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Evaluation of Antioxidants Activity of Some Natural Polyphenolic Compounds By using Briggs-Rauscher Reaction

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The macrocyclic complex catalyzed Briggs-Rauscher (BR) oscillator was used to determine the antioxidants activity of natural polyphenolic compounds (tannic acid, chlorogenic acid, and luteolin) in this paper. The complex Ni catalyst is donated by $NiL(ClO_4)_2$ where the ligand L in the complex is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The overall reaction pH was maintained at 2, which is similar to the pH of the human stomach. Experimental results have shown that as per addition of the above antioxidants into the BR system, the temporarily cessation of oscillation was noticed and inhibition time linearly depends on the concentration of antioxidants added. The evaluation of natural polyphenolic compound, antioxidants activity was tested successfully. The three natural polyphenolic compounds tested are tannic acid, chlorogenic acid, and luteolin. In these three natural compounds, the chlorogenic acid was found the most proficient antioxidant. The perturbation mechanism involving $HOO^{\bullet}$ radical based on FCA model was suggested.

Keywords: Antioxidants activity, naturally phenolic compounds, Evaluation, Briggs-Rauscher reactions

1. INTRODUCTION

The involvement of Free radicals (FR) and reactive oxygen species (ROS) is important and effective factor toward some human diseases such as cancer, central nervous system injury, inflammatory and degenerative diseases [1-4]. Antineoplastic or malignant cell and poisonous of environmental xenobiotic agents are responsible to free radicals [5]. Polyphenolic antioxidants stop these diseases caused by free radicals and are utilized for employment for health and traditional medicine [6]. Antioxidants have classified mainly into two kinds, synthetic antioxidant, and natural antioxidants which have relatively low side-effects on the human body [7]. Fruits, vegetable and most kind of vitamins (vitamin B complex, C, E and K) are considered as natural antioxidants having less level of attached ring structure which is responsible for antioxidant activity [8-10].

The basic techniques used to determine the antioxidant activity are the utilizing different free radicals containing TOSC (total oxidant scavenging capacity) [11], ORAC (oxygen radical absorbance capacity) [12], TRAP (Total radical trapping parameter) and TEAC (Trolox equivalent antioxidant capacity) [12] based on antioxidant properties of cyanidine [2-(-,4-dihydroxyyphenyl)-3,5,7-trihydroxyflavonol] which exists in strawberries and cherries [13,14]. TEAC technique works on pH 7.4, which is analogous to the pH of blood while the other methods are working at a higher pH value [15]. All the technique is based on the formation of free radical in the reaction mixture of and their detection points.

Recently, the inhibitory effect (immediate cessation of oscillation) of soy antioxidants on an oscillating reaction of the Briggs-Rauscher (BR) type was reported in which Mn^{2+} ion was used as catalyst [16, 17]. And such inhibitory effect was imitated by is directly proportional to the concentration of antioxidants and initiated the free radical scavenging mechanism. In particular study, the B-R system has been utilized to measure the antioxidants activity of ten phenolic compounds namely pyrocatechol (PC), ferulic acid (FA), caffeic acid (CA), 2,6-dihydroxybenzoic acid (2,6-DHBA), homovanillic acid (HA), 3,4-dihydroxybenzoic acid (3,4-DHBA), resorcinol (Re), 2,4-dihydroxybenzoic acid (2,4-DHBA), 3,5-dihydroxybenzoic acid (3,5-DHBA) and 2,5-dihydroxybenzoic acid (2,5-DHBA), on the basis of inhibition time [18].

With the contrast to Manganese –catalyzed BR oscillator, the $[NiL](ClO_4)_2$-catalyzed BR reaction is considered good catalyst because their cyclic structure is similar to porphyrin (exist in numerous metallic comprising enzymes) [19]. One of these complex called $NiL(ClO_4)_2$ where the ligand L in the complex is 5,7,7,12,14,14- hexamethyl -1,4,8,11-tetraazacyclotetraeca-4,11-diene. The reagents (Sulfuric acid –potassium iodate–malonic acid–$NiL(ClO_4)_2$) was mixed in order to get oscillation patterns, just on the slight variation of {[Ni(III))]/[Ni(II)L]} values [20]. Both Mn(II)-catalyzed and macrocyclic NiL-complex-catalyzed B-R system including various intermediate species, like HOI, HOIO, IO_2 and hydroperoxyl radical ($HOO^{\bullet}$). The involvement of ($HOO^{\bullet}$) is responsible for causing inhibition time (t_{in}) which becomes the tool to determine the antioxidant activity of compounds.

