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The dual role of phenolic compounds in oxidative changes in fruit products

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Abstract

This study was conducted to reconcile the controversial scientific evidence indicating the dual role of phenolic compounds in oxidative changes in fruit products. The hypothesis has been substantiated, according to which the functioning of flavonoids as redox-systems, is strictly connected with the ability of fruit phenolic compounds to inhibit the free-radical processes of the oxidation of substrates; this is due to the semiquinone presence in the equilibrium system. Terminology and appropriate methods of studying, in respect of the antioxidant effect of natural, as well as added compounds in fruit products, were analysed. The effect of redox-properties of the antioxidant agent, on studying the inhibition of the enzymatic oxidation of phenolic compounds with this agent, has been analysed. It was shown that this field of study is vital for improving the concepts of browning inhibitors in foodstuffs, as well as for improving the theory of interactions between components in canned foodstuffs.

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Introduction

Terms in respect of fruit phenolic compounds

Depending on the type of carbon skeletons, fruit phenolic substances were divided into three groups: flavonoids with C_6-C_3-C_6 structure; cinnamic acid derivatives with C_6-C_3 structure; phenolcarbonic acids with C_6-C_1 structure (Zaprometov, 1964). The term "fruit polyphenols" is used to define phenolic compounds in their monomeric forms such as cyanidin; pelargonidin, etc. and their glycosides (Sioud and Luh, 1966; Scoricova, 1973; Tsao, 2010; Watson *et al.*, 2014). Contemporary authors also call them polyphenolic substances (Kratchanova, 2010; Georgieva and Mihaylova, 2015), phenolic compounds (Martinez and Whitaker, 1995; Zheng and Wang, 2001; Balasundrama *et al.*, 2006; Mertz *et al.*, 2007; Wojdylo *et al.*, 2007; Huand *et al.*, 2010; Cheynie, 2012), and polyphenolic compounds (Handique and Baruah, 2002; Ignat *et al.*, 2011; Sasikumar *et al.*, 2015; Sripakdee *et al.*, 2015). The chemical structure of flavonoids allows them to be classified as diphenols. The term 'polyphenol' is historically used and is well matched with 'polyphenol oxidase (PPO)', which is used for the enzyme catalysing oxidation process in plants, and fruit pulps (Yoruk and Marshall, 2003; Kolodziejczyk *et al.*, 2010). Therefore, the terms 'phenolic compound', and 'polyphenol' are both acceptable for describing the monomeric forms of flavonoids, cinnamonic acid derivaties, and phenolcarbonic acids. Today, the term 'polyphenol' not only includes phenolic acids, and flavonoids, but also stilbenes, lignans, and polymeric lignans (Gharras, 2009; Bahadoran *et al.*, 2013; Keerthi *et al.*, 2014). The polymeric forms of fruit phenolic compounds are often referred to as tannins (Martinez and Whitaker, 1995; Caballero, 2013).

Comparative characteristics and terms in respect of the antioxidant effect of fruit phenolic compounds

The antioxidant effect of fruit phenolic substances has been extensively studied (Van Acker *et al.*, 1996; Calado *et al.*, 2015; Georgieva and Mihaylova, 2015; Korotkova *et al.*, 2015). The common definition 'antioxidant' is used for substances, which prevent or inhibit the oxidation process (Choe and Min, 2009; Flora, 2009). The antioxidant effect has been defined as an ability to protect against free radicals (Georgieva and Mihaylova, 2015). The modern quantitative methods of antioxidant activity evaluation are based on free radical absorbance capacity (Fedina *et al.*, 2010; Korotkova *et al.*, 2015).

The classical definition of antioxidants, according to which antioxidants must be readily oxidized (Housecroft and Constable, 2006) will be used in this article. Such substances include hydroquinone (Housecroft and Constable, 2006). The substances with low redox potential are classical antioxidants

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(Vetter, 1967). The classical antioxidant used in the fruit canning industry is ascorbic acid (Ramaswamy and Marcotte, 2005; Flaumenboum *et al.*, 2006; Adria, 2009). The mechanism of antioxidant action includes transforming the antioxidant into its oxidized form while other substances convert from its oxidized form into reduced form. For such an ability of antioxidants there is another definition referred to as the reducing power (Georgieva and Mihaylova, 2015). There is data of measuring this parameter in comparison with vitamin C (Georgieva and Mihaylova, 2015).

As can be seen from the above, there is not a unified approach to the characterisation of the antioxidant properties of phenolic substances of fruit products. However, there is no doubt about the antioxidant properties of cathechins as redox systems, and as an inhibitor of free radical oxidation of substrates (Zaprometov, 1964; Akannia *et al.*, 2014; Preedy, 2014).

Negative role of fruit phenolic compounds and methods for reducing oxidative browning

It has been shown that among the main negative changes, which take place in raw fruit materials during processing, there are oxidative polyphenol conversions, and polymerisation of products of oxidative reaction (Marh *et al.*, 1985; Sharma *et al.*, 2002; Boekel *et al.*, 2010). Indeed, the damage to cell structures during processing leads to a stopping of the Palladin scheme. The interaction between: phenolic compounds, enzymes, and oxygen, during grinding, heating, or freezing of raw materials leads to the forming of brown pigments. It has been shown that dark-coloured compounds can be formed due to the interactions between quinones with proteins (Scoricova, 1973). It has been demonstrated that the monomeric forms of plant phenolic substances, such as catechins, and anthocyanins, affect negative colour changes in fruit products during processing and storage (Manach *et al.*, 2004; Brownmiller, 2008). The browning of canned fruit products, because of non-enzymatic oxidation of phenolic compounds, has been shown to be an essential part in quality deterioration during storage (Sharma *et al.*, 2002; Bharate, 2014).

