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INFLUENCE OF HYDROXYCINNAMIC ACIDS ON THE OXY-RADICAL GENERATED IODIDE/HYDROGEN PEROXIDE REACTION SYSTEM

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ABSTRACT

The influence of hydroxycinnamic acids (HCA): caffeic acid, chlorogenic acid, and p-coumaric acid, on the potassium iodide/hydrogen peroxide system was investigated. A linear correlation between absorption maximum of triiodide (I_3^-) at 351 nm and HCA concentration was found. In the presence of HCA, reaction yield of I_3^- was found to increase in following order p-coumaric < chlorogenic \leq caffeic acid. This is attributing to their oxy-radical scavenging activity. Results obtained in this study have showed correlation between antioxidant activities of HCA and their ability to enhanced I_3^- production.

INTRODUCTION

Recent investigations have showed that KI/H₂O₂ reaction system abound with free radical species. Namely, the EPR spin-trapping investigation of KI/H₂O₂ reaction system have provided clear evidence on the existence of hydroperoxyl radical (HOO \cdot) and hydroxyl radical (HO \cdot) as intermediary species [1,2]. Thus, KI/H₂O₂ reaction system can be considered as an easy available laboratory source of reactive oxygen species (ROS). It will be of great interest to investigate the effect of most famous antioxidant compounds on the oxy-radicals generated KI/H₂O₂ reaction. It is well-known that the function of antioxidants is to intercept and react with free radicals at a rate faster than substrate [3]. Therefore, antioxidants can be considered as free radical scavengers. Phenolic compounds, widely present in plant kingdom, stand out as the most efficient group of antioxidants [4,5].

EXPERIMENTAL

The chemicals used in this study were: potassium iodide, KI (p.a grade, Merck), hydrogen-peroxide, H₂O₂ (30%, p.a. Merck) and caffeic acid, p-coumaric acid and chlorogenic acid (all used HCA were from Sigma-

Aldrich, p.a. grade). The solutions were prepared with deionised water with resistivity 18.2 M Ω cm (Milli-Q purification system). The stock solutions were: 0.06 mol dm⁻³ KI, 0.125 mol dm⁻³ H₂O₂, and the hydroxycinnamic acids: 1.66 $\times 10^{-4}$ mol dm⁻³ caffeic, 1.97 $\times 10^{-4}$ mol dm⁻³ *p*-coumaric, and 1.47 $\times 10^{-4}$ mol dm⁻³ chlorogenic acid. The reaction mixture is always contained the same concentration of KI and H₂O₂, while the concentration of particular HCA was varied. Volume of reaction mixture was 3 cm³. The characteristic UV/VIS absorption peak was recorded at 351 nm, wavelength of I₃⁻ absorption maximum. The iodide – peroxide – hydroxycinnamic acid system was monitored for 180 s with 10 s step size. All experiments were done at ambient temperature (23 °C).

RESULTS AND DISCUSSION

The UV/VIS absorption spectra of the KI/H₂O₂ reaction system in the presence of *p*-coumaric acid, in various concentrations, are shown in the Fig. 1. The absorption spectra were recorded 180 s after the reaction initiation. The increase of I₃⁻ yield (increase of absorption at 351 nm) with the increasing concentration of caffeic acid can be observed. The same trend is obtained when caffeic or chlorogenic acid are introduced in to the iodide-peroxide system. [5].

Since certain amount of I₃⁻ will be generated even in the absence of HCA, spectra denoted with 0 $\mu\text{mol dm}^{-3}$ concentration in Fig. 1, the absorbance at 351 nm which originate from generated I₃⁻ in the absence of HCA (A_0^{351}) should be taken as background, and subtracted from the measured absorbance value (A_{HCA}^{351}) in the presence of HCA. Therefore, the difference ΔA_{351} , $\Delta A_{351} = A_{HCA}^{351} - A_0^{351}$, will be used in this study As shown in Fig. 2, the linear correlation between ΔA_{351} and concentration of HCA was observed in all cases. It is noteworthy that magnitude of enhanced I₃⁻ production in the system was found to increase in following order *p*-coumaric acid < chlorogenic acid \leq caffeic acid.