In the present work, we have successfully estimated the antioxidants performance of three naturally occurring polyphenolic samples containing tannic acid, chlorogenic acid, and luteolin by using the Ni-complex catalyzed B-R oscillator. The relative antioxidants activity of antioxidants was

determined on the basis of inhibition time t_{in}. The t_{in} is a concentration dependent phenomenon, meaning as the amount of natural polyphenolic antioxidants added into BR system increases, the t_{in} increases.

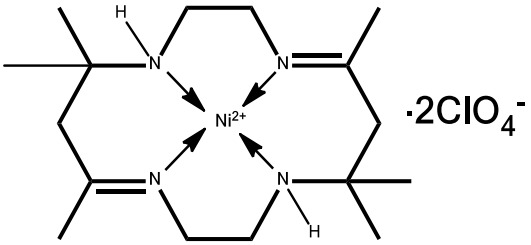

Figure 1. Structure of [NiL] $(ClO_4)_2$

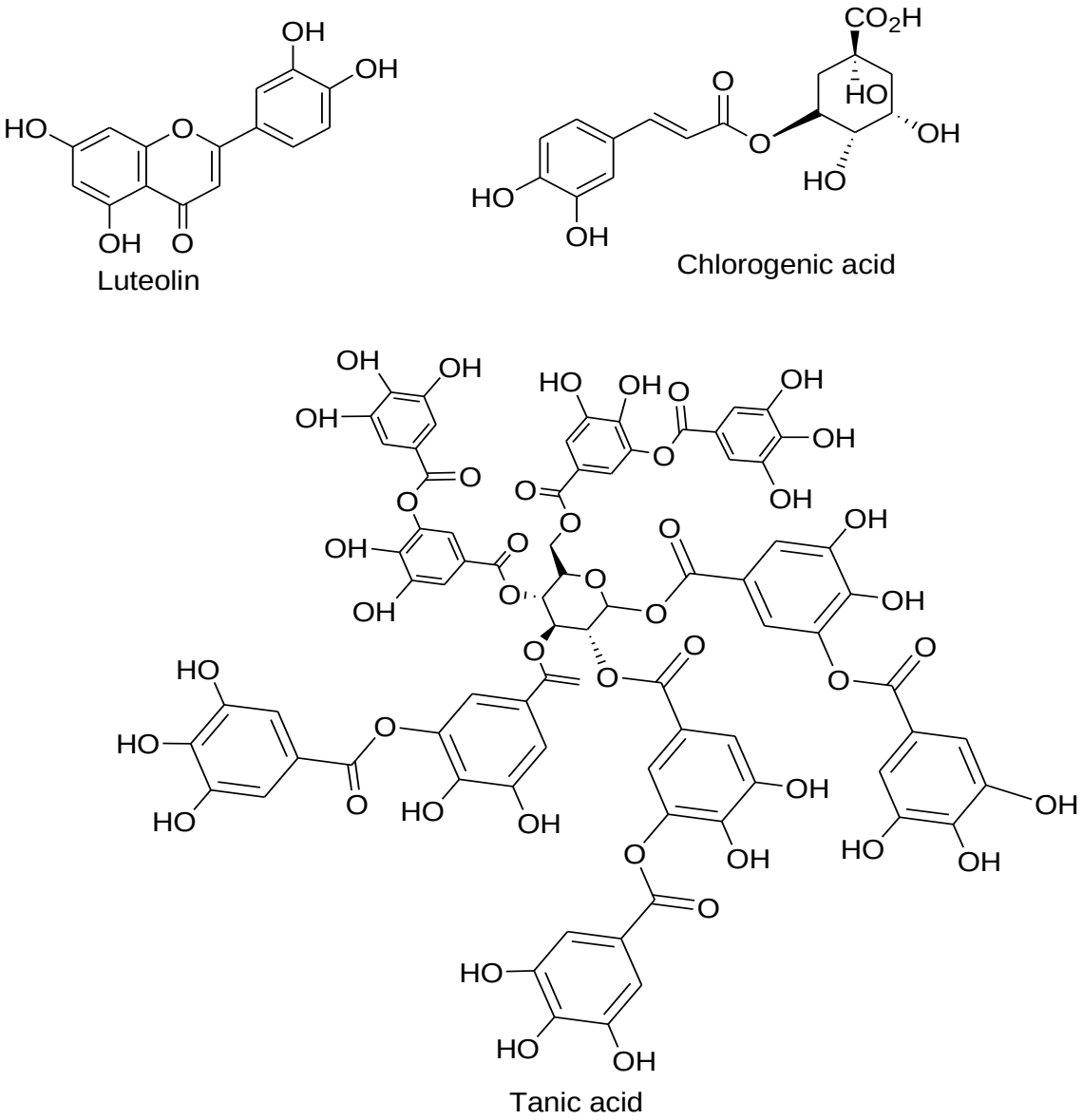

Figure 2. The structure of the three natural polyphenolic antioxidants

A recent highly developed TEAC method [21 is used to evaluate the antioxidants activities]. The measurement range for such technique is μ mol L^{-1} which is same to that of our B-R based method, which is easy to handle. The study of different antioxidants capacity, the BR method has many advantages: the analysis is rapid, inexpensive and the apparatus and reagent are generally used in all chemical laboratories.

2. EXPERIMENTAL SECTION

2.1 Reagent

All the reagents, malonic acid, potassium iodate, hydrogen peroxide, and sulphuric acid were of analytical grade without further purification. The chlorogenic acid (MW = 354.31 g/mol, ≥ 98%), (Shanghai Macklin Biochemical Co; Ltd.), Tannic acid (MW = 1701.20 g/mol, ≥ 98%), (Aladdin Chemistry Co.Ltd.) Luteolin (MW = 286.24 g/mol, ≥ 98%), (Aladdin Industrial Corporation Shanghai, China) were purchased, except Ni-macrocyclic catalyst, which was synthesized in the laboratory as per literature [22,23] and identified by IR and elemental analysis.

2.2. Apparatus

BR oscillator consists of a 50 ml glass reactor, two electrodes. One is platinum electrode (model 213 Shanghai, China) having a function of working electrode and 2nd is SCE (Saturated Calomel Electrode) (Model 217 Shanghai, China) used as a reference electrode. Such electrodes were put into a 50 ml glass reactor under constant