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One-pot multicomponent reactions of isatins: Green synthesis of cyclopentatriazine derivatives by employing $Ag/Fe_3O_4/SiO_2$@MWCNTs MNCs as an efficient catalyst

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ABSTRACT

Using a multicomponent reaction of isatin or benzaldehydes, malononitrile, ethyl 2,4-dioxo-4-arylbutanoate, ammonium acetate, and hydrazonoyl chlorides in aqueous media at room temperature in the presence of $Ag/Fe_3O_4/SiO_2$@MWCNTs MNCs, this research produced cyclopentatriazines as new derivatives with a high yield. Another investigation in this work examines the antioxidant properties of the produced cyclopentatriazine. The applied method for producing cyclopentatriazine demonstrated a number of desirable traits, including quick reactions, high yields of the final product, and straightforward separation of the product and catalyst from the reaction mixture.

1. Introduction

Heterocyclic organic compounds are among the most significant families molecules because they are used in medicinal chemistry and have a wide range of biological functions [1-12]. As a result of the significance of these compounds; numerous methods for the synthesis of heterocyclic compounds have been identified. Multicomponent reactions (MCRs) are a useful technique for producing physiologically active heterocyclic chemical molecules [13, 14]. MCRs are crucial because they offer advantages like atom efficiency and high yields for the synthesis of heterocyclic compounds when compared to other methods [15-17]. The abundance of spirocyclic molecules in both natural and synthetic substances, as well as the fact that many of them exhibit pharmacological and biological action, makes them of great interest to synthetic and medicinal chemists.[18] Additionally, due to their rigid structure, spiro-molecules are ideal for medicinal chemistry and can be utilized as ligands or catalyst forms in the production of organic compounds [19]. We must keep in mind that the many of multicomponent reactions wasn't performed without catalyst or have low yield without catalyst. Due to high surface area, chemical and electrochemical permanence, and contributions to technology and applied research, nanostructures play an essential role among catalyst [20]. Due to the huge surface and high adsorption capacity of Multi-walled

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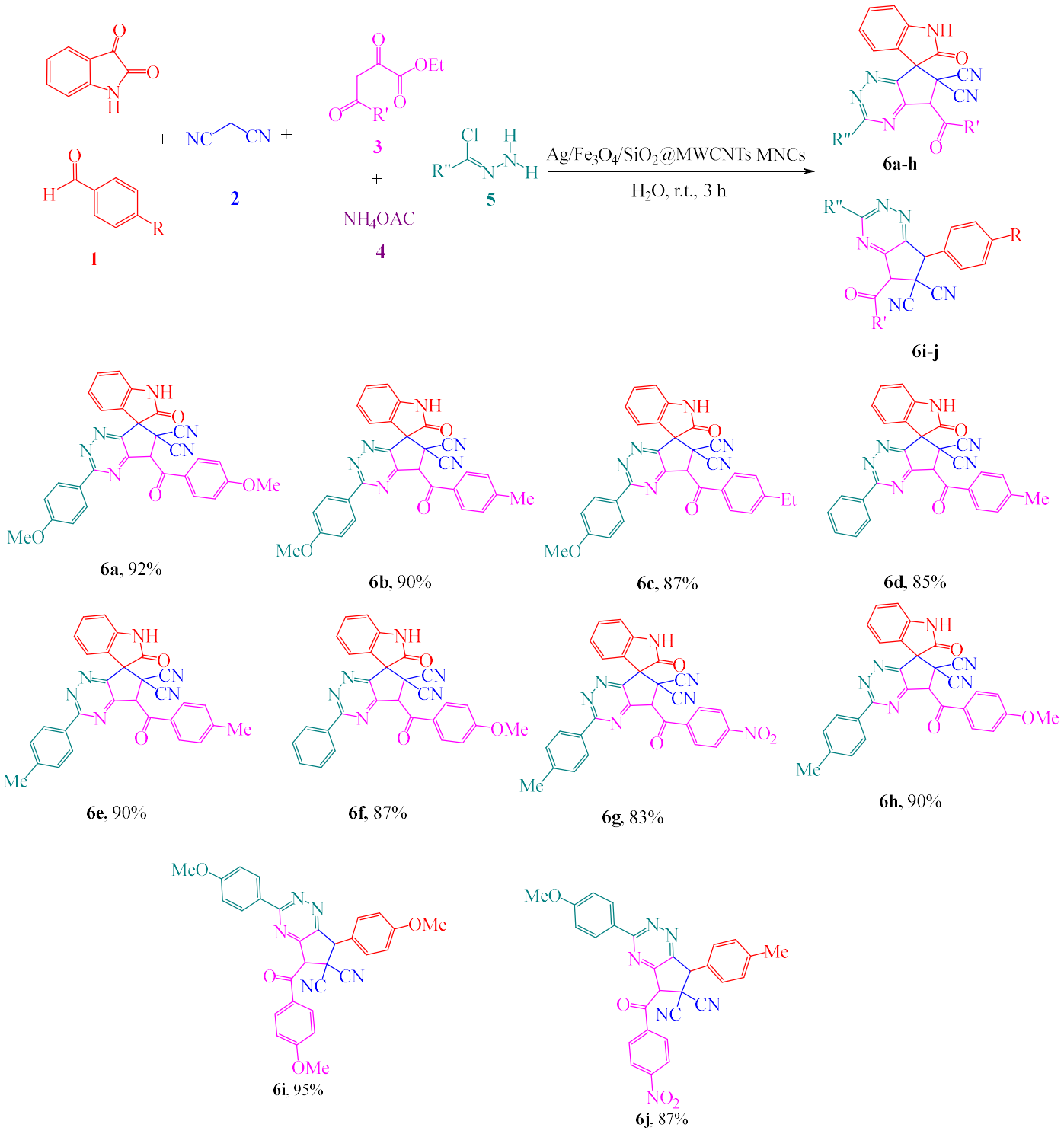

Scheme 1. Synthesis of new cyclopentatriazine catalyzed by $Ag/Fe_3O_4/SiO_2$@MWCNTs MNCs.

2. Experimental

General

Material and methods. Without additional purification, Fluka and Merck Company provided all the starting materials, reagents, and solvents required for the synthesis of cyclopentatriazine in this study. $Ag/Fe_3O_4/SiO_2$@MWCNTs MNCs were synthesized and the catalyst structure was confirmed using spectroscopy analysis, including XRD, SEM, EDX, and VSM. Melting points were measured on an Electrothermal 9100 apparatus. To analyze synthetic cyclopentatriazine using FT-IR (KBr medium), a Shimadzu IR-460 spectrometer was used. The Bruker DRX-500 AVANCE spectrometer was used to provide ^{1}H-NMR and ^{13}C-NMR, which is another method for verifying the structure of synthesized compounds. $CDCl_3$ and TMS were used as the solvent and internal standard, respectively, in the 500 MHz NMR measurements. MAT 8430 spectrometer made by Finnigan having an ionization potential of 70 eV For the purpose of providing mass spectra, of synthesized compounds. To perform elemental analysis, we applied Heraeus CHN–O-Rapid analyzer.

Generation of $Ag/Fe_3O_4/SiO_2$@MWCNTs

$AgNO_3$ (1.5 g) was added to the mixture of $FeCl_3.6H_2O$ (1.5 g) and tetraethyl orthosilicate (3 mL) which had been dissolved in the *Petasites hybridus rhizome* water extract (5 mL) after 30 min and the new mixture was heated to 100 °C in a round bottom flask and stirred for 1 h. Once the reaction was finished, the temperature of the reaction was lowered to room temperature. The produced precipitate ($Ag/Fe_3O_4/SiO_2$) was then centrifuged for around 10 minutes at 7000 rpm after cooling to eliminate the undesirable organic molecules. The produced $Ag/Fe_3O_4/SiO_2$ (0.1 g) and the MWCNTs (0.1 g) were added to 100 mL of water extract from *Petasites hybridus rhizome* and mixed at 150 °C for 1 hour to create $Ag/Fe_3O_4/SiO_2$@MWCNTs MNCs. After using an external magnet to separation of the $Ag/Fe_3O_4/SiO_2$@MWCNTs magnetic nanocomposite which required cooling to room temperature and could be washed with a 50:50 solution of water and ethanol. After washing the catalyst, it was separated by using an external magnet and dried for 24 hours and then calcined it for 45 minutes at 300 °C.

Reusability of $Ag/Fe_3O_4/SiO_2$@MWCNTs

For evolution of reusability of synthesized catalyst, in model reaction (synthesis of compound 6a) after completing the reactions, the catalyst was separated by external magnet from mixture of reaction and washed with a 50:50 solution of water and ethanol and used in the model reaction again. This work was performed many times until the yields of model reaction was decreased (Table 3).