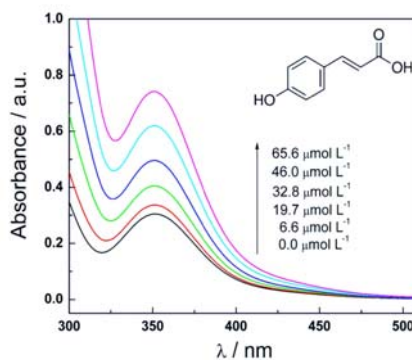


Figure 1. Absorption spectra of the KI/H₂O₂ system, in the presence of different concentrations of *p*-coumaric acid.

Accordingly, it seems to be possible connecting the antioxidant activity of investigated acids with their ability to enhance production of I_3^- . Some rough calculations of the Bond Dissociation Enthalpies (BDE) of O-H bonds in these molecules were complete, using the additively rules proposed by Wright et al. [6]. As the reaction with radicals and generic antioxidant (ArOH) becomes more exothermic, the energy barrier necessary for reaction occurring should

decrease, and the antioxidant will react faster with the radicals, thus preventing reaction with substrate. Phenolic compounds which contain only one hydroxyl group attached to their aromatic ring are less effective antioxidants if compared with ones that possess second hydroxyl in the ortho or para position [6,7]. Therefore, caffeic and chlorogenic acid, with two OH groups, are a better free-radical scavenger than coumaric acid (one OH group). Due to BDE theory CAFF and CGA acids have a similar antioxidant activity $\Delta BDE = (-9.2-4.7) \text{ kcal/mol} = -13.9 \text{ kcal/mol}$, while *p*-CM is weaker antioxidant $\Delta BDE = -4.7 \text{ kcal/mol}$ [6]. In the calculations we assimilate the side chain has the same effect as $-\text{CH}=\text{CH}_2$ group, since Wright claimed that groups three bonds far from an OH group have little effect on BDE. The results which suggest that CAF is slightly better free radical scavenger than CGA obtained in this study are supported by work Chen et al. [7].

CONCLUSION

The influence of hydroxycinnamic acids on oxy-radical generated iodide-peroxide reaction was investigated. This influence was considered by monitoring the formation of I_3^- as the final product of iodide-peroxide reaction. The linear correlation between I_3^- absorption (ΔA_{352}) and the concentration of hydroxycinnamic acids was found. The different HCA cause the different increases of triiodide production ($p\text{-CM} < \text{CGA} \leq \text{CAF}$). Our preliminary results show that it should be possible to connect the antioxidant activity of these acids with their ability to produce more I_3^- .

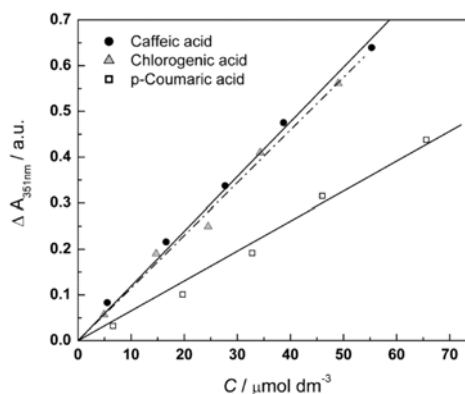


Figure 2. Linear correlation between ΔA_{352} and the concentration of hydroxycinnamic acids.

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REFERENCES

- [1] D. Stanisavljev, M. Milenkovic, M. Mojivic, A. Popovic-Bijelic, *Journal Physical Chemistry A*, 2011, 115, 2247-2249.
- [2] D. Stanisavljev, M. Milenkovic, M. Mojivic, A. Popovic-Bijelic, *Journal of Physical Chemistry A*, 2011, 115, 7955-7958.
- [3] S. Wright, E. Johnson, G. DiLabio, *Journal of American Chemical Society*, 2001, 123, 1173-1183.
- [4] R. Cervellati, C. Renyulli, M. Guerre, E. Speroni, *Journal of Agricultural and Food Chemistry*, 2002, 50, 7504-7509.
- [5] S.Ž. Gorjanović, M.M. Novaković, N.I. Potkonjak, I. Leskošek-Čukalović, D.Ž. Sužnjević, *Journal of Agricultural and Food Chemistry*, 2010, 58, 744-751.
- [6] S. Wright, E. Johnson, G. DiLabio, *Journal of American Chemical Society*, 2001, 123, 1173-1183.
- [7] J. H. Chen, C.-T. Ho, *Journal of Agricultural and Food Chemistry*, 1997, 45, 2374-2378.