magnetic stirring (Jiangsu China) at the 600-700 stirring rate. The magnetic bar was used to homogenize the solution in the glass reactor at zero degree. The two electrode were lined to a Go!Link sensor interface (Vernier, USA) and amplifier (Vernier, USA). The data was recorded potentially vs time on PC through Logger Lite data-acquisition programmer.

2.3. Procedure

For the BR oscillating reaction required: 2.00 mol L^{-1} malonic acid, 0.14 mol L^{-1} potassium iodate, 4.00 mol L^{-1} H_2O_2 and 0.0173 mol L^{-1} nickel (II) complex $[NiL](ClO_4)_2$ catalyst. All the reagent was dispersed into 0.025mol L^{-1} sulphuric acid. The sulphuric acid solution was prepared in double-distilled deionized water. The chlorogenic acid, tannic acid, and carvacrol were dissolved in ethanol. In 50 ml glass reactor, a total 40 ml mixed volume was gotten by pouring into reactor with the following reagents in following order: 15.5 ml H_2SO_4, 6.5 ml KIO_3, 2.5 ml malonic acid, 1.5 ml nickel (II) complex and 14 ml H_2O_2. Magnetic stirrer was used incessantly to stir the mixture solution, and typically potential oscillation was recorded *versus* time. At 9th oscillation cycle, different amount of antioxidants were used to perturb the oscillation profile.

3. RESULTS AND DISCUSSION

The typical oscillation was achieved (as shown in Figure 3a) by the mixing of the reagents in the above-stated order. Under 0˚C, the typical oscillation profile for $NiL(ClO_4)_2$-catalyzed BR oscillators was not interfered in the concentration conditions of 20µl of ethanol. The average oscillations cycle is approximately 38 to 43 cycles and the average oscillation time is 28 to 32 s. The low energy (46.844kj/mol) exhibits in this oscillating system [24]. The solution color was incessantly changed from yellow to brown and from brown to yellow, and this is because of the transfer of one electron procedure between $[NiL]^{2+}$ and $[NiL]^{3+}$. The brown color of the solution is due to dissolved of I_2 generated during the sequence of the oscillation.

