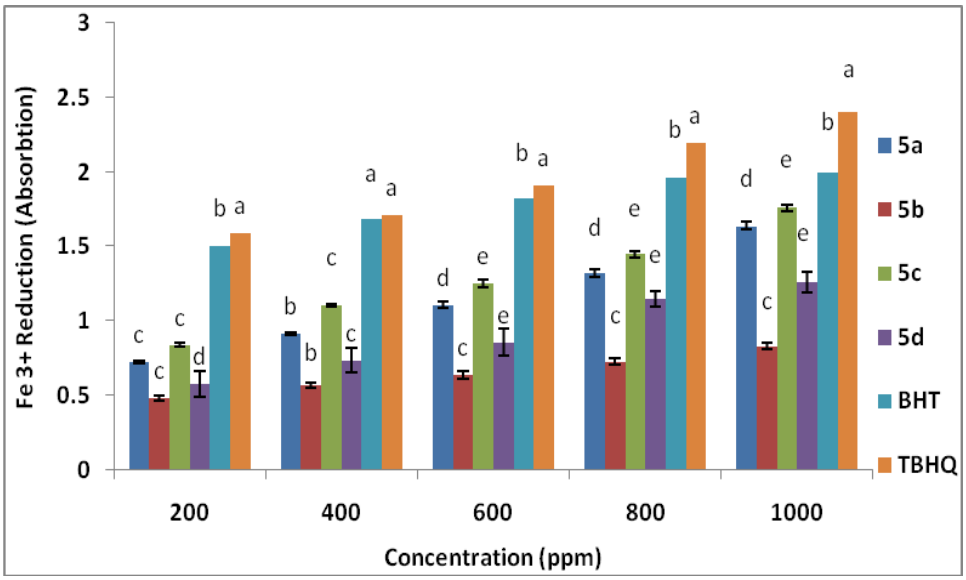


Figure 2: Ferric ions (Fe^{3+}) reducing antioxidant power (FRAP) of compounds **5a-5d.**

Conclusion

Regarding results of this study, an efficient, green and environmentally benign method has been developed for the synthesis of functionalized quinolines derivatives *via* a one pot three components condensation reaction between aniline, diethyloxalate, activated acetylenic compounds and amines in the presence of KF/CP (NPs) as a heterogeneous base nanocatalyst, at room temperature in water. The advantages of proposed method are the mild and clean reaction conditions, low catalyst loading, use of natural catalyst and cost efficiency which make this approach an interesting alternative to the existing methods.

Experimental

Material and Methods:

All chemicals used in this work purchased from Fluka (Buchs, Switzerland) and used without further purification. Clinoptilolite obtained from Afrandtooska Company in the region of Semnan. Elemental analyses for C, H, and N performed using a Heraeus CHN–O-Rapid analyzer. Mass spectra recorded on a FINNIGAN-MAT 8430 spectrometer operating at an ionization potential of 70 eV. IR spectra measured on a Shimadzu IR-460 spectrometer. The morphology of nanoparticles of KF/Clinoptilolite was characterized by scanning electron microscopy (SEM) using a Holland Philips XL30 microscope. Crystalline structure of KF/CP (NPs) was characterized by X-ray diffraction (XRD) analysis at room temperature using a Holland Philips Xpert X-ray powder diffractometer, with $CuK_{\square}$ radiation (λ=0.15406 nm), with 2θ ranging from 20 to 80°. The average crystallite size was calculated using Scherrer's formula; D= 0.9λ/β cosθ, where D is the diameter of the nanoparticles, λ (CuK_{α}) =1.5406 Å and β is the full-width at half-maximum of the diffraction lines. ^{1}H, and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1 and 125.8 MHz, respectively. ^{1}H and ^{13}C spectra obtained for solutions in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard.

Preparation of Nano KF/Clinoptilolite:

Nano sized natural Clinoptilolite zeolite was prepared by grinding in a planetary ball mill using a zirconia vial set in dry conditions with a time period of about 20 min. Then, the KF/CP (NPs) catalyst was prepared according to previously reported procedure [28-29].

General procedure for the preparation of 5a-5e:

A mixture of aniline (2 mmol) **1** and diethyl oxalate **2** (2 mmol) and activated acetylenic compound **3** (2 mmol) in water (5 mL) was added to a stirred mixture of the amine **4** (2 mmol) and KF/CP (NPs) (10% w/w, 0.38 g) in water (5 mL) at room temperature. After completion of the reaction [8 h; TLC (EtOAc/hexane 2:1)], water (15 ml) was poured into the mixture of reaction. The solid phase was filtered, washed with diethyl ether. The solvent was evaporated, and the residue was purified by column chromatography [silica gel (230–240 mesh; Merck), hexane/EtOAc 4:1)].