Preparation process of cyclopentatriazine 6a–j

In the presence of $Ag/Fe_3O_4/SiO_2$@MWCNTs MNCs (0.01 g) in water (5 mL) as the solvent, the ethyl 2,4-dioxo-4-arylbutanoate **3** (2 mmol) and the ammonium acetate **4** (2 mmol) were combined and stirred for 30 min at room temperature. Isatin **1** (2 mmol) and malononitrile **2** (2 mmol) were added to water as the solvent in a different pot along with $Ag/Fe_3O_4/SiO_2$@MWCNTs MNCs (0.01 g) and mixed for 30 minutes at room temperature. This mixture was added to the earlier one, and the two were stirred together for 45 minutes. After this, the hydrazonoyl chloride 5 (2 mmol) was added, and the finished mixture was agitated for 1 hour. After three hours of TLC monitoring, the reaction was complete. At this point, the catalyst was separated by external magnet and solid residue was washed by EtOH and Et_2O to prepare purified cyclopentatriazine **6**.

5-(4-methoxybenzoyl)-2'-oxo-(4-methoxyphenyl)-spiro [cyclopenta [e][1,2,4]triazine-7,3'- indoline]-6,6(5H)-dicarbonitrile **(6a):** Yellow powder, m.p. 139-141 °C, Yield: 95%. IR (KBr) (ν_{max}/cm^{-1}): 2195, 1728, 1725, 1697, 1485, 1378 and 1292 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 3.83 (6 H, s, 2 MeO), 5.03 (1 H, s, CH), 6.96-7.28 (5 H, m, 5 CH), 7.30-7.44 (2 H, m, 2 CH), 7.85-8.17 (5 H, m, 5 CH), 10.23 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 195.17, 174.11, 165.12, 163.05, 161.88, 155.06, 148.49, 141.47, 130.50, 129.74, 129.21, 129.02, 127.75, 126.01, 125.87, 122.35, 114.05, 113.70, 111.30, 110.53, 62.62, 61.30, 55.34, 55.33, 52.26 ppm. MS, *m/z* (%): 528 (M^+, 15), 147 (48), 31 (100). Anal. Calcd for $C_{30}H_{20}N_6O_4$ (528.53): C, 68.18; H, 3.81; N, 15.90; Found: C, 68.26; H, 3.96; N, 15.96 %.

3-(4-methoxyphenyl)-5-(4-methylbenzoyl)-2'-oxospiro[cyclopenta[e][1,2,4]triazine-7,3'-indoline]-6,6(5H)-dicarbonitrile **(6b):** Yellow powder, m.p. 143-145 °C, Yield: 0.96 g (95%). IR (KBr) (ν_{max}/cm^{-1}): 2232, 1729, 1728, 1697, 1589, 1487, 1358 and 1296 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 2.38 (3 H, s, Me), 3.83 (3 H, s, OMe), 5.81 (1 H, s, CH), 6.94-8.17 (12 H, m, 12 CH), 10.42 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): 195.36, 174.11, 165.12, 161.88, 155.06, 148.49, 143.90, 141.47, 131.14, 129.74,

129.53, 129.21, 129.14, 129.02, 126.01, 125.87, 122.35, 114.05, 111.30, 110.53, 62.62, 61.27, 55.33, 52.27, 21.34 ppm. MS, *m/z* (%): 512 (M^+, 10), 147 (48), 31 (100). Anal. Calcd for $C_{30}H_{20}N_6O_3$ (512.53): C, 70.30; H, 3.93; N, 16.40; Found: C, 70.42; H, 4.08; N, 16.53 %.

5-(4-ethylbenzoyl)-3-(4-methoxyphenyl)-2'-oxospiro[cyclopenta[e][1,2,4]triazine-7,3'-indoline]-6,6(5H)-dicarbonitrile **(6c):** Pale **y**ellow powder, m.p. 153-154 °C, Yield: 92%. IR (KBr) (ν_{max}/cm^{-1}): 2175, 1732, 1727, 1996, 1586, 1485, 1368 and 1295 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (3 H, t, $^3J_{HH}$ = 7.3 Hz, Me), 2.70 (2 H, q, $^3J_{HH}$ = 7.3 Hz, CH_2), 3.83 (3 H, s, OMe), 5.81 (1 H, s, CH), 6.94-8.16 (12 H, m, 12 CH), 10.37 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 195.24, 174.11, 165.12, 161.88, 155.06, 148.49, 146.64, 141.47, 131.93, 129.74, 129.21, 129.09, 129.02, 128.28, 126.01, 125.87, 122.35, 114.05, 111.30, 110.53, 62.62, 61.27, 55.33, 52.27, 28.61, 15.30 ppm. MS, *m/z* (%): 526 (M^+, 10), 147 (48), 31 (100). Anal. Calcd for $C_{31}H_{22}N_6O_3$ (526.56): C, 70.71; H, 4.21; N, 15.96; Found: C, 70.71; H, 4.21; N, 15.96 %.

5-(4-methylbenzoyl)-2'-oxo-3-phenylspiro[cyclopenta[e][1,2,4]triazine-7,3'-indoline]-6,6(5H)-dicarbonitrile **(6d):** Yellow powder, m.p. 163-165 °C, Yield: 85%. IR (KBr) (ν_{max}/cm^{-1}): 2195, 1734, 1728, 1698, 1595, 1485, 1376 and 1293 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 2.38 (3 H, s, Me), 5.82 (1 H, s, CH), 6.94-8.19 (13 H, m, 13 CH), 10.48 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 195.36, 174.11, 165.21, 155.06, 148.49, 143.90, 141.47, 134.24, 131.14, 131.10, 129.53, 129.21, 129.14, 128.89, 128.77, 126.01, 125.87, 122.35, 111.30, 110.53, 62.62, 61.27, 52.27, 21.34 ppm. MS, *m/z* (%): 482 (M^+, 10), 147 (48), 31 (100). Anal. Calcd for $C_{29}H_{18}N_6O_2$ (482.50): C, 72.19; H, 3.76; N, 17.42; Found: C, 72.26; H, 3.85; N, 17.56%.

5-(4-methylbenzoyl)-2'-oxo-3-(p-tolyl)-spiro[cyclopenta[e][1,2,4]triazine-7,3'-indoline]-6,6(5H)-dicarbonitrile **(6e):** Yellow powder, m.p. 163-165 °C, Yield: 90%. IR (KBr) (ν_{max}/cm^{-1}): 2198, 1732, 1725, 1695, 1588, 1498, 1378 and 1298 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 2.38 (3 H, s, Me), 2.39 (3 H, s, Me), 5.81 (1 H, s, CH), 6.94-7.99 (12 H, m, 12 CH), 7.02 (2 H, d, $^3J_{HH}$ = 7.6 Hz, 2 CH), 7.18-7.24 (4 H, m, 4 CH), 7.36 (2 H, d, ^3J = 7.8 Hz, 2 CH), 7.42 (2 H, d, ^3J = 7.6 Hz, 2 CH), 10.52 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 195.36, 174.11, 165.01, 155.06, 148.49, 143.90, 141.47, 138.96, 132.48, 131.14, 129.53, 129.21, 129.14, 128.98, 128.47, 126.01, 125.87, 122.35, 111.30, 110.53, 62.62, 61.27, 52.27, 21.34, 21.23 ppm. MS, m/z (%): 496 (M^+, 10), 147 (48), 31 (100). Anal. Calcd for $C_{30}H_{20}N_6O_2$ (496.53): C, 72.57; H, 4.06; N, 16.93; Found: C, 72.72; H, 4.24; N, 17.08 %.

5-(4-methoxybenzoyl)-2'-oxo-3-phenylspiro[cyclopenta[e][1,2,4]triazine-7,3'-indoline]-6,6(5H)-dicarbonitrile **(6f):** Yellow powder, m.p. 171-173 °C, Yield: 87%. IR (KBr) (ν_{max}/cm^{-1}): 2237, 1734, 1726, 1697, 1597, 1488, 1387 and 1292 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm: 3.85 (3 H, s, MeO), 6.57 (1 H, s, CH), 6.92 (2 H, d, ^3J = 7.8 Hz, 2 CH), 7.12-7.16 (4 H, m, 4 CH), 7.23-7.28 (3 H, m, 3 CH), 7.34 (2 H, d, ^3J = 7.8 Hz, 2 CH), 7.37-7.42 (2 H, m, 2 CH), 10.36 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 195.17, 174.11, 165.21, 163.05, 155.06, 148.49, 141.47, 134.24, 131.10, 130.50, 129.21, 128.89, 128.77, 127.75, 126.01, 125.87, 122.35, 113.70, 111.30, 110.53, 62.62, 61.30, 55.33, 52.26 ppm. MS, *m/z* (%): 498 (M^+, 10), 147 (48), 31 (100). Anal. Calcd for $C_{29}H_{18}N_6O_3$ (498.50): C, 69.87; H, 3.64; N, 16.86; Found: C, 69.97; H, 3.83; N, 16.98%.

