ANTIOXIDANT POTENTIAL OF SELECTED PHENOLIC ACIDS – A THEORETICAL APPROACH

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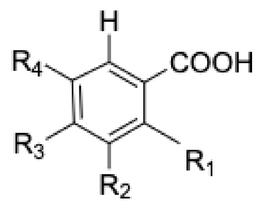
Introduction

Phenolic acids are a group of phenolic compounds and can be found in various fruit, vegetables and nuts. Their structure is composed of a benzene ring connected to carboxylic functional group and they can be grouped into two groups: hydroxybenzoic and hydroxycinnamic acids. Hydroxybenzoic acids contain 7 C atoms, while hydroxycinnamic acids have 9 C atoms (Fig. 1.). Aside from that, phenolic acids differ in the number and position of substituents, e.g. hydroxyl and methoxyl groups, on the aromatic ring. These are highly bioactive compounds with different types of bioactivity, such as antiviral, antioxidant, anticancer, antidiabetic activity, etc. Antioxidant activity has great importance in fighting diseases based on oxidative stress, such as cardiovascular and neurodegenerative diseases, some types of cancer, age-related diseases, diabetes, etc.



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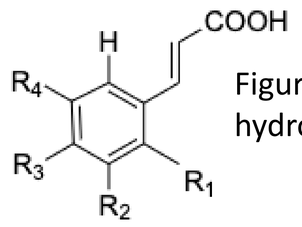

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Figure 1. Structure of hydroxybenzoic (1.) and hydroxycinnamic acids (2.).

Mechanisms of antioxidant activity

Until now, many mechanism of antioxidant activity have been proposed. They can be generally grouped into two types of processes – processes based on hydrogen atom donation and processes based on radical adduct formation. In this work, several mechanisms based on both types of processes have been studied. They are hydrogen atom donation (HAT), single electron transfer followed by proton transfer (SET-PT), sequential proton loss electron transfer (SPLET) and radical adduct formation (RAF) mechanism.

Brief review of theoretical studies of antioxidant potential of hydroxybenzoic acids

Authors	Year	Studied compound	Computational method	Mechanisms	Results
Zhang *et al.*	2011	ellagic acid, it's derivates and metabolites	B3LYP/6-31+G(d,p)	HAT, SET-PT, SPLET	ellagic acid and derivates have better antioxidant activity than metabolites, SET-PT and SPLET less favourable that HAT
Kalita *et al.*	2012	gallic acid (GA), methyl gallate (MEG), ethyl gallate (EG), 4,5-dihydroxy-3-methoxy benzoic acid (OME)	B3LYP/6-31G(d,p)/PCM	HAT, SET	For BDE: GA > OME > MEG > EG For IP: GA > MEG > EG > OME
Mazzone *et al.*	2013	isonasutin, nasutin A, ellagic acid and it's derivate	B3LYP/6-311++G (3df,2p)/ CPCM	HAT, SET-PT, SPLET	ellagic acid derivative showed the best antioxidant activity (lowest BDE), HAT preferred in all studied solvents
Milenković *et al.*	2017	6 DHBA	M05-2X/6-311++G(d,p)/SMD	HAT, SET-PT, SPLET	HAT preferred in nonpolar medium, SPLET in polar, SET-PT inoperative mechanism

Brief review of theoretical studies of antioxidant potential of hydroxycinnamic acids

Authors	Year	Studied compound	Computational method	Mechanisms	Results
Urbaniak *et al.*	2012	trans-*p*-coumaric and trans-sinapic acid	B3LYP/6-311+G(2d,2p)/CPCM	HAT, SET-PT, SPLET	SET-PT not preferred, SPLET preferred in polar medium
Urbaniak *et al.*	2013	stereoizomers of ferulic scid	B3LYP/6-311++G (2d,2p)/ PCM	HAT, SET-PT, SPLET	HAT optimal in vacuum, SPLET preferred in polar medium
Mazzone *et al.*	2015	caffeic and ferulic acid and their derivates	M05-2X/6-311++G(d,p)/SMD	HAT, SET-PT, SPLET	caffeic acid slightly better than ferulic, HAT preferred
Saqib *et al*.	2016	chlorogenic acid	B3LYP/6-311G	HAT, SPLET	HAT optimal in vacuum, SPLET preferred in polar medium
Borgohain *et al*.	2016	ferulic acid and its esters	B3LYP/6-31+G(d,p)/PCM	HAT, SET	HAT preferred in nonpolar, SET in polar medium, esters show better antioxidant activity than ferulic acid
Tošović *et al*.	2017	chlorogenic acid	M06-2X/6-31++G(d,p)/CPSM	HAT, SET-PT, SPLET, RAF	SPLET preferred in polar, H AT and RAF slightly dependant on solvent polarity
Amić *et al*.	2017	quercetin, caffeic, hydrocaffeic, homoprotocatechuic, protocatechuic acid, 4-methylcatehol, catechol	M05-2X/6-31++G(d,p)/SMD	HAT, SPLET	catechol metabolites more efficient that quercetin, SPLET preferred in polar medium
Mansouri *et al.*	2020	caffeic, ferulic, sinapic and *p*-coumaric acid	M05-2X/6-31+G(d,p)/SMD	HAT, SET-PT, SPLET	HAT preferred in vacuum, SPLET preferred in pentyl ethanoate, ethanol and water

Conclusion

Phenolic acids are a group of phenolic compounds that show significant antioxidant potential. Based on analysed studies, mechanism underlying antioxidant potential of phenolic acids in nonpolar medium is HAT, while in polar medium preferred mechanism is SPLET. However, it is important it note that studies presented here refer to thermodynamics only and don't take kinetics of studied processes into account.