Spectral data of products

Trimethyl 2,3,4-quinoline tricarboxylate (5a):

Orange oil, yield 90%. IR (KBr) (γ_{max}/cm^{-1}): 1697, 1614, 1569, 1532, 1488, 1189 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.89 (3H, s, MeO), 3.98 (6 H, s, MeO), 7.63 (1 H, t, ^{3}J = 7.2 Hz, CH), 7.77 (1 H, t, ^{3}J = 7.2 Hz, CH), 7.95 (1 H, d, ^{3}J = 8.4 Hz, CH), 8.16 (1 H, d, ^{3}J = 8.5 Hz, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.9 (MeO), 53.0 (MeO), 53.2 (MeO), 122.8 (C), 123.5 (C), 125.4 (CH), 129.8 (CH), 130.2 (CH), 131.9 (CH), 139.8 (C), 147.4 (C), 147.7 (C), 165.5 (C=O), 165.6 (C=O), 165.7 (C=O). MS (EI, 70 eV): m/z (%) = 303 (M+, 10), 273 (88), 258 (49), 244 (65), 187 (82), 129 (100). Anal.Calcd for $C_{15}H_{13}NO_6$ (303.26): C, 59.41; H, 4.32; N, 4.62. Found: C, 59.67; H, 4.24; N, 4.55.

4-Ethyl 2,3-dimethyl 2,3,4-quinolinetricarboxylate (5b):

Yellow Oil, yield 91%. IR (KBr) (γ_{max}/cm^{-1}): 1722, 1718, 1706, 1533, 1445, 1384 cm^{-1}. ^{1}H NMR(500 MHz, $CDCl_3$): δ = 1.40 (3 H, t, ^{3}J = 7.3, Me), 3.98 (3H, s, MeO), 4.03 (3H, s, MeO), 4.51 (2H, q, ^{3}J = 7.3, OCH_2), 7.70 (1H, t, ^{3}J = 7.4 CH), 7.84 (1 H, t, ^{3}J = 7.4, CH), 8.05 (1 H, d, ^{3}J =7.5, CH), 8.24 (1 H, d, ^{3}J=7.4, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ=13.9 (Me), 52.8 (MeO), 53.2 (MeO), 62.6 (CH_2O), 122.3 (C), 123.5 (C), 125.4 (CH), 129.7 (CH), 131.9 (CH), 133.0 (CH), 140.1 (C), 147.5 (C), 147.7(C), 165.1 (C=O), 165.3 (C=O), 165.7 (C=O). EI-MS: 317 (M^{+}, 15), 129 (100). Anal.Calcd for $C_{16}H_{15}NO_6$ (317.29): C, 60.57; H, 4.76; N, 4.41; found: C, 60.23; H, 5.12; N, 4.33%.

2,3-Diethyl4-methyl 2,3,4-quinolinetricarboxylate (5c):

Yellow Oil, yield 90%. IR (KBr) (γ_{max}/cm^{-1}): 1744, 1707, 1676, 1599, 1487 cm^{-1}. ^{1}H NMR (500 MHz,

$CDCl_3$): δ = 1.38 (3 H, t, ^3J = 7.2, Me), 1.43 (3 H, t, ^3J = 7.2, Me), 4.04 (3H, s, MeO), 4.41 (2 H, q, ^3J = 7.2, CH_2O), 4.50 (2 H, q, ^3J = 7.2, CH_2O), 7.70 (1 H, t, ^3J =7.6, CH), 7.85 (1H, t, ^3J =7.6, CH), 7.99 (1 H, d, ^3J=7.8, CH), 8.25 (1 H, d, ^3J=7.8, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ=13.8 (Me), 13.9 (Me), 53.0 (MeO), 62.3 (CH_2O), 62.4 (CH_2O), 122.5 (C), 123.7 (C), 125.4 (CH), 129.7 (CH), 130.3 (CH), 131.7 (CH), 140.2 (C), 147.5 (C), 149.7 (C), 165.1 (C=O), 165.3 (C=O), 165.9 (C=O). EI-MS: 331 (M^+, 23), 129 (100). Anal.Calcd for $C_{17}H_{17}NO_6$ (331.32): C, 61.63; H, 5.17; N, 4.23; found: C, 61.54; H, 5.08; N, 4.05%.