5-(4-nitrobenzoyl)-2'-oxo-3-(p-tolyl)spiro[cyclopenta[e][1,2,4]triazine-7,3'-indoline]-6,6(5H)-dicarbonitrile **(6g):** Yellow powder, m.p. 187-189 °C, Yield: 83%. IR (KBr) (ν_{max}/cm^{-1}): 2218, 1729, 1726, 1694, 1584, 1469 and 1296 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm: 2.47 (3 H, s, Me), 6.58 (1 H, s, CH), 6.92 (2 H, d, ^3J = 7.7 Hz, 2 CH), 7.06-7.11 (4 H, m, 4 CH), 7.26 (2 H, d, ^3J = 7.7 Hz, 2 CH), 7.34-7.37 (2 H, m, 2 CH), 8.06 (2 H, d, ^3J = 7.7 Hz, 2 CH), 10.42 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 194.76, 174.11, 165.01, 155.06, 150.01, 148.49, 141.47, 138.96, 138.35, 132.48, 129.98, 129.21, 128.98, 128.47, 126.01, 125.87, 123.99, 122.35, 111.30, 110.53, 62.62, 61.28, 52.27, 21.23 ppm. MS, *m/z* (%): 527 (M^+, 10), 147 (56), 31 (100). Anal. Calcd for $C_{29}H_{17}N_7O_4$ (527.50): C, 66.03; H, 3.25; N, 18.59; Found: C, 66.18; H, 3.38; N, 18.72 %

5-(4-methoxybenzoyl)-2'-oxo-3-(p-tolyl)spiro[cyclopenta [e][1,2,4]triazine-7,3'-indoline]-6,6(5H)-dicarbonitrile **(6h):** Pale **y**ellow powder, m.p. 149-151 °C, Yield: 90%. IR (KBr) (ν_{max}/cm^{-1}): 2278, 1726, 1698, 1578, 1364 and 1289 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 2.37 (3 H, s, Me), 3.87 (3 H, s, OMe), 6.62 (1 H, s, CH), 6.93 (2 H, d, ^3J = 7.7 Hz, 2 CH), 7.14 (2 H, d, ^3J = 7.7 Hz, 2 CH), 7.22-7.26 (2 H, m, 2 CH), 7.36 (2 H, m, 2 CH), 7.43 (2 H, d, ^3J = 7.8 Hz, 2 CH), 7.56 (2 H, d, ^3J = 7.8 Hz, 2 CH), 10.56 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 195.17, 174.11, 165.01, 163.05, 155.06, 148.49, 141.47, 138.96, 132.48, 130.50, 129.21, 128.98, 128.47, 127.75, 126.01, 125.87, 122.35, 113.70, 111.30, 110.53, 62.62,

61.30, 55.33, 52.26, 21.23 ppm. MS, *m/z* (%): 512 (M^+, 15), 147 (48), 31 (100). Anal. Calcd for $C_{30}H_{20}N_6O_3$ (512.53): C, 70.30; H, 3.93; N, 16.40; Found: C, 70.43; H, 4.07; N, 16.54%.

5-(4-methoxybenzoyl)-3,7-bis(4-methoxyphenyl)-5,7-dihydro-6H-cyclopenta[e][1,2,4]triazine-6,6-dicarbonitrile **(6i):** Yellow powder, m.p. 168-170 °C, Yield: 95%. IR (KBr) (ν_{max}/cm^{-1}): 2195, 1728, 1725, 1697, 1485, 1378 and 1295 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 3.75 (3 H, s, Me), 3.78 (3 H, s, Me), 3.83 (3 H, s, Me), 6.24 (1 H, s, CH), 6.98 (2 H, d, ^3J = 7.7 Hz, 2 CH), 7.24-7.36 (4 H, m, 4 CH), 7.45-7.56 (4 H, m, 4 CH), 7.68 (2 H, d, ^3J = 7.7 Hz, 2 CH), 10.56 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 192.74, 163.05, 161.88, 161.70, 159.08, 158.26, 157.83, 130.50, 129.74, 129.58, 129.02, 128.45, 127.44, 114.05, 113.88, 113.70, 112.15, 62.75, 57.78, 55.35, 55.34, 55.33, 52.37 ppm. MS, *m/z* (%): 517 (M^+, 10), 147 (48), 31 (100). Anal. Calcd for $C_{30}H_{23}N_5O_4$ (517.54): C, 69.62; H, 4.48; N, 13.53; Found: C, 69.78; H, 4.56; N, 13.64%.

3-(4-methoxyphenyl)-5-(4-nitrobenzoyl)-7-(p-tolyl)-5,7-dihydro-6H-cyclopenta[e][1,2,4]triazine-6,6-dicarbonitrile **(6j):** Yellow powder, m.p. 171-173 °C, Yield: (85%). IR (KBr) (ν_{max}/cm^{-1}): 2196, 1729, 1725, 1697, 1589, 1487, 1358 and 1296 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* ppm: 2.34 (3 H, s, Me), 3.83 (3 H, s, MeO), 6.54 (1 H, s, CH), 7.16 (2 H, d, ^3J = 7.7 Hz, 2 CH), 7.18-7.34 (6 H, m, 6 CH), 7.42-8.12 (4 H, m, 4 CH), 10.63 (1 H, s, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): 192.42, 161.88, 161.70, 158.26, 157.43, 150.01, 139.12, 137.63, 130.45, 130.09, 129.74, 129.52, 129.02, 128.44, 123.99, 114.05, 112.15, 62.93, 57.55, 55.33, 52.33, 21.06 ppm. MS, *m/z* (%): 516 (M^+, 10), 147 (48), 31 (100). Anal. Calcd for $C_{29}H_{20}N_6O_4$ (516.52): C, 67.44; H, 3.90; N, 16.27; Found: C, 67.56; H, 4.06; N, 16.36%.

Evaluation of antioxidant property *via* DPPH

As noted above, Shimada et al. methods were used to evaluate the antioxidant properties of various produced cyclopentatriazine **6a-6d**.[42] The concentration of cyclopentatriazine **6a–6d** was chosen to be between 200 and 1000 ppm in accordance with the Shimada method, and an equal volume of methanolic DPPH solution (1 mmol/L) was added. After the new combination had been blended at room temperature for 30 minutes, it was placed in a dark area where its absorbance had reached 517 nm. We employed methanol (3mL) as a substitute for synthetic chemicals when comparing the antioxidant activity of the cyclopentatriazine **6a–6d**, BHT and TBHQ. Using the Yen and Duh [43] equation, the inhibition percentage of the DPPH radical trapping experiment was calculated.

Evaluating FRAP process of cyclopentatriazine antioxidant activity

The FRAP process, developed by Yildirim et al., examines the quantities of iron (III) reduction by produced cyclopentatriazine **6a–6d**. This is another way to examine the cyclopentatriazine' antioxidant properties.[44] According to the method employed by Yildirim et al., the cyclopentatriazine solution (1 mL), ferricyanide solution (2.6 mL), and buffer of phosphate (2.6 mL) were utilized in this experiment to assess antioxidant activity. The temperature of the mixture was kept at 55 oC for 35 minutes after the addition of Trichloroacetic acid (2.5 mL), and the new mixture was agitated for 10 minutes. At 700 nm, the mixture of $FeCl_3$ (0.6 mL) and supernatant (2.5 mL) in aqueous medium (2.6 mL) was measured to have an absorbance. Results revealed that substances with a high capacity have a significant ability absorbance. To confirm the calculations, they were computed in three times. We ran the SPSS software version 18.0 to compute analysis of variance (ANOVA) for synthesizing cyclopentatriazine data, which endorsed samples and standard variation. For separation, we also applied Duncan multiple range tests with 95% ($P < 0.05$).

3. Result and discussions

In the present study, five component reactions of isatin or benzaldehydes **1**, malononitrile **2**, ethyl 2,4-dioxo-4-arylbutanoate **3**, ammonium acetate **4**, and hydrazonoyl chloride **5**, in the vicinity of $Ag/Fe_3O_4/SiO_2$@MWCNTs MNCs in aqueous media at room temperature, were used to efficiently produce the new cyclopentatriazine **6**. The catalyst was prepared by using *Petasites hybridus* rhizome water extract.

Petasites hybridus rhizome water extract was used in the synthesis of catalyst and was mentioned in the experimental section in the procedure for synthesis of catalyst. The *Petasites hybridus* rhizome water extract metabolites such as Flavonoids, terpenoids, polyphenols, alkaloids, phenolic acids, and proteins play as reducing agent. It should be mentioned that the catalyst could be synthesized with water but yields of reaction are lower relative to using plants. We employed SEM, XRD, EDX, and TEM images of produced $Ag/Fe_3O_4/SiO_2$@MWCNTs MNCs to

confirm the nanoparticle's structure. In the study of nanomaterials, field emission scanning electron microscopy (FESEM) is a secondary electron detection method used in conjunction with a field emission source to produce high-resolution surface imaging. In this process, a strong electric field causes the release of electrons from a conductor's surface. Figure 1 depicts the surface morphology of $Ag/Fe_3O_4/SiO_2$@MWCNTs as determined by the FESEM approach.

