Iron-polyphenol interaction: Its role in catalyzing colour development during sugar manufacturing

SUMMARY

of

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The polyphenols chosen for the study in this thesis are commonly found in sugar cane juice. Although, iron present in traces (5-15 ppm) in sugar. However, iron introduces in the system from equipment and machinery. Due to the presence of oxidative enzymes iron changes from ferrous to ferric and when it come contact with polyphenols. Complex formation takes place, consequently, colour is developed which imparts colour to the end product. Iron and polyphenolic compounds are important for human. However, these are considered enemy for sugar processing. Sugarcane contains many colourant compounds that could be extracted from its juice [Rupa T. R., 2008]. In 1971, a study on sugarcane juice identified chlorogenic acid, cinnamic and flavones as coloured compounds [Farber *et. al.*, 1971]. Those coloured substances (pigments) are derived from plants and can be found in raw sugar after processing [Bourzutschky, 2005]. The work embedded in this thesis concludes that polyphenols present in sugar cane juice are mainly responsible for colour development during sugar process. There is a general update that fast caramalisation catalyzed by iron and relationship between polyphenols and uptake of iron is only hypothesis without experimental data on iron polyphenols interaction which can complement the above hypothesis that as and when polyphenols comes in contact with iron is accompanied by colour formation during sugar processing. In the present study, the caffeic acid, syringic acid, chlorogenic acid, 7-hydroxy-4-methylcoumarine and 4-hydroxycoumarine were chosen as representative selection of polyphenols commonly present in cane juice and their reaction with iron was investigated with emphasis on colour development. The role of electron transfer reaction in catalysing colour formation has been proved beyond doubt that the reaction between iron and polyphenols are mainly responsible for development of colour during sugar manufacturing [Farber and Carpenter, 1972]. This study would provide substantial experiment evidences of colour formation by iron-polyphenols which can be extended to systems of significant importance such as role of electron transfer reactions in catalysing colour formation during sugar manufacturing. Therefore, their complete removal during clarification must be ensured so that the quality of the end product could be maintained [Senpei Yang, 2014]. This study hopefully appears to generate kinetic data where the application will eventually lead to the introduction of the coating of an inactive material in the surface of iron which remains in contact with cane juice and undergoes various operations and complete removal of polyphenols from cane juice must be ensured [Hurrell *et.al.*, 1999]. Such preventive measure would also be helpful in minimizing the colour development during storage of sugar as well. The objective of the present study, therefore, is to substantiate the mechanistic aspects of the interactions between Fe(III) and caffeic acid, syringic acid, chlorogenic acid, 7-hydroxy-4-methylcoumarin, 4-hydroxycoumarin employing experimental and theoretical study.

A detailed study of the complexes of the various polyphenols (caffeic acid, syringic acid, chlorogenic acid, 7-hydroxy-4-methylcoumarine and 4-hydroxycoumarine) commonly present with Fe(III) in cane juice have been synthesized, characterized, using spectral techniques.

The organization of the thesis is given below:

Chapter 1: Introduction and review of literature

Chapter 2: Experimental methods and characterization techniques

Chapter 3: Kinetics of complex formation of Fe(III) with caffeic acid: Experimental and theoretical study

Chapter 4: Kinetics of complex formation of Fe(III) with syringic acid: Experimental and theoretical study

Chapter 5 Kinetics of complex formation of Fe(III) with chlorogenic acid: Experimental and theoretical study

Chapter 6: Kinetics of complex formation of Fe(III) with 4-Hydroxycoumarine: Experimental and theoretical study

Chapter 7: Kinetics of complex formation of Fe(III) with 7-Hydroxy-4-methylcoumarine: Experimental and theoretical study

The study will broadly follow the scheme as given above. The summary of research work carried out is as follows:

Chapter 1

In this proposed work, attempt has been made to understand the role of electron transfer (E.T.) reactions in catalysing colour development in sugar processing where iron-polyphenols play an important role as control or elimination of colour formation in sugar processing is of high technical importance. Keeping in view the above problem of the sugar processing following have been proposed:-

1. To determine the kinetics and mechanism of iron-polyphenols interaction taking caffeic acid, syringic acid, chlorogenic acid, 7-hydroxy-4-methylcoumarin, 4-hydroxycoumarin as representative selection of polyphenols commonly present in cane juice.