3.1 Relative Antioxidant Activity Calculations

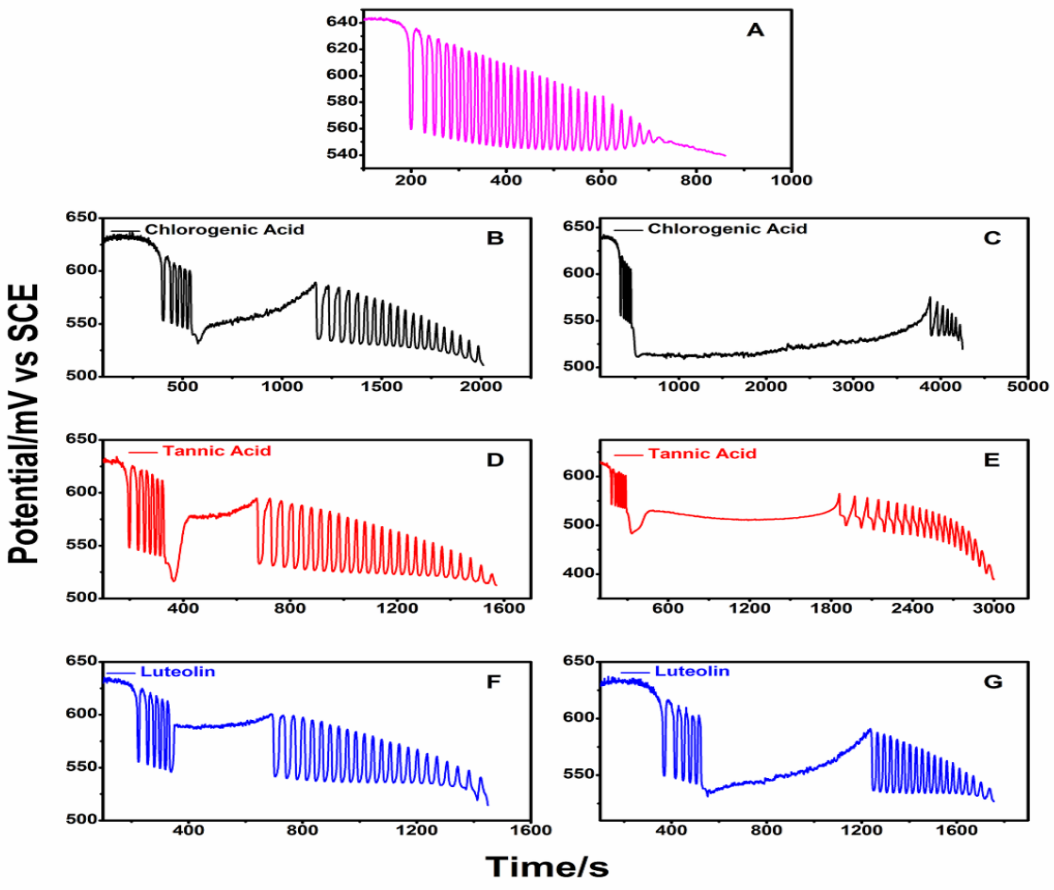

Figure 3. (a) The typical oscillations of potential of the bright-Pt vs. SCE in deionize solution . (b) Perturb oscillation by injection of 7.75×10^{-6} M [tannic acid]; (c) Perturb oscillation by injection of 3.10×10^{-5} M [tannic acid]; (d) Perturb oscillation by injection of 6.0×10^{-6} M [Chlorogenic acid]; (e) Perturb oscillation by injection of 1.50×10^{-5} M [Chlorogenic acid]; (f) Perturb oscillation by injection of 8.75×10^{-6} M[Luteolin]; (g) Perturb oscillation by injection of 2.37×10^{-5} M [Luteolin]; Common condition: $[H_2SO_4]$ = 0.025 M, $[KIO_3]$ = 0.0238 M, [MA] = 0.15 M, $[NiL]^{2+}$ = 0.000778 M, $[H_2O_2]$ = 1.32 M. Temperature = 0 ± 0.1 ˚C.

We investigate the injection of polyphenolic compounds into active B-R system. It results temporary cease of oscillation, the immediately quenching and succeeding regeneration of oscillations after the t_{in}. The quenching of oscillation is due to the scavenging action of the antioxidants against ($HOO^{\bullet}$) radicals into B-R oscillatory system. Therefore, the cessation of oscillation is defined as the inhibition time (t_{in}), the time lapsed at the beginning of the damping of oscillation the first regeneration of oscillations.