The surface morphological growth of MWCNT on $Ag/Fe_3O_4/SiO_2$ is visible in the SEM picture of the $Ag/Fe_3O_4/SiO_2$@MWCNTs (Figure 1). Due to the magnetic characteristics of the $Ag/Fe_3O_4/SiO_2$ the highly agglomerated nature of the nanoparticles was observed.

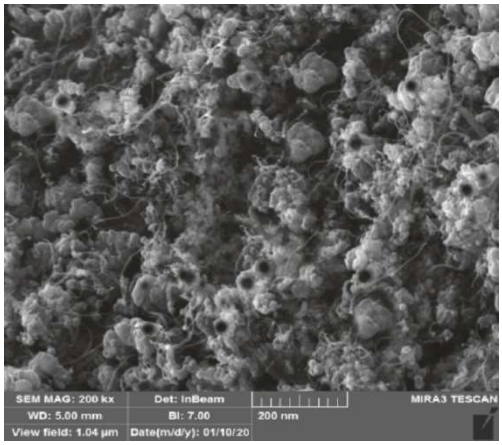

Fig. 1. SEM image of $Ag/Fe_3O_4/SiO_2$@MWCNTs

Figure 2 displays the XRD analysis of the $Ag/Fe_3O_4/SiO_2$@MWCNTs. The diffraction peaks at $2\theta = 35.0°$, 44.0°, 57.2°, and 63.0° in the XRD pattern for the synthesized $Ag/Fe_3O_4/SiO_2$@MWCNTs (Figure 2) suggest the presence of Fe_3O_4 MNPs (JCPDS No. 19-629). The face-centered cubic lattice of metallic Ag (JCPDS file no. 04-0783) has peaks at 2θ=38.3 and 46.2° planes that can suggest the presence of Ag NPs in the composites. The characteristic peak of MWNTs (JCPDS No. 41-1487) was detected as a broad crystalline peak of MWNTs between 26.0° and 43.5°. SiO_2 NPs illustrate amorphous behavior, owing to lack of any sharp diffraction peak in the range of 2θ angle according to (JCPDS No. 00-016-1157). According to the Debye-Scherrer equation, the $Ag/Fe_3O_4/SiO_2$@MWCNTs' average crystallite size was around 33.4 nm.

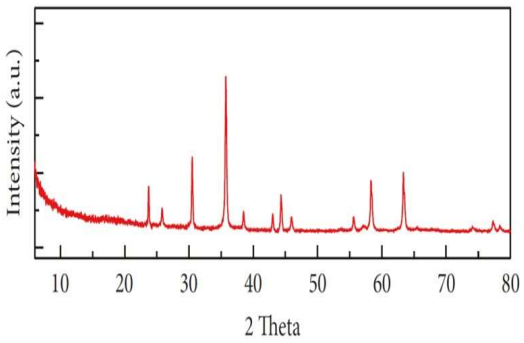

Fig. 2. XRD spectra of $Ag/Fe_3O_4/SiO_2$@MWCNTs

The samples were examined by TEM, as shown in Figure 3, to further study the morphology of the $Ag/Fe_3O_4/SiO_2$@MWCNTs.

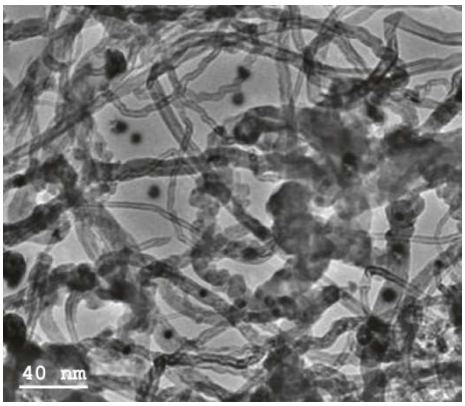

Fig. 3. TEM image of the $Ag/Fe_3O_4/SiO_2$@MWCNTs

Energy dispersive X-ray spectroscopy (EDS) was used to analyze the elemental composition of $Ag/Fe_3O_4/SiO_2$@MWCNTs which was proven to contain C, Si, Ag, Fe, and oxygen (Figure4).

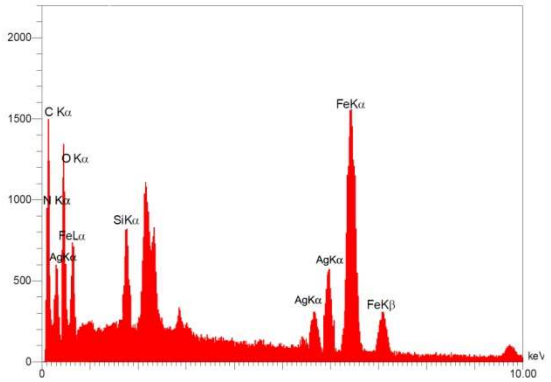

Fig. 4. EDX image of $Ag/Fe_3O_4/SiO_2$@MWCNTs

The saturation magnetization (Ms) values of the pure Fe_3O_4 MNPs and the magnetic $Ag/Fe_3O_4/ZnO$@MWCNT MNPs are shown in Figure 5. Each sample had typical superparamagnetic

characteristics with very little coercivity and remanence. In contrast to pure Fe_3O_4 NPs (52.3 emu/g), the Ms of the Ag/Fe_3O_4/ZnO@MWCNT (19.3 emu/g) has an attenuated value, as illustrated in Figure 5.

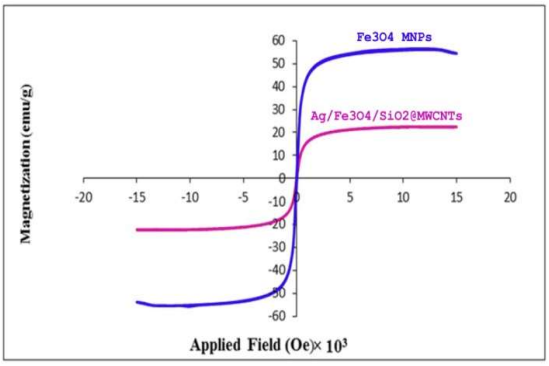

Fig. 5. VSM analysis of the Ag/Fe_3O_4/SiO_2@MWCNTs

By creating cyclopentatriazine, the Ag/Fe_3O_4/SiO_2@MWCNTs' catalytic abilities were assessed. The crucial problem in all organic reactions is acquiring the appropriate conditions to carry out the reactions. The multicomponent reaction involving isatin **1a**, malononitrile **2**, ethyl 2,4-dioxo-4-phenylbutanoate **3a**, ammonium acetate **4**, and 4-methoxyhydrazonoyl chloride **5a** was initially selected as the model reaction to accomplish this purpose (Table 1). Without a catalyst, chemical **6a** synthesis remained inactive even after 10 hours (entry 1, Table 1). The reaction temperature was raised to 100 °C in order to achieve the optimal temperature for the sample reaction, but this did not significantly affect the efficiency of dihydrospirotriazine **6a** (Entry 2, Table 1). Additionally, these reactions did not occur without a catalyst. Fe_3O_4 MNPs (0.02 g) were added as a catalyst to the combination process to support this assertion. Dihydrospirotriazine **6a** was produced after 4 hours with great efficiency (entry 4, Table 1). Therefore, a catalyst was required for the conduct of these reactions. For this reason the available catalyst (Ag NPs, SiO_2 NPs, Fe_3O_4 MNPs, MWCNTs,) was tested for model reaction. For more investigation the some new catalysis was synthesized such as Fe_3O_4/SiO_2@MWCNTs, Fe_3O_4/Ag NPs, Fe_3O_4/SiO_2 and Ag/Fe_3O_4/SiO_2@MWCNTs. These catalysts have Lewis acid and Lewis base cite and the more the number of sites increased the yields of reactions therefore Ag/Fe_3O_4/SiO_2@MWCNTs have best catalytic effect on model reaction. The selected these catalysts are based on the novelty of the catalyst otherwise, other catalysts that have Lewis acid and base properties such as ZnO, TiO_2 do this reaction. For the synthesis of dihydrospirotriazine **6a**, the catalyst Ag/Fe_3O_4/SiO_2@MWCNTs was chosen as a best nanocatalyst and improved product efficiency.

Ag/Fe_3O_4/SiO_2@MWCNT quantities were increased from 0.02-0.03g, however there was no discernible change in the reaction's efficiency. As a result, 0.02 g of Ag/Fe_3O_4/SiO_2@MWCNTs were required for the highly efficient production of dihydrospirotriazine (entry 13, Table 1), and after 3 hours, compound **6a** had a 92% yield.