2. Spectrophotometric, kinetics and analytical techniques will be used to investigate the kinetics of chelate formation between iron and aforesaid polyphenols.

3. Physiochemical analysis of the iron-polyphenol chelates such as pH stability, solubility, molecular weight, gustatory properties, etc. will be investigated.

4. To determine the various parameters of the isolated complexes such as hardness, electronegativity, softness, total energy, dipole moment and point group symmetry, Density Functional Theory (DFT) was used.

5. To corroborate the experiment findings of the isolated chelates in the pure chemical system by the theoretical study.

This study hopefully appears to generate kinetic data where the application will eventually lead to the introduction of the coating of an inactive material in the surface of iron which remains in contact with cane juice and undergoes various operations and complete removal of polyphenols from cane juice must be ensured. Such preventive measure would also be helpful in minimizing the colour development during storage of sugar as well.

The objective of the present study, therefore, is to substantiate the mechanistic aspects of the interactions between Fe(III) and caffeic acid, syringic acid, chlorogenic acid, 7-hydroxy-4-methylcoumarin, 4-hydroxycoumarin commonly found in cane juice employing experimental and theoretical study.

Chapter 2

Following instrumental techniques have been carried out for the characterization of synthesized Fe(III)-polyphenols complexes during research period are discussed.

a) *Scanning Electron Microscopy*: SEM examination yields information about surface features of the isolated complexes. Morphological study such as shape and size of the synthesize complexes have been carried out.

b) *UV-Visible Spectroscopy:* Colorimetric and kinetics studies of Fe(III) with polyphenols have been carried out by this spectral technique.

c) *Fourier Transform Infrared (FT-IR) Spectroscopy*: It is used to identify the types of chemical bonds in iron-polyphenols complexes.

d) *Density Functional Theory (DFT):* The theoretical study of iron-polyphenols complexes have been carried out by Gaussian 09 software.

Chapter 3

Kinetic study on the complexation of caffeic acid with ferric chloride was performed in aqueous solution at pH 9.0.

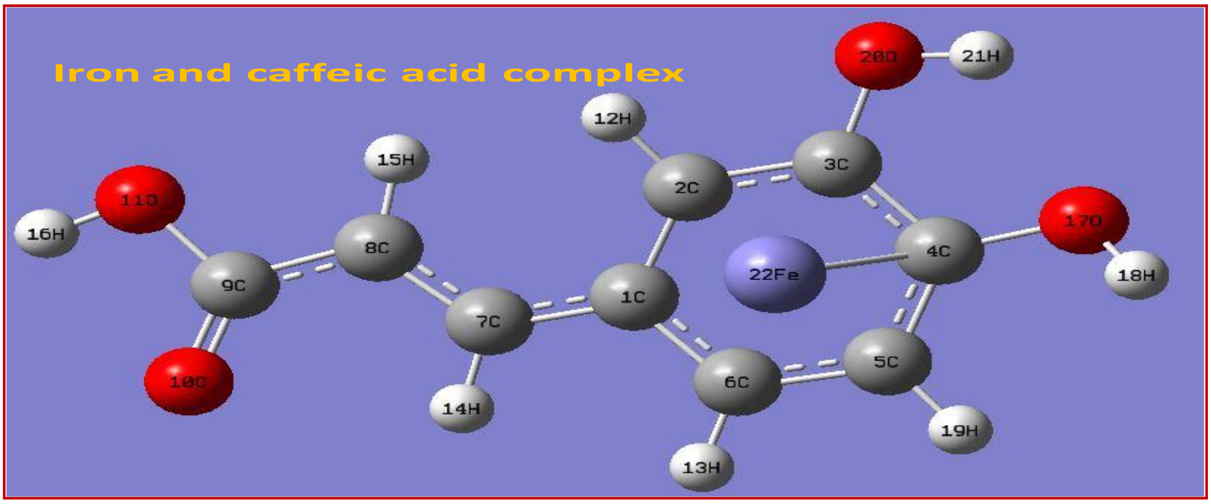


Fig. 1. Image showing complexation reaction between Fe(III) and caffeic acid by DFT method