The t_{in} of the experiment is associated with the concentration of three antioxidants. We notice that the t_{in} is dependent on the concentrations of antioxidants over a wide concentration range.

The linear regression curves exist regarding the relationship of inhibition time and the specific antioxidants concentration. For tannic acid, t_{in} dependence on the concentration of tannic acid was determined in the straight-line range of 3.87×10^{-6} to 3.1×10^{-5} M. The linear relationship between the t_{in} and concentration of chlorogenic acid is in the range of 1.5×10^{-6} to 1.25×10^{-5} M. The linear relationship between inhibition times and concentration range of luteolin is from 1.25×10^{-6} to 1.5×10^{-5} M. The graphs t_{in} versus concentration of distinguishable antioxidants are described in **Figure 4.**

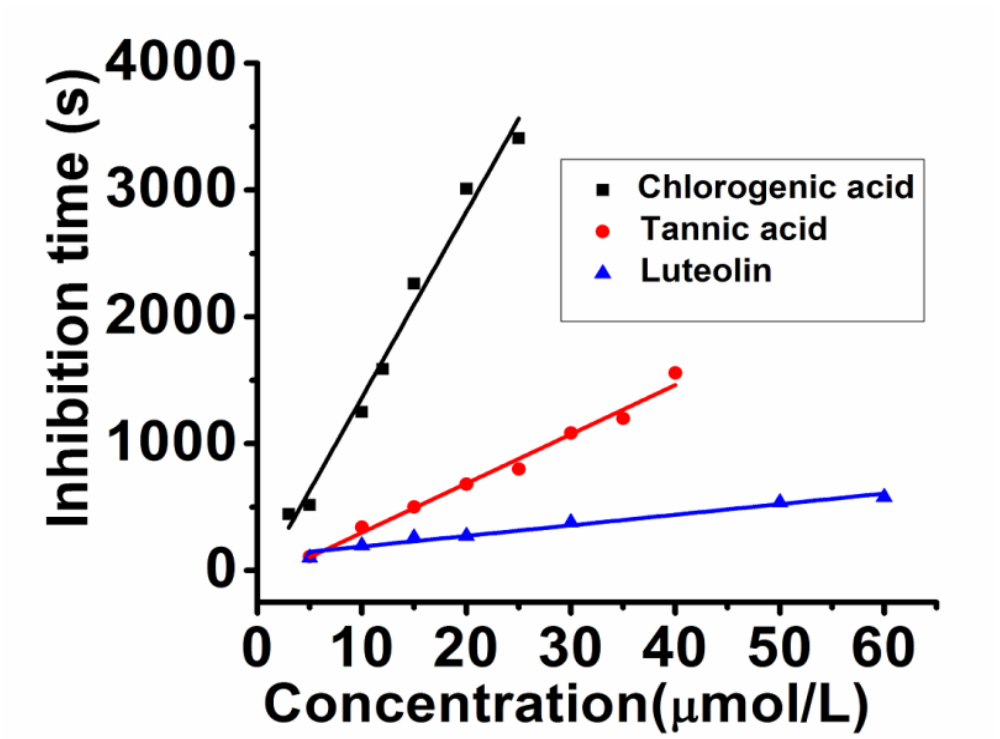

Figure 4. Linear fits of the time inhibition vs concentration for antioxidant studied.

The experimental data has proven that by adding different concentration of polyphenolic compounds in B-R system, different compounds behave differently to give diverse linearity. The low concentration of antioxidants added having no inhibition is measured [25]. We consider that under the low limits of concentrations, the linear lines cure near to zero. When the concentration is high enough to a certain value (which is the different for each antioxidant), the oscillation does not restart,

representing that the reaction has reached its end point not being able to produce radical. This action is due to the scavenging action of added antioxidants against $HOO^{\bullet}$ radical formed in BR oscillation.

The linear parameters of the line, collectedly with correlation coefficients, are shown in **table 1.** The linear regression of each line is different. The single t_{in} is related to the concentration of each analyst. The t_{in} is due to the involvement of ($HOO^{\bullet}$).

The single t_{in} is an easy parameter to be used to determine the relative antioxidant activity of each antioxidant [26, 27]. The relative antioxidant activity is compared by the concentration of a sample with the concentration of a chosen standard that gives the same (t_{in}), which is called relative activity with respect to concentration (rac). Rac is shown in the following ratio [28-33].