Therefore, the oxidative browning of food products is an inevitable process caused by the nature of these foodstuffs. The importance of organoleptic properties of foodstuffs causes the fact that scientists today are still investigating new methods and new substances to reduce oxidative processes in fruit products (Dyidogan and Bayindirli, 2004; Gacche et al., 2004; Suh and Park, 2011; Wu, 2014).

Among these methods are the removal of phenolic compounds by β-cyclodextrins (Osuga *et al.*, 1994), or by ultrafiltration (Alper and Acar, 2004), as well as eliminating phenolic compound activity by methylation (Bezusov *et al.*, 2002). However, the changes in chemical structure could affect the polyphenols' capacity to protect against free-radical oxidation of substrates.

Among methods, which could reduce oxidative processes, the most effective are inactivating the plant enzyme systems, and adding antioxidants (Thutnham, 1992; Pizzocaro, 1993; Leopoldini *et al.*, 2011). It was reported on the heat inactivation of PPO (1, 2-benzenediol: oxygen oxidoreductase) by applying temperatures of >50^{o}C (Martinez and Whitaker, 1995). There are recommendations of using the antioxidant agents, such as glutathione, to prevent browning in different products, including apple juice (Gacche *et al.*, 2004), grape juice (Wu, 2014); meat products (Wu, 2013), and white wine (El Hosry *et al.*, 2009). The authors explanations are different in respect of the positive effect of glutathione on browning inhibition, and include the antioxidant properties (Kishkovsky and Skurihin, 1988; El Hosry *et al.*, 2009) of glutathione as well as the inhibition of the enzyme activity by glutathione (Gacche *et al.*, 2004). It was reported on the capacity of glutathione to prevent both enzymatic and non-enzymatic browning (Wu, 2013, 2014). The controversies in explanations of the browning inhibition data with glutathione show the difficulties of investigation of PPO activity inhibition in the case of using antioxidants as enzyme inhibitors.

The importance of the investigation of the real process can be proved by the fact that the incorrect conclusion in respect of substance to be the PPO inhibitor can cause a high level of browning of canned foodstuffs processed at low heat level.

Positive role of fruit phenolic compounds

The positive effect of plant phenolic compounds was mentioned by many authors (Block and Patterson, 1992; Van Acker *et al.*, 1996; Ren *et al.*, 2003; Siriwoharn *et al.*, 2004; Ivanova *et al.*, 2005; Katalinic *et al.*, 2006; Celiktar *et al.*, 2007; Heinonen, 2007; Wojdylo *et al.*, 2007; Céspedes, 2008; Atawodi *et al.*, 2009; Dai and Mumper, 2010; Girones-Vilaplana, 2012).

The wide spectrum of the positive role of phenolic compounds could be recognized according to the following facts: first, diatomic phenols can inhibit the processes of liquid-phase oxidation of carbohydrates (Nikolaevskiy, 1978); second, there are facts about positive effect of phenols on the inhibition of the processes of enzymatic oxidation of substrates (Krylov *et al.*, 1993; Araji *et al*., 2014); third, it has been proved the antioxidant capacity of fruit polyphenolic substances (Pastrana-Bonilla *et al*., 2003; Du and Ma, 2009; Ramful et al. 2011; Murillo, 2012; Sasikumar *et al*., 2015); fourth, our previous data (Bocharova, 2008) showed the positive effect of phenolic compounds of citrus fruits on vitamin C stability, and in this way conserving the biological value of products. Previous data (Bocharova *et al*., 2016) showed that reducing ability of phenolic compounds of fruit juices redox systems affected different types of spontaneous redox reactions, which is vital for fruit foodstuffs containing benzoates in respect of the products of benzoic acid reduction.

Such a scientific controversy, in respect of the positive and negative roles of phenolic compounds in fruit products quality formation, influences the necessity of detailed analysis of this subject. The methods of preventing oxidative browning should not cause deterioration of the positive properties of fruit phenolic compounds. This substantiates the importance of the above mentioned objective.

Research task formulation

As can be seen from the above, the contradiction between the positive and negative effects of phenolic compounds on the quality of fruit products necessitates the forming of a hypothesis, which could reconcile the controversial scientific evidence. The conflicting new data necessitates forming a hypothesis on studying the browning prevention in fruit products, with respect to using an antioxidant agent as an oxidative enzyme inhibitor. This field of study is especially important for providing the competitiveness of fruit foodstuffs, as well as for establishing a scientific base for fruit products manufacturing.

To achieve the objectives of the study, it is necessary to perform the following tasks:

(1) to analyse the role of phenolic compounds as participants of oxidative changes in fruit products;

(2) to analyse the possible connection between the functioning of flavonoids as redox-systems and the ability of plant phenolic compounds to inhibit the free-radical processes of oxidation of substrates;

(3) to analyse the possibility of glutathione