The isolated Fe(III)-caffeic acid complex was characterized with IR, UV-Vis spectroscopic and FE-SEM techniques. The complexation reaction was found to be a first-order with rate constants for k (formation) $2.86x10^{-2}$ min^{-1}[Bukhari et.al., 2006]. This solution had a salty and slight caramel taste but again no metallic taste. The gustatory properties of the isolated complex were investigated and complex showed solution had a salty and slight caramel taste but again no metallic taste. The isolated complex was stable at pH 9.0. The apparent activation energy of the complexation reaction was evaluated to be 150 kcal/mol. However, this activation energy is inconsistent with the chemistry of Fe(III) with polyphenols which is supposed to mimic the interaction of Fe(III) with transferrin in biological media. Various parameters of the complex such as hardness, electronegativity, softness, total energy, dipole moment and point group symmetry were calculated employing Density Functional Theory (DFT) and evaluated as 0.04465, 0.2130, 22.39, 0.5201×10^{-8} eV, 15.13 Debye and C1, respectively.

Chapter 4

Kinetic study on the complexation of syringic acid with Fe(III) was performed in aqueous solution at pH 9.0. The complex was characterized with IR, UV-Vis spectroscopy and FE-SEM techniques.

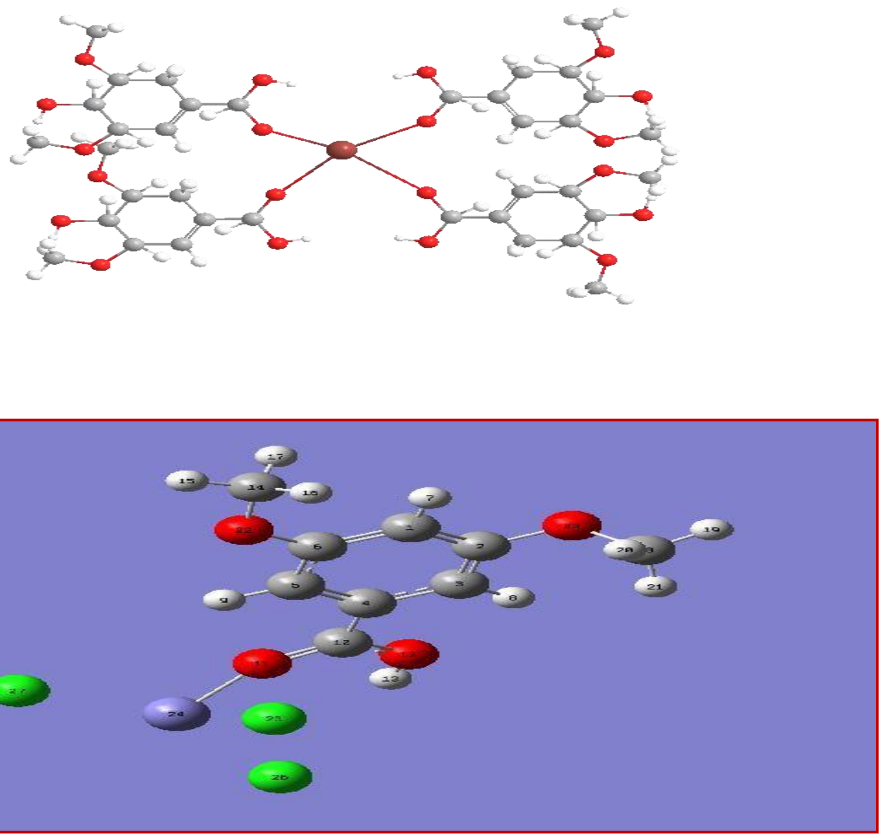


Fig. 2. Image showing complex formation of Fe(III) and syringic acid by DFT method

The complexation reaction was found to be a first-order with rate constants for k_1 (formation) 3.67×10^{-2} min^{-1}. This solution had a salty and slight caramel taste but again no metallic taste. The gustatory properties of the isolated complex were investigated and complex showed no metallic taste. Isolated complex showed tetrahedral geometry. The isolated complex was stable at pH 9.0. The apparent activation energy of the complexation reaction was evaluated to be 168 kcal/mol. Various parameters of the complex such as hardness, electronegativity, softness, total energy, dipole moment, chemical potential, electrophilicity index and point group symmetry were calculated and found as 0.153, 0.0.484, 6.52, 0.889×10^{-9} eV, 11.03 Debye, -0.484, 0.764 and C1, respectively.

Chapter 5

The kinetic study of the complexation of chlorogenic acid with ferric chloride was performed using UV–Vis absorption spectroscopy.