Table 1. Determining the most optimal conditions for preparation of compound **6a**

Entry	Catalyst	Temp.(°C)	Catalyst (g)	Time (h)	Yield%[a]
1	none	r.t.	-	10	-
2	none	100	-	8	-
3	Fe_3O_4-MNPs	r.t.	0.015	5	53
4	Fe_3O_4-MNPs	r.t.	0.02	4	65
5	Fe_3O_4-MNPs	r.t.	0.025	4	65
6	Ag-NPs	r.t.	0.02	4	58
7	Fe_3O_4/Ag NPs	r.t.	0.02	4	78
8	SiO_2/Fe_3O_4 NPs	r.t.	0.02	3	70
9	Ag/SiO_2 NPs	r.t.	0.02	3	65
10	MWCNTs	r.t.	0.02	5	28
11	SiO_2/Fe_3O_4@MWCNTs MNPs	r.t.	0.02	4	78
12	Ag/Fe_3O_4@MWCNTs MNPs	r.t.	0.02	3	85
13	**Ag/SiO_2/Fe_3O_4@MWCNTs MNPs**	**r.t.**	**0.02**	**3**	**92**

The effects of the solvents on the production of chemical **6a** were also studied in this investigation. According to Table 2's findings, water is the most effective solvent for carrying out the reaction.

Table 2. Determining the most excellent solvent for production of **6a**

Entry	Solvent	Time (h)	Yield%[a]
1	EtOH	15	85
2	CH_2Cl_2	8	60
3	$CHCl_3$	5	68
4	**H_2O**	**3**	**92**
5	Solvent-free	8	58
6	DMF	12	30
7	toluene	12	68
8	CH_3CN	5	90

As shown in Tables 1 and 2, the optimum catalyst for producing compound **6a** at room temperature and in aqueous media is $Ag/Fe_3O_4/SiO_2$@MWCNTs (0.02 g). An crucial step in the synthesis of organic compounds is the reuse of produced catalyst. In this study, dihydrospirotriazine **6a** was produced using the manufactured nanocatalyst three times (Table 3). The final results demonstrated that the catalyst's power could be used four more times with little alteration (Table 3).

The catalyst was taken out of the mixture of reactions after each run in order to synthesis chemical **6a**, washed, and then reused. Because to the reduction in catalyst and subsequent separation after each cycle, the yield of compound **6a** dropped after three runs.

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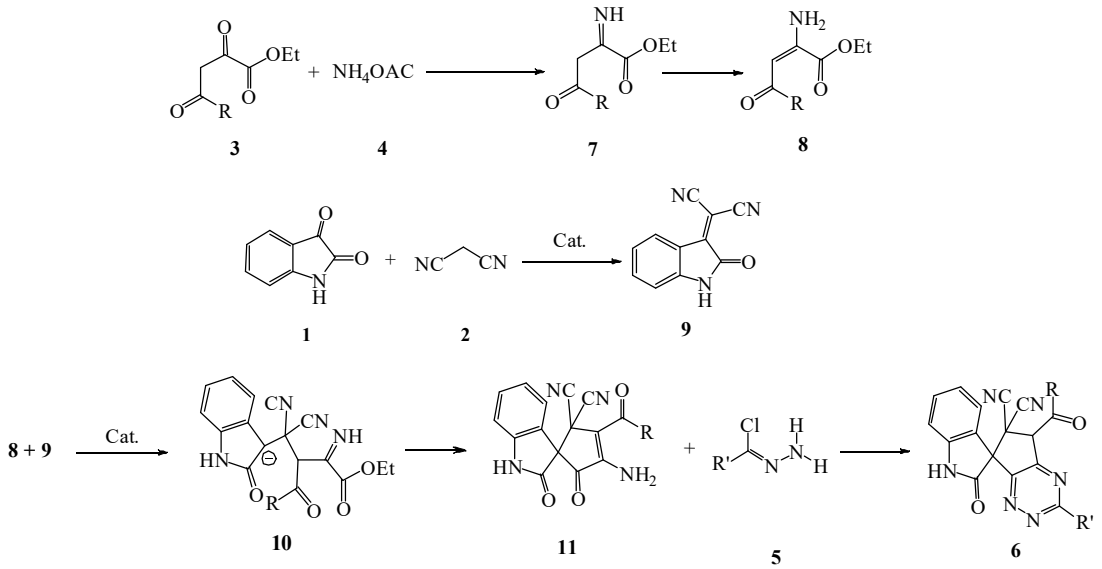
Table 3. How often catalyst is reused for synthesis of compound **6a**

Run	% Yield[a]
1	92
2	92
3	90
4	87
5	85

It should be noted that while the catalyst's form and size may not change after separation, the amount of catalyst may. The effectiveness of compound **6a** is largely affected by reducing the catalyst ratios. In order to confirm the results, the structures of the synthesized cyclopentatriazine **6** were analyzed using ^{1}H NMR, ^{13}C NMR, IR, elemental analysis, and mass spectrometry. Cyclopentatriazine **6a** showed one singlet for two methoxy protons in their ^{1}H NMR spectra at 3.83 ppm. The one singlet appeared at 5.03 ppm for CH protone and several signals for aromatic protons at 6.96-8.17 ppm. Four resonances were visible in the carbonyl moiety in the ^{13}C NMR spectra of **6a** at 195.2 and 174.1 ppm. The IR spectrum is yet another method for verifying the presence of carbonyl groups in compounds that have been produced. In Scheme 2, the following preparation method for the produced compounds **6** is suggested.



Scheme 2. Recommended mechanism for preparation of **6**

At first, enaminone **8** was produced from ethyl 2,4-dioxo-4-arylbutanoate **3** and ammonium acetate **4** at room temperature. Isatin **1** reacts with malononitrile to form intermediates **9** which then react with intermediate **8** to produce intermediates **10** that converted to intermediate **11** by intermolecular cyclization. Spiro cyclopentatriazine **6** were created via the reaction of intermediate **11** with hydrazonoyl chloride **5** by intermolecular cyclization. According to procedure for the synthesis of these compounds, the intermediate **8** and **9** weren't separated and the mixture of one pot was added to second pot and the reaction was continued. For confirming the reaction mechanism, the intermediate **8** and **9** in model reaction (synthesis of compound **6a**) was separated and combined again but yield of reaction was lower than MCRs.

Evaluating antioxidant property of prepared cyclopentatriazine by 2,2-diphenyl-1-picrylhydrazyl (DPPH)

Additionally, the goal of this inquiry was to examine the antioxidant properties of synthetic cyclopentatriazine, and DPPH was employed to accomplish this. It should be noted that we used the DPPH radical scavenging test for a variety of reasons, including determining the antioxidant activity of foods, biological structures, and synthetic chemical compounds.[44,45] This was done by removing an electron or hydrogen atom by the DPPH free radical. In the presence of a DPPH radical, the produced cyclopentatriazine lose one electron or the hydrogen atom, indicating that they exhibit antioxidant properties. The order of antioxidant activity is demonstrated by the synthesized cyclopentatriazine' percentage of DPPH free radical trapping. With the help of this investigation, we looked at the antioxidant activity of several synthetic compounds, including **6a-6d**, and compared it to that of the more commonly used antioxidants, BHT and TBHQ. The antioxidant activity of these compounds was demonstrated by their ability to absorb electrons or hydrogen from the DPPH free radical. The absorbance of DPPH is reduced by 517 nm when an electron or hydrogen atom is adsorbed. Overall, the cyclopentatriazine derivatives **6a–6d** was shown to have the following antioxidant capacity: TBHQ≈BHT>**6b**>**6a**>**6c**>**6d** (Figure 6).

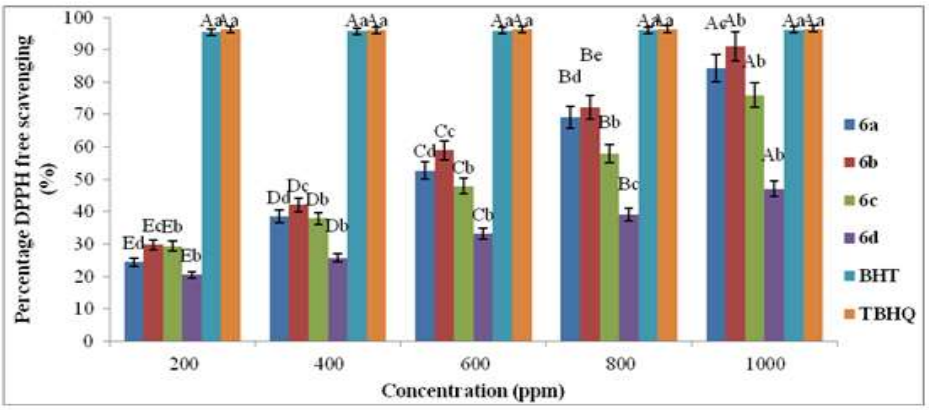


Fig. 6. Order of antioxidant activity of **6a-6d** using DPPH

Figure 6 demonstrated that there were significant variations between the concentrations of cyclopentatriazine compared to BHT and TBHQ as common antioxidants. When compared to BHT and TBHQ, compound **6b** from the tested cyclopentatriazine **6a–6d** performed well.