2,3-Dimethyl 4-propyl2,3,4-quinoline tricarboxylate (5d);

Yellow Oil, yield 92%. IR (KBr) (γ_{max}/cm^{-1}): 1740, 1583, 1490, 1407, 1366, 1294 cm^{-1}. ^{1}H NMR(500 MHz, $CDCl_3$): δ = 0.90 (3 H, t, ^3J = 7.3, Me), 1.70 (2 H, m, CH_2), 3.86 (3 H, s, MeO), 3.95 (3 H, s, MeO), 4.32 (2 H, t, ^3J = 7.3, CH_2O), 7.59 (1 H, t, ^3J = 8.0, CH), 7.73 (1 H, t, ^3J = 8.2, CH), 7.94 (1 H, d, ^3J = 8.5, CH), 8.12 (1 H, d,^3J = 8.5, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ=10.2 (Me), 21.6 (CH_2), 52.9 (MeO), 53.1 (MeO), 68.2 (CH_2O), 122.7 (C), 123.6 (C), 125.4 (CH), 129.8 (CH), 130.3 (CH), 131.9 (CH), 140.3 (C), 147.4 (C), 147.8 (C), 165.2 (C=O), 165.6 (C=O), 165.7 (C=O). EI-MS: 331 (M+, 18), 129 (100). Anal.Calcd for $C_{17}H_{17}NO_6$ (331.32): C, 61.63; H, 5.17; N, 4.23; found: C, 61.33; H, 5.12; N, 4.12%.

Triethyl 2,3,4-quinoline tricarboxylate (5e);

Yellow Oil, yield 93%. IR (KBr) (γ_{max}/cm^{-1}): 1727, 1660, 1607, 1567, 1477, 1351 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (3 H, t, ^3J = 7.2, Me), 1.34 (3 H, t, ^3J = 7.2, Me), 1.37 (3 H, t, ^3J = 7.2, Me), 4.35 (2 H, q, ^3J = 7.2, CH_2O), 4.42 (2 H, q, ^3J = 7.2, CH_2O), 4.46 (2 H, q, ^{3}J = 7.2, CH_2O), 7.63 (1 H, t, ^3J = 7.8, CH), 7.78 (1 H, t, ^3J = 7.8, CH), 7.95 (1 H, d, ^3J = 8.4, CH), 8.15 (1 H, d, ^3J = 8.2, CH). ^{13}C NMR(125 MHz, $CDCl_3$):δ= 13.8 (Me), 13.9 (Me), 14.0 (Me), 62.3 (CH_2O), 62.4 (CH_2O), 62.5 (CH_2O), 123.5 (C), 124.3 (C), 125.4 (CH), 129.7 (CH), 130.2 (CH), 131.9 (CH), 147.4 (C), 148.6 (C), 150.5 (C), 165.1 (C=O), 165.3 (C=O), 165.4 (C=O). EI-MS: 345 (M+, 25), 129 (100). Anal.Calcd for $C_{18}H_{19}NO_6$ (345.35): C, 62.60; H, 5.55; N, 4.06; found: C, 61.98; H, 5.45; N, 4.04%.

Determination of antioxidant activity using radical trapping test by (DPPH):

The radical trapping experiment by DPPH was employed for valuation of antioxidant ability for some generated compounds such as **5a-5d** as indicated by Shimada et al [44] procedure. For achieving to this purpose, different concentrations (200–1000 ppm) of compounds **5a-5d** were added to DPPH methanolic solution (1 mmol/L) with an equal volume. The mixture was mixed for 30 min at ambient temperature and after this time putted in a gloomy space and the mixture absorbance was recorded at 517 nm. The compounds **5a-5d** was exchanged with methanol (3 mL) in the standard type. The standard antioxidants in this experiment are Butylated hydroxytoluene (BHT) and 2-tertbutylhydroquinone (TBHQ). By using Yen and Duh [45] formula, the percentage of inhibition for the radical of DPPH was measured.

Evaluation of reducing ability for synthesized compounds:

The ability of reducing iron (III) was evaluated for the compounds **5a-5d** using Yildirim et al. method. [46] For this purpose, the samples (1 mL), potassium ferricyanide ($K_3Fe(CN)_6$; 2.5 mL, 10g/L) and buffer of phosphate (2.5 mL, 0.2 mol/L, pH 6.6) were combined together and sustained for 30 min at 50 ^{o}C. Then, to the previous solution was added trichloroacetic acid (2.5 mL, 10% w/v) and centrifuged for 10 min. In the end, the supernatant (2.5 mL), distilled water (2.5 mL) and $FeCl_3$ (0.5 mL, 1 g/L) mixed together and at 700 nm the samples absorbance was measured. The higher reducing power was attributed to higher absorbance. For accuracy of calculating, each calculation was performed in three times. The SPSS software version 18.0 by running one way study of variance (ANOVA) was used for data analyzing of compounds that confirmed variation of samples and control. Separation mean with the importance quantity of 95% ($P < 0.05$) was done by Duncan multiple range experiments.

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