(Relative activity with respect to concentration) rac = [std] / [smp]

Relative activity with respect to concentration [rac] is representing the ratio, where [smp] is the concentration of the sample put into the BR to produce a certain (t_{in}), and [std] is the concentration of the standard that could create the same inhibition time (t_{in}). The latter concentration is achieved from the linear line equation of the antioxidants which is chosen as a standard. For a rac calculation reason, the t_{in} must also be in the straight line linear range of the standard and all of the observed substance. Tannic acid is selected as a standard antioxidant.

Table 1. Parameters of the line equation (t_{inhib}=A[concentration] + B) and the R^2

Substance	A(μmol^{-1} l)	B	R^2
Tannic acid	38.7928	-88.7142	0.9835
Chlorogenic acid	146.583	-101.07	0.9814
Luteolin	7.8421	-128.570	0.9901

Table 2. rac (relative activity with respect to concentration) values for the antioxidants studies

Antioxidants	t_{in} (s)	Concentration (µM)	rac
Tannic acid	560	19.5	0.63
Chlorogenic acid	560	8.5	1.14
Luteolin	560	47.2	0.13

The studied rac values are described in **table 2.** The order of relative activity for the polyphenolic antioxidant are calculated, and (t_{in}) of 560 s is selected to obtain following result:

Chlorogenic acid (1.14) > Tannic acid (0.63) > Luteolin (0.13)

We observed that in an acidic medium the Chlorogenic acid is most effective and is considered as highest antioxidant capacity in these three polyphenolic compounds. The Luteolin is considering as a lowest antioxidant capacity in these three polyphenolic compounds.

For determination of antioxidants activity, many analytical methods were developed which is based on free radicals in the reaction mixture. Recently Schlesier and coworkers [34] published valuation of antioxidants activity by means of six different methods. (TEAC Trolox equivalent antioxidant capacity; TRAP Total radical-trapping antioxidant parameters; DPPH 2,2-diphenyl-1-picryl-hydroxyl; DMPD N,N-dimethyl-p-phenylenediamine; PCL Photochemiluminescence; FRAP Ferric reducing the ability of plasma). These methods were used to evaluate antioxidants and were also applied to test the several beverages. These methods work under the pH (3.3-10.5), but our method (B-R oscillator) is work in acidic medium (2 pH), which was kept at pH of stomach fluids in the human body.

3.2. Mechanistic Interpretation

The B-R reaction mechanism is complex and was first offered by Noyes and Furrow (NF model) in 1982 [35], representing the basic feature of the oscillation. At the same time, De Kepper and Epstein (DF) proposed a mechanism for chemical oscillation called DF model [36], describing the variety of phenomena seen in continuous-flowed stirred tank reactor (CSTR). Recently Furrow and coworkers [37] improved the NF mechanism based on importance role played by $HOO^{\bullet}$ radical within B-R oscillation reaction [38] and named it as FCA model. The detail reaction mechanism is mentioned as under:

Iodine involvement reaction

I1 $HOI + I^- + H^+ \leftrightarrow I_2 + H_2O$

I2 $HIO_2 + I^- + H^+ \rightarrow 2HOI$

I3 $IO_3^- + I^- + 2H^+ \leftrightarrow HIO_2 + HOI$

I4 $2HIO_2 \rightarrow IO_3^- + HOI + H^+$

I5 $IO_3^- + HIO_2 + H^+ \leftrightarrow 2IO_2^{\bullet} + H_2O$

Oxygen involvement reaction

O2 $2HOO^{\bullet} \rightarrow H_2O_2 + O_2$

D1 $HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O$

Catalyst involvement reaction

M1 $IO_2^{\bullet} + [NiL]^{2+} + H^+ \leftrightarrow [NiL]^{3+} + HIO_2$

M2 $H_2O_2 + [NiL]^{3+} \rightarrow [NiL]^{2+} + HOO^{\bullet} + H^+$

Iodate reaction/Organic substrate

C3 $CH_2(COOH)_2 \rightarrow (COOH)=C(OH)_2$ (enol)