Assessment of cyclopentatriazine antioxidant activity using Fe^{3+} reducing

Another approach was used to verify the cyclopentatriazine **6a–6d** antioxidant ability. Cyclopentatriazine **6b** showed good effect in comparison to BHT and TBHQ in reducing ferric ions (Fe^{3+}), and levels of reducing were assessed based on reduction of Fe^{3+}/ferricyanide to the Fe^{2+}/ferrous at 700 nm. The antioxidant activity of cyclopentatriazine **6a–6d** is displayed in Figure 7 as follows:

TBHQ > BHT > **6b** > **6a** > **6c** > **6d**.

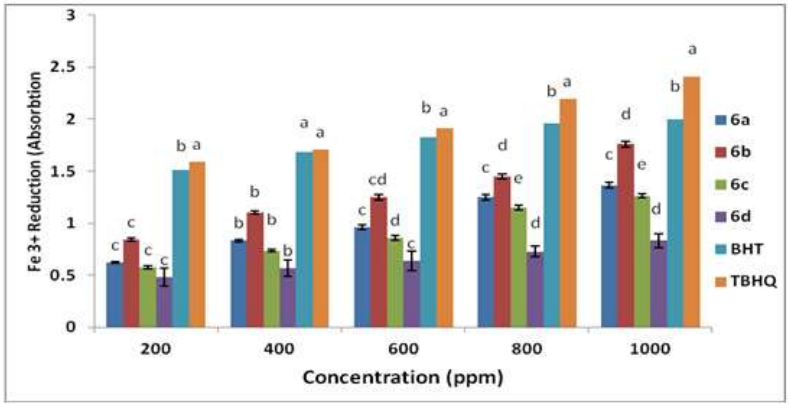


Fig. 7. Ferric ions (Fe^{3+}) decreasing antioxidant ability (FRAP) of compounds **6a-6d**

4. Conclusions

This work focused on efficient, environmentally friendly reactions that produced novel derivatives of cyclopentatriazine in aqueous media at room temperature. These reactions involved isatin or benzaldehydes, malononitrile, ethyl 2,4-dioxo-4-arylbutanoate, ammonium acetate, and hydrazonoyl chlorides. Additionally, two techniques were used to assess the antioxidant capacity of the created cyclopentatriazine **6a–6d**. The ability of produced compounds to trap DPPH radicals and reduce Fe^{+3} proved they possessed strong antioxidant properties compared to other antioxidants. According to the findings of antioxidant research, synthetic cyclopentatriazine show good biological action. As a result, this method of making cyclopentatriazine has a number of benefits, including a high rate of reaction, high yield output, green process, easy separation of the product from the reaction mixture, and simple product purification, which are the main factors in making cyclopentatriazine.

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Supplementary material

^{1}H NMR and ^{13}C NMR data of synthesized compounds are available with the article through the journal Web site.

References

[1] A. K. O. Aldulaimi, H. R. Saud, M. Ubaid, M. H. Sami, A. H. Adhab, F. Shahimi, Recent investigations in synthesis of α-hydroxycarboxylic acids by reductive carboxylation of aldehydes with CO2 (microreview) *Chem. Rev. Lett.,* 7 (2024) 148-158.10.22034/crl.2024.431476.1273

[2] (a) P. N. Kalaria, S. C. Karad, D. K. Raval, Eur. J. Med. Chem. 2018, 158, 917–936; (b)N. Desai, A. Trivedi, U. Pandit, A. Dodiya, V. K. Rao, P. Desai, Mini. Rev. Med. Chem. 2016, 16, 1500–1526; (c) M. M. Fouad, E. R. El-Bendary, G. M. Suddek, I. A. Shehata, M. M. El-Kerdawy, Bioorg. Chem. 2018, 81, 587–598. doi: 10.1016/j.bioorg.2018.09.022; (d) K. D. Issa, Rostam Rasul Braiem, Green and Highly Efficient Synthetic Approach for the Synthesis of 4-Aminoantipyrine Schiff Bases, *Chem. Rev. Lett.* 6 (2023) 2-6. 10.22034/crl.2022.347066.1171

[3] A. K. O. Aldulaimi, A. H. Hussein, M. J. Mohammed, H. R. Saud, H. Bahair; F. Shahimi, Direct hydroxyazidation of alkenes: A viable strategy for the synthesis of β-azido alcohols, *Chem. Rev. Lett.,* 7 (2024) 53-64. 10.22034/crl.2024.430494.1270.

[4] (a) P. Martins, J. Jesus, S. Santos, L. R. Raposo, C. Roma-Rodrigues, P. V. Baptista, A. R. Fernandes, Molecules 2015, 20, 16852–16891; (b) N. Siddiqui, S. Andalip Bawa, R. Ali, O. Afzal, M. J. Akhtar, B. Azad, R. Kumar, J. Pharm. Bioallied. Sci. 2011, 3, 194–212; (c) A. S. Sokolova, O. I. Yarovaya, N. I. Bormotov, L. N. Shishkina, N. F. Salakhutdinov, Med. Chem. Comm. 2018, 9, 1746–1753; (d) A. Goel, N. Agarwal, F. V. Singh, A. Sharon, P. Tiwari, M. Dixit, R. Pratap, A. K. Srivastava, P. R. Maulik, V. Ram, J. Bioorg. Med. Chem. Lett. 2004, 14, 1089–1092; (e) M. Amir, S. A. Javed, H. Kumar, Indian. J. Pharm. Sci. 2007, 69, 337–343; (f) O. Pouralimardan, H. Bahir, S. M. Saeed, A. H. Adhab, R. Sadeghzadeh, Sulfinic esters: Novel and versatile sulfenylating agents for biologically important thioethers synthesis, *Chem. Rev. Lett.* 6

(2023) 95-104. 10.22034/crl.2023.390623.1213; (g) L. Sreerama, E. Vessally, F. Behmagham, Oxidative lactamization of amino alcohols: an overview, *J. Chem. Lett.* 1(1) (2020) 9-18. (h) S. Majedi, L. Sreerama, E. Vessally, F. Behmagham, Metal-free regioselective thiocyanation of (hetero) aromatic CH bonds using ammonium thiocyanate: an overview, Journal of Chemistry Letters 1(1) (2020) 25-31; (i) N. A. A. Salman, A. H. Adhab, H. Bahir, M. H. Sami, R. sadeghzadeh, Oxidative Decarboxylation of Arylacetic Acids: Novel Approach to the Synthesis of Aryl Aldehydes and Ketones, *Chem. Rev. Lett.* 6 (2023) 139-149. 10.22034/crl.2023.390701.1214

[5] R. J. Mohamed, A. K. O. Aldulaimi, S. A. Aowda, Synthesized of new alkaloid compounds and study their anticancer activity. Paper presented at the *AIP Conference Proceedings,* 2660 (2022) 020082. doi:10.1063/5.0108821.

[6] A. K. O. Aldulaimi, A. H. Idan, A. A. Majhool, M. J. Jawad, Z. H. Khudhair, S. M. Hassan, S. S. S. A. Azziz, Synthesis of new antibiotic agent based on mannich reaction. *Int. J. Drug Deliv. Tec., 12*(3) (2022) 1428-1432. doi:10.25258/ijddt.12.3.83.

[7] (a) W. Li, S. J. Zhao, F. Gao, Z. S. Lv, J. Y. Tu, Z. Xu, Chemistry Select 2018, 3, 10250–10254; (b) X. Zhao, S. T. Chaudhry, J. Mei, Heterocyclic building blocks for organic semiconductors. Heterocyclic chemistry in the 21st Century a Tribute to Alan Katritzky 2017, 121, 133–171; c) Zainab A. K. Al-Messri Chemical Methodologies 2023, 7, 581-593. Doi:10.22034/chemm.2023.393061.1669; (d) T. A. Khattab, M. A. Rehan. Egypt. J. Chem. 2018, 61, 989–1018; e) C. Lamberth, J. Dinges, Bioactive heterocyclic compound classes: agrochemicals. Wiley-VCH Verlag GmbH & Co, KGaA, 2012.

[8] A. K. O. Aldulaimi, A. A. Majhool, I. S. Hasan, M. Adil, S. M. Saeed, A. H. Adhab, New MCRs: Preparation of Novel Derivatives of Pyrazoloazepines in Ionic Liquid and Study of Biological Activity, *Polycycl. Aromat. Comp.,* (2023). DOI: 10.1080/10406638.2023.2254903.