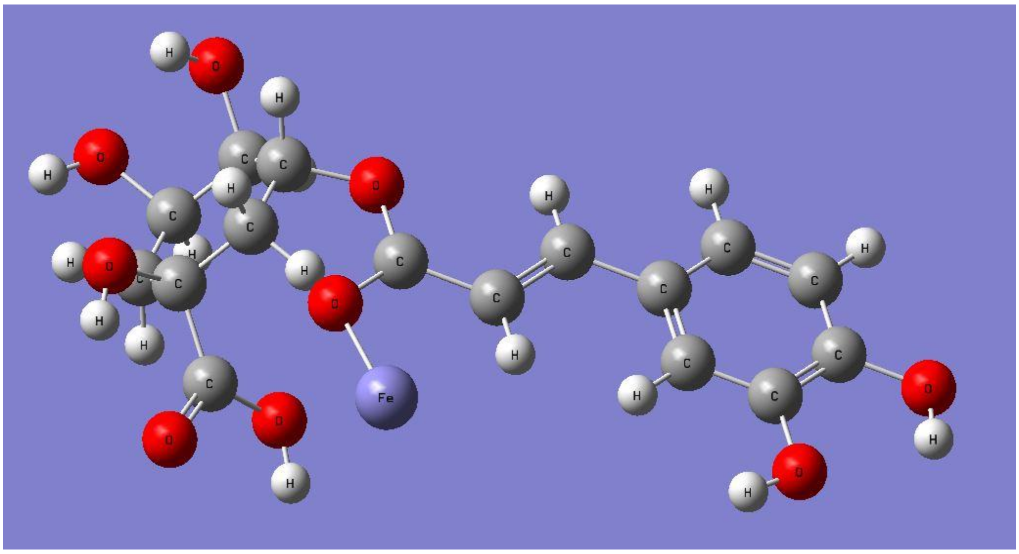


Fig. 3. Image showing complex formation of Fe(III) and syringic acid by DFT method

The colour complexation reaction was found to be first-order with rate constants for k (formation) 2.4×10^{-2} min^{-1} for Fe(III)-chlorogenic acid complex. The gustatory property of the isolated complex was investigated and complex showed no metallic taste. The isolated complex was stable at pH 12.0. The isolated complex was stable at pH 12.0. The DFT study of Fe(III)-chlorogenic acid complex provided hardness (1.0121), electronegativity (0.456), softness (8.26), total energy (0.106×10^{-9} eV), dipole moment (16.62 Debye), chemical potential (-0.456), electrophilicity index (0.859) and point group symmetry (C1).

Chapter 6

Kinetic study on the complexation of 4-Hydroxycoumarine with Fe(III) was described in aqueous solution at pH 11.0 together with a reappraisal of spectral evidence for chelate formation.