C4 $I_2 + MA(enol) \rightarrow MAI(IMAI) + I^- + H^+$

Overall chemical equcation is as following

I $IO_3^- + 2H_2O_2 + CH_2(COOH)_2 + H^+ \rightarrow ICH(COOH)_2 + 3H_2O + 2O_2$

Overall reaction step I are

II $IO_3^- + 2H_2O_2 + H^+ \rightarrow HIO + O_2 + H_2O$

III $HIO + CH_2(COOH)_2 \rightarrow ICH(COOH)_2 + H_2O$

Step II is rapidily reaction through radical route

I5 $2IO_3^- + 2HIO_2 + 2H^+ \rightarrow 4IO_2^{\bullet} + 2H_2O$

M1 $IO_2^{\bullet} + [NiL]^{2+} + H^+ \leftrightarrow [NiL]^{3+} + HIO_2$

M2 $H_2O_2 + [NiL]^{3+} \rightarrow [NiL]^{2+} + HOO^{\bullet} + H^+$

O2 $2HOO^{\bullet} \rightarrow H_2O_2 + O_2$

Step III reaction

II $HOI + H_2O_2 + I^- + H^+ \leftrightarrow I_2 + H_2O$

C3 $CH_2(COOH)_2 \rightarrow (COOH)=C(OH)_2$ (enol)

C4 $(COOH)=C(OH)_2$ (enol) $+ I_2 \rightarrow IHC(COOH)_2 + I^- + H^+$

In B-R oscillating system, hydroperoxyl radical ($HOO^{\bullet}$) plays a vital role, which shows a possible mechanism between antioxidant and ($HOO^{\bullet}$) in the presence of macrocyclic nickel (II) complex-catalyzed Briggs-Rauscher system. Ar-OH is considered as the replacement of antioxidant. The first reaction involves the transfer of an electron from the antioxidant to ($HOO^{\bullet}$) radical. The Ar-OH becomes radical cation of antioxidants and $HOO^{\bullet}$ radical forms hydroperoxyl anion [39-43]:

$$Ar - OH + HOO^{\cdot} \rightarrow Ar - OH^{\cdot +} + HOO^{-}$$

The second reaction is a faster reaction

$$Ar - OH^{\cdot +} \rightarrow Ar - O^{\cdot} + H^{+}$$

The proton reacts instantly with the hydroperoxyl anion to form H_2O_2:

$$H^+ + HOO^- \rightarrow H_2O_2$$

4. CONCLUSIONS

The antioxidant capacity of natural polyphenolic antioxidants were evaluated by using macrocyclic nickel (II) complex-catalyst Briggs-Rauscher oscillation system, in which the temporary cessation of the oscillation was caused by addition of antioxidants. The oscillation stopped for a period of time due to scavenging action of antioxidants added against the ($HOO^{\bullet}$) radical. The inhibition time is proportional to the concentration of added antioxidants. Finally, we successfully established the method to evaluate the antioxidants capacity of natural polyphenolic antioxidants (tannic acid, chlorogenic acid, and luteolin). By the comparison with TEAC method, such a method is sample, sensitive and easy in operation.