[9] A.K.O. Aldulaimi, M. J. Jawad, S. M. Hassan, T. S. Alwan, S. S. S. A. Azziz, Y. M. Bakri,. The potential antibacterial activity of a novel amide derivative against gram-positive and gram-negative bacteria. *Int. J. Drug Deliv. Tec., 12*(2) (2022) 510-515. doi:10.25258/ijddt.12.2.8

[10] A.K.O. Aldulaimi, AA Majhool, I Sabeeh Hasan, M Adil, S Mahmood Saeed, ... New MCRs: Preparation of Novel Derivatives of Pyrazoloazepines in Ionic Liquid and Study of Biological Activity, Polycyclic Aromatic Compounds, 1-12, 2023, 10.1080/10406638.2023.2254903.

[11] M. Y. Saleh, A.K.O. Aldulaimi, S.M. Saeed, A.H. Adhab, TiFe2O4@SiO2–SO3H: A novel and effective catalyst for esterification reaction, Heliyon, 4(2024) https://doi.org/10.1016/j.heliyon.2024.e26286.

[12] C.-Y. Hsu, A. K. O. Aldulaimi, H. Bahir, A. H. Adhab and S. K. Saraswat, Hydrazinosulfonylation of aryl electrophiles: a straightforward approach for the synthesis of aryl N-aminosulfonamides, RSC adv. 13 (2023) 18546-18560.

[13] a) A. Domling and I. Ugi, Angew. Chem., Int. Ed., 2009, 39, 3168–3210. DOI: 10.1002/1521-3773(20000915); b) O. Ghashghaei, F. Seghetti and R. Lavilla, Beilstein J. Org. Chem., 2019, 15, 521–534. doi.org/10.3762/bjoc.15.46.

[14] I. A. Ibarra, A. Islas-Jácome, E.González-Zamora, Org. Biomol. Chem. 2018, 16, 1402–1418. Doi:10.1039/C7OB02305G.

[15] L. F. Tietze, C. Bsasche, K. M. Gericke, Domino reactions in organic synthesis. Wiley-VCH, Weinheim, 2006.

[16] a) Israa Sattar Gatea, Entesar. O. Al-Tamimi; Chemical Methodologies 2022, 6, 446-456. DOI:10.22034/CHEMM.2022.335635.1465.

[17] R. P. Herrera, Marqués-López, E. Multicomponent reactions: concepts and applications for design and synthesis. Wiley, Hoboken 2015.

[18] (a) Y.-S. Chong, S. Anwar and K. Chen, Mini-Rev. Org. Chem., 2018, 15, 364. DOI: 10.2174/1570193X15666171228145726; (b) D. Jo and S. Han, Chem. Commun., 2018, 54, 6750. doi.org/10.1039/C8CC02315H. (c) A. Quintavalla, Curr. Med. Chem., 2018, 25, 917. doi: 10.2174/0929867324666171106162259. ; (d) E. Chupakhin, O. Babich, A. Prosekov, L. Asyakina and M. Krasavin, Molecules, 2019, 24, 4165. https://doi.org/10.3390/molecules 24224165; (e) S. Mandal and B. Thirupathi, Org. Biomol. Chem., 2020, 18, 5287. doi.org/10.1039/D0OB00954G.

[19] a) Y. Zheng, C. M. Tice and S. B. Singh, Bioorg. Med. Chem. Lett., 2014, 24, 3673–3682. Doi:10.1016/j.bmcl.2014.06.081; b) Y. J. Zheng and C. M. Tice, Expert Opin. Drug Discovery, 2016, 11, 831–834. doi: 10.1080/17460441.2016.1195367; c) Milad Edraki, Issa Mousazadeh Moghaddampour, Mohammad Banimahd Keivani, Milad Sheydaei, Characterization and antimicrobial properties of Matcha green tea. Chem Rev Lett 5 (2022) 76-82.

[20] a) R. Sahay, J. Sundaramurthy, P. Suresh Kumar, V. Thavasi, S. G. Mhaisalkar, S. Ramakrishna, J. Solid State Chem., 2012, 186, 261; b) Seyed Jalal Hoseyni, Mahboobeh Manoochehri, Maryam Daghighi Asli, Synthesis and Crystal Structure of Dibromido{[(2-Pyridyl) methyl] (pethylphenyl)amine} Zinc. Chem Rev Lett 5 (2022) 99-105; (c) P. O. Ameh, Synthesized iron oxide nanoparticles from Acacia nilotica leaves for the sequestration..., *J. Chem. Lett.* 4 (2023) 38-51. 10.22034/jchemlett.2023.360137.1083; (d) Milad. Sheydaei, M. Edraki, Poly(butylene trisulfide)/CNT nanocomposites: synthesis and effect of CNT content on thermal properties, *J. Chem. Lett.* 3 (2022) 159-163. 10.22034/jchemlett.2023.380990.1101; (e) M. Sheydaei, M. Edraki, Vinyl ester/C-MMT

nanocomposites: investigation of mechanical and antimicrobial properties, *J. Chem. Lett.* 3 (2022) 95-98. 10.22034/jchemlett.2022.350678.1074; (f) E. Vessally, M. R. Ilghami, M, Abbasian, Investigation the Capability of Doped Graphene Nanostructure in Magnesium and Barium Batteries with Quantum Calculations, Chem. Res. Technol., 1 (2024) 10.2234/chemrestec.2024.436837.1007; (h) P. R. A. Selvan, M. Praveendaniel, Synthesis and Application of TiO2-Phosphomolybdic acid nanocomposite, *J. Chem. Lett.* 4 (2023) 10.22034/jchemlett.2023.395693.1114;

[21] a) B.T. Zhang, X. Zheng, H.-F. Li, J.-M. Lin, Anal. Chim. Acta, 2013, 784, 1. doi: 10.1016/j.aca.2013.03.054; b) Kamran Ghasemi, Mostafa Emadi, Asghar Bagheri, Mehdi Mohammadi, Evaluation of antioxidant properties of button mushroom in different harvest and morphological stages. Chem Rev Lett 5 (2022) 106-112.

[22] a) T. Xin, M. Ma, H. Zhang, J. Gu, S. Wang, M. Liu, Q. Zhang, Appl. Surf. Sci. 2014, 288, 51. doi: 10.1016/j.apsusc.2013.09.108.b) Adibe Khezri, Ladan Ejlali, Moosa Eshaghi, Mohammad Taghi Vardini, Hadi Basharnavaz, Inhibiting effect of a synthesized organic compound, [3-(4methoxyphenyl)isoxazole-5-yl]-methanol, on copper in 1 M sulfuric acid solution. Chem Rev Lett 5 (2022) 113-118.

[23] J. Jing, J. Li, J. Feng, W. Li, W.W. Yu, Chem. Eng. J. 2013, 219, 355. Doi:10.1016/j.cej.2012.12.058

[24] K. Mandel, F. Hutter, C. Gellermann, G. Sextl, Sep. Purif. Technol. 2013, 109, 144. Doi:10.1016/j.seppur.2013.03.002.

[25] A. B. Djurišić, X. Chen, Y. H. Leung, A. Man, J. Mater, Chem., 2012, 22, 6526-6535. doi.org/10.1039/C2JM15548F.

[26] (a) B. Halliwell, Free Radical Res. 1999, 31, 261–272. DOI: 10.1080/10715769900300841; (b) F. Ahmadi, M. Kadivar, M. Shahedi, Food Chem. 2007, 105, 57–64. doi:10.1016/j.foodchem.2007.03.056.

[27] M. A. Babizhayev, A. I. Deyev, V. N. Yermakovea, I.V. Brikman, J. Bours, Drugs R D 2004, 5, 125–139. doi: 10.2165/00126839-200405030-00001.

[28] L. Liu, M. Meydani, Nutr. Rev. 2002, 60, 368–371. DOI: 10.1301/00296640260385810.

[29] (a) E. Ezzatzadeh, E. Pourghasem, S. Fallah Iri Sofla, Journal of Essential Oil 2014, 17, 577-583. doi.org/10.1080/0972060X.2014.901616; b) S. Naderi, R. Sandaroos; S. Peiman; B. Maleki, Chem. Methodol. 2023, 7, 392-404. DOI:10.22034/CHEMM.2023.385248.1651; c) E. Ezzatzadeh, Z.S. Hossaini, R. Rostamian, S. Vaseghi, S. F. Mousavi, Journal of Heterocyclic Chemistry 2017, 54 (5), 2906-2911. https://doi.org/10.1002/jhet.2900; d) M. Mohammadi, F. Alirezapour, A. Khanmohammadi, Theoretical Chemistry Accounts 2021, 140 (8), 104. DOI: 10.1007/s00214-021-02813-1

[30] (a) M. Mohammadi, A. Khanmohammadi, Theoretical Chemistry Accounts 2019, 138 (8), 101. Doi.org/10.1007/s00214-019-2492-4; b) S. Saeednia, P. Iranmanesh, M. Hatefi Ardakani, M. Mohammadi, Gh. Norouzi, Materials Research Bulletin 2016, 78, 1-10. DOI: 10.1016/j.materresbull.2016.02.010; c) A. Khanmohammadi, M. Mohammadi; Journal of the Chilean Chemical Society 2019, 64 (1), 4337-4344. doi.org/10.4067/s0717-97072019000104337; d) M Pirgheibi, M Mohammadi, A Khanmohammadi, Structural Chemistry 2021, 32 (4), 1529-1539. Doi.org/10.1007/s11224-021-01728-8.