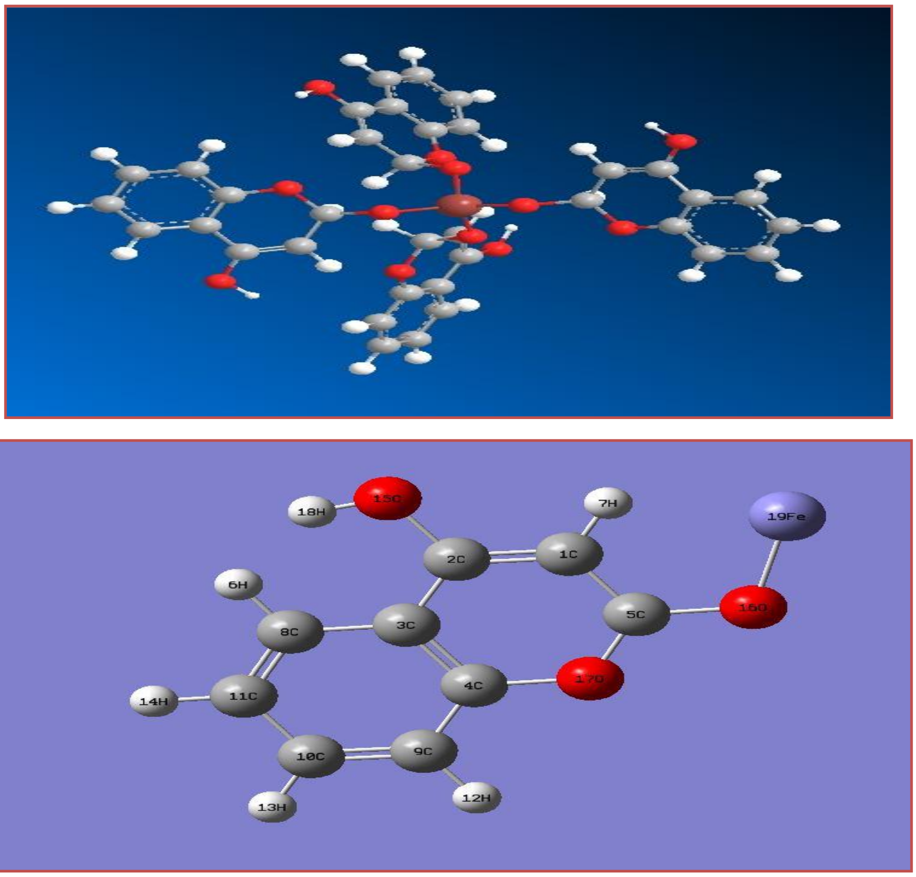
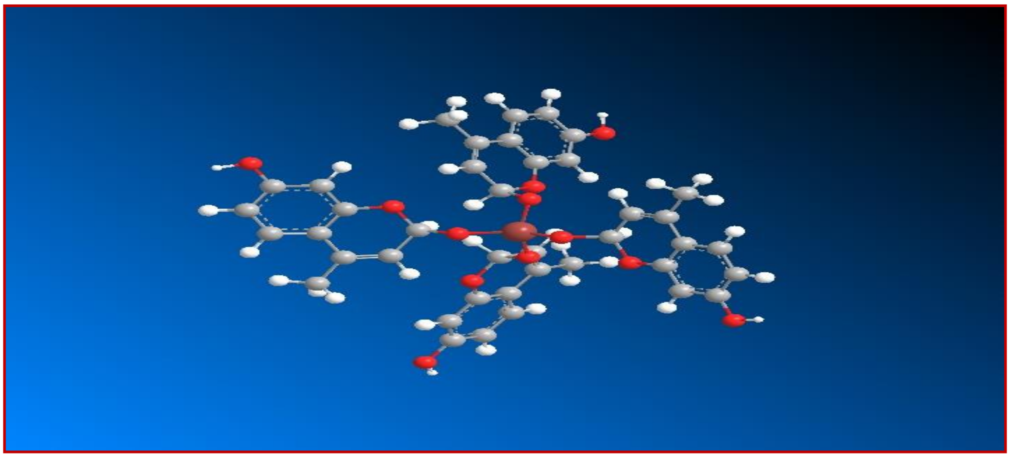


Fig. 4. Image showing complex formation of Fe(III) and 4-hydroxycoumarin by DFT method

The complexation reaction betbeen Fe(III)-4-hydroxycoumarine was found to be a first-order with rate constants for k_1 (formation) 4.35×10^{-4} min^{-1}. Additionally the effect of concentration and temperature on the complexation reaction was investigated [Fiallo Marina, 1999]. The gustatory properties of the isolated complex were investigated and complex showed no metallic taste. The complex was stable in tetrahedral geometry. The isolated complex was stable at pH 11.0. The apparent activation energy of the complexation reaction was evaluated to be 181 kcal/mol. The DFT study used for evaluation of various parameters of the studied complex showed hardness (0.153), electronegativity (0.484), softness (6.52), total energy (0.889×10^{-9} eV), dipole moment (11.03 Debye), chemical potential (-0.484), electrophilicity index (0.764) and point group symmetry (C1).

Chapter 7

Kinetic study on the complexation of 7-hydroxy-4-methylcoumarine with Fe(III) was described in aqueous solution at pH 10.0 together with a reappraisal of spectral evidence for chelate formation. The complexation reaction was found to be a first-order with rate constants for k_1 (formation) 6.1×10^{-4} min^{-1} [Hynes. M.J. and Coinceanainn M.O., 2004. The dried compound was only slightly salty with no metallic taste whatever. This solution had a salty and slight caramel taste but again no metallic taste. The gustatory properties of the isolated complex were investigated and complex showed no metallic taste. The isolated complex was stable at pH 10.0. The apparent activation energy of the complexation reaction was evaluated to be 995 kcal/mol. The isolated complex showed tetrahedral geometry. DFT study shows that the isolated complex of Fe(III) and 7-hydroxy-4-methylcoumarine was formed in tetrahedral geometry. Various parameters of the isolated complex such as hardness, electronegativity, softness, total energy, dipole moment, chemical potential, electrophilicity index and point group symmetry were evaluated using DFT method and were found as 0.2264, 0.4793, 4.41, 0.179×10^{-9} eV, 9.78 Debye, -0.4793, 0.5066 and C1, respectively.