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References

1. G. Block, B. Petterson and A. Subar, *Nutr. Cancer,* 18 (1192) 1.
2. M. L. Burr, *J. Hum. Nutr. Diet*., 7 (1994) 409.
3. S. R. J. Maxeell, H. Thomason, D. Sandler. C. Leguen, M. A. Baxter, G. H. G. Thorpe and A. H. Barnett, *Eur. J. Clin. InVest.,* 26 (1997) 484.
4. S. E. Vollset and S. E. Bjelke, *Lancet,* 2 (1983) 742.
5. C. E. Cross, B. Halliwell, E. T. Borish, W. A. Pryor. B. N. Ames, R. L. Saul, J. M. McCord and D. Harman, *Ann. Intern. Med.,* 107 (4) (1987) 526.
6. P. Scartezzini and E. Speroni, *J. Ethnopharmacol.,* 71 (2000) 23.
7. S. Nieto, A. Garrido, J. Sanhueza, L. A. Loyola, G. Morales, F. Leighton and A. Valenzuela., *J. Am. Oil Chem. Soc.,* 70 (8) (1993) 773.
8. J. W. M. Wu, H. C. Lee, T. Ho and S. S. Chang., *J.A.O.C.S.,* 59 (1982) 339.
9. Z. Formanek, A. Lynch, K. Galvin, J. Farkasand J. P. Kerry, *Meat Science*, 58 (2001) 433.
10. V. Cody, J. B. Harborne, E. Middleton and *E. A. Liss., New York.*, (1986) 15.
11. F. Regoli and G. W. Winston, *TAAP.,* 156 (1999) 96.
12. V. D. Berg, R. M. M. Haenen, D. Berg and A. Bast., *Food Chem.*, 66 (1999) 511.
13. C.A. Rice-Evans, N. J. Miller and G. Paganga, *Free. Radical. Biol. Med.*, 20 (1996) 933.
14. N. J. Millner, C. A. Rice-Evans, M. J. Davies, V. Gopinathan and A. Milner, *Clin. Sci.*. 84 (1993) 407.
15. A. Roda, C. Russo, P. Pasini, F. piazza, G. Feroci, L. J. Kricka and M. Baraldini, *J. Biolumin. Chemilumin.,* 13 (1998) 327.
16. R. Cervellati, N. Crespi-Perellino and S. D. Furrow., *Helv. Chim. Acta*, 83 (2000) 3179.
17. T.S. Briggs and W.C. Rauscher, *J. Chem. Educ.,* 50 (1973) 496.
18. R. Cervellati, K. Honer, S. D. Furrow, C. Neddens and S. Costa, *Helv. Chim. Acta.*, 84 (2001) 3533.
19. J. Barbee and A. E. Kuznetsov, *Comput Theor Chem.*, 1 981 (2012) 73.
20. L. Tikhonova, S. Rosokha and E. Bakay, *React. Kinet. Catal. Lett.*, 63 (1998) 129.
21. R. Re. N. Pellegrini, A. Proteggente, A. Pannala, M. Yang and C. Rice-Evans, *Free. Rad. Biol.Med.,* 26 (1999) 1231.
22. N. F. Curtis and R. W. Hay, *Chem. Commun.,* 0 (1966) 524.
23. N. F. Curtis, *Dalton Trans*., 13 (1972) 1357.
24. G. Hu, L. Zhu, M. M. Guo and H. Liu, *Asian J. Chem.*, 22 (2010) 6393.
25. R. Cervellati, N. Crespi-Perellino and S. D. Furrow, *Helv. Chim. Acta*, 83 (2000) 3179.
26. M. Li, G. Hu and Y. Chen, *Food Chem.,* 197 (2016) 987.
27. R. Cervellati, C. Renzulli, M. C. Guerra and E. Speroni, *J. Agric. Food Chem*., 50 (2002) 7504.
28. R. Cervellati, K. Honer, S. D. Furrow, C. Neddens and S. Costa., *Helv. Chim. Acta*, 84 (2001) 3533.
29. J. S. Zlabur, N. Dobricevic, M. Brncic, F.J. Barba, J. M. Lorenzo, D. Franco, A. G. Atanasov, S. Voca and S. R. Brncic, *Molecules,* 24 (2019) 1202.
30. A. A. Boligon, M. M. Machado and M. L. Athayde, *Med. Chem*., 4 (2014) 517.
31. J. Lu, P. Qin, X. Han, Y. Wang and Z. Li, *Eur. Food Res. Technol*., 240 (2015) 301.
32. I. Pinchuk, H. Shoval, Y. Dotan and D. Lichtenberg, *Chem. Phys. Lipids.,* 165 (2012) 638.
33. P. Chao, S. Lin, K. Lin, Y. Liu, J. Hsu, C. Yang and J. Lai, *Nutrients*.,6 (2016) 2115.
34. K. Schlesier, M. Harwat, V. Bohm and R. Bitsch, *Free Radical Res*., 36 (2002), 177.

35. R. M. Noyes and S. D. Furrow, *J. Am. Chem. Soc*., 104 (1982) 45.
36. P. D. Kepper, and I. R. Epstein, *J. Am. Chem. Soc*., 104 (1982) 49.
37. S. D. Furrow, R. Cervellati and G. Amadori, *J. Phys. Chem. A.,* 106 (2002) 5841.
38. R. Cervellati, N. Crespi-Perellino, S. D. Furrow and A. Minghetti., *Helv. Chim. Acta*,83 (2000) 3179.
39. R.Cervellati and S.D. Furrow, *Russ. J. Phys. Chem. A.,* 87 (2013) 2121.
40. R.Cervellati, E. Greco, S. M. Blagojevic, S.N. Blagojevic, S. Anic and Z. D. Cupic, *Reac. Kinet. Mech. Cat.,* 123 (2018) 125.
41. M. Leopoldini, N. Russo and M. Toscano, *Food Chem*., 125 (2011) 288.
42. A. Munin and F. Edwards-Levy*, Pharmaceutics*, 3 (2011) 793.
43. K. Honer, R. Cervellati and C. Neddens, *Eur. Food. Res. Technol*., 214 (2002) 356.