[31] a) N. Karami Hezarcheshmeh, F. Godarzbod, N. Faal Hamedanii, S. Vaseghi, Polycyclic Aromatic Compounds, 2023, 1-23. Doi.org/10.1080/10406638.2022.2162553; b) N. Karami Hezarcheshmeh, J. Azizian Polycyclic Aromatic Compounds 2022, 42 (10), 7686-7696. Doi.org/10.1080/10406638.2021.2006250; c) N. K. Hezarcheshmeh, J. Azizian, Molecular Diversity 2022, 26 (4), 2011-2024. Doi:10.1007/s11030-021-10311-6. d) Kamran Ghasemi, Mostafa Emadi, Asghar Bagheri, Mehdi Mohammadi, Evaluation of antioxidant properties of button mushroom in different harvest and morphological stages. Chem Rev Lett 5 (2022) 106-112.

[32] a) F. Sheikholeslami-Farahani, A. S. Shahvelayati, Bulg. Chem. Commun 2015, 47, 830-836; b) F. Sheikholeslami-Farahani, Asian Journal of Nanosciences and Materials 2022, 5, 132-143. Doi.org/10.26655/AJNANOMAT.2022.2.5; c) E. Ezzatzadeh, F. Sheikholeslami-Farahani, K. Yadollahzadeh, S. Rezayati; Combinatorial Chemistry & High Throughput Screening 2021, 24 (9), 1465-1475. Doi.org/10.2174/1386207323666201007154343.

[33] a) S. Esfahani, J. Akbari, S. Soleimani-Amiri, M. Mirzaei, AG Gol, Diamond and Related Materials 135, 109893. https://doi.org/10.1016/j.diamond.2023.109893; b) M. Z. Kassaee, E. Motamedi, M. Majdi, A. Cheshmehkani, S. Soleimani-Amiri, F. Buazar, Journal of Alloys and Compounds 2008, 453 (1-2), 229-232. Doi.org/10.1016/j.jallcom.2007.06.002; c) S. Soleimani-Amiri, Z. S. Hossaini, M. Arabkhazaeli, H. Karami, Journal of the Chinese Chemical Society 2019, 66 (4), 438-445. https://doi.org/10.1002/jccs.201800199.

[34] a) M. Ghashghaee, M. Ghambarian, Z. Azizi, Black phosphorus: synthesis, properties and applications, 2020, 59-72. DOI:10.1007/978-3-030-29555-4; b) S Reihani, Z Azizi, M Khaleghian, H Passdar, L Pishkar, R Ahmadi, Journal of Physical & Theoretical Chemistry 2007, 4 (2), 51-56; c) S. Soleimani-Amiri, M. Koohi, Z. Azizi Journal of the Chinese Chemical Society 2018, 65, 1453-1464. Doi.org/10.1002/jccs.201800163.d) Hojat Jafari,

Elham Ameri, Majid Rezaeivala, Mohammad Hassan Vakili, Nader Mokhtarian, Synthesized Schiff base acted as eco-friendly inhibitor for mild steel in 1N H_2SO_4. Chem Rev Lett 5 (2022) 119-126.

[35] a) MZ Kassaee, M Ghambarian, SM Musavi, FA Shakib, MR Momeni Journal of Physical Organic Chemistry 2009, 22 (10), 919-924. Doi.org/10.1002/poc.1540; b) M Ghadiri, M Ghashghaee, M Ghambarian Physical Chemistry Chemical Physics 2020, 22 (27), 15549-15558. Doi.org/10.1039/D0CP02013C; c) M Ghambarian, Z Azizi, M Ghashghaee Black phosphorus: synthesis, properties and applications, 2020, 1-30. DOI:10.1007/978-3-030-29555-4. d) Hojat Jafari, E. Ameri, M. Rezaeivala, M. H. Vakili, N. Mokhtarian, Synthesized Schiff base acted as eco-friendly inhibitor for mild steel in 1N H_2SO4. Chem Rev Lett 5 (2022) 119-126.

[36] a) F.K. Feizabad, K. Khandan-Barani, A. Hassanabadi, Journal of Chemical Research 2017, 41, 673-675. https://doi.org/10.3184/174751917X151056906628; b) M.T. Maghsoodlou, K. Khandan-Barani, N. Hazeri, S.M. Habibi-Khorasani, Research on Chemical Intermediates 2014, 40, 779-785. https://doi.org/10.1007/s11164-012-1002-2; c) Shahad M. Dhiaa, S. K. Mohammed, H. Bahair, A. H. Hameed, E. A. Mahmood, F. Abedinifar, E. B.Rezaei, Recent Advances in Bioactive 1,5-Benzothiazepine-based Compounds: Highlights from 2012 to 2022. Chem Rev Lett 6 (2023) 390-402.

[37] a) M. Moreno, S. K. Mohammed, A. Hussein A., O. Pouralimardan, F. Behmagham, Recent trends in the deformylative C-H arylation/alkylation of (hetero)arenes with aldehydes. Chem Rev Lett 6 (2023) 390-400; b) I Yavari, Z Hossaini, E Karimi, Monatshefte für Chemie-Chemical Monthly 2007, 138, 1267-1271. Doi:10.1007/s00706-007-0711-5; c) B Azizi, MRP Heravi, Z Hossaini, A Ebadi, E Vessally RSC advances 2021, 11 (22), 13138-13151. DOI: 10.1039/D0RA09848E; d) R Katal, S Masudy-Panah, M Sabbaghan, Z Hossaini, MHDA Farahani Separation and Purification Technology 2020, 250, 117239. doi.org/10.1016/j.seppur.2020.117239.

[38] a) B. Norouzi, A. Malekan, M. Moradian, Russ. J. Electrochem. 2016, 52, 330-339. /doi.org/10.1134/S1023193516040108; b) S.M.H. Khorassani, M.T. Maghsoodlou, A. Ebrahimi, H. Roohi, Phosphorus, Sulfur, and Silicon 2006, 181 (5), 1103-1115. DOI:10.1080/10426500500326446; c) T Pezeshkvar, B Norouzi, M Moradian, A Mirabi Journal of Solid State Electrochemistry 2022, 26 (6-7), 1479-1492. DO:10.1007/s10008-022-05182-2; d) B Norouzi, M Moradian, A Malekan Portugaliae Electrochimica Acta 2015, 33 (2), 111-124. DOI: 10.4152/pea.201502111.

[39] a) MR Nazari, V Abdossi, FZ Hargalani, K Larijani Scientific Reports 2022, 12, 6156. https://doi.org/10.1038/s41598-022-10109-y; b) M Abbasi, F Zamani Hargalani, S Afrashteh, R Rostamian Canadian Journal of Chemistry 2019, 97, 848-855. https://doi.org/10.1139/cjc-2019-0167; c) Nahid Shajari, Reza Ghiasi, Ali Ramazani, Experimental and computational insights for identification of dialkyl 5-oxo-5H[1,3] thiazolo[3,2-a]pyrimidine-2,3-dicarboxylates. Chem Rev Lett 6 (2023) 24-28.

[40] a) Mohammad M. Al-Tufah; Shakhawan Beebaeny; Saad Salem Jasim; Bari Lateef Mohammed, Chem. Methodol. 2023, **7**, 408-418. doi.org/10.22034/chemm.2023.388126.1654.

[41] a) F. A. Nashaan, M. S. Al-Rawi, C*hem. Methodol.* 2023, 7, 267-276. Doi:10.22034/chemm.2023.366582.1619; b) B. Baghernejad, F. Nuhia, A new approach to the facile synthesis of 1,8-dioxooctahydroxanthene using nano-TiO2/ CNT as an efficient catalyst. Chem Rev Lett 5 (2022) 268-277.

[42] K. Shimada, K. Fujikawa, K. Yahara, T. Nakamura, J. Agric. Food Chem. 1992, 40, 945–948. https://doi.org/10.1021/jf00018a005.

[43] Yen G. C.; Duh P. D.; J. Agric. Food Chem. 1994, 42, 629–632. Doi;10.1021/jf00039a005.

[44] Yildirim A.; Mavi A.; Kara A. A.; J. Agric. Food Chem., 2001, 49, 4083-4089. DOI: 10.1021/jf0103572

[45] Saundane A. R.; Nandibeoor M. K.; Monatsh Chem. 2015, 146, 1751. https://doi.org/10.1007/s00706-015-1440-9

[46] Bidchol A. M.; Food Bioprocess Techol,. 2011, 4, 1137. DOI:10.1007/s11947-009-0196-9.