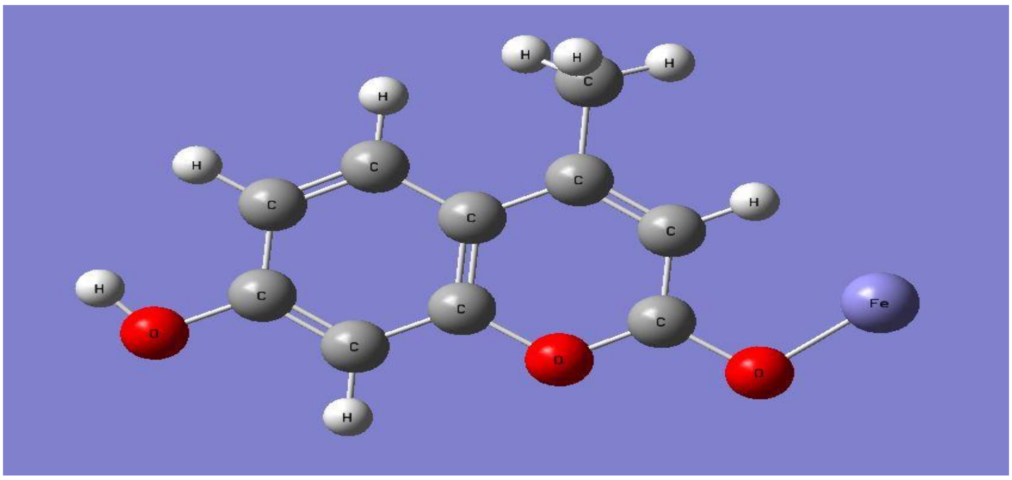


Fig. 5. Images complex formation of Fe(III) and 7-hydroxy-4-methylcoumarin by DFT method

Reference

1. Bourzutschky H.C.C. Color formation and removal - Options for the sugar and sugar refining industries: a review. *Zuckerind..*, 130 **(2005)** 470-475.
2. Farber L, Carpenter, FG. Mcdonald, E J., Separation of colorants from cane sugar. *Int. Sug. J.*, 69 **(1971)** 323-328.
3. Farber L., Carpenter, F.G., Mcdonald E J., Separation of colorants from cane sugar. *Int. Sug. J.*, 69 **(1972)** 323-328.
4. Rupa T. R., Asokan S., Effect of rind pigments and juice colorants on juice claribility, settling time and mud volume of sugarcane., *Sugar Tech*., 10 **(2008)** 109-113.
5. Victor R. Deitz, Color Evaluation in the Cane Sugar Industry, *J. Res. Nat. Bur. Std..*, 57 (3) **(1956)** 159-170.
6. Hurrell R.F., Reddy M., Cook J.D., Inhibition of non-haem iron absorption in man by polyphenolic-containing beverages., *Brit. J. Nutr.*, 81 **(1999)** 289– 295.
7. Senpei Yang., The interaction of phenolic acids with Fe(III) in the presence of citrate as studied by isothermal titration calorimetry., *Food Chem*., 157 **(2014)** 302–309.
8. Bukhari S. B., Memonb S., Tahir M. M., Bhanger M. I., Synthesis, characterization and antioxidant activity copper-quercetin complex., *Spectrochim. Act. A*., 71 (2006) 1901–1906.
9. Fiallo Marina M. L., Drechsel Hartmut., Solution Structure of Iron (III)-Anthracycline Complexes., *J. Med. Chem*., 42 **(1999)** 2844-2851.
10. Hynes. M.J. and Coinceanainn M.O., The kinetics and mechanisms of reactions of iron (III) with caffeic acid, chlorogenic acid, sinapic acid, ferulic acid and naringin., *J. Inorg. Biochem*., 98 **(2004)** 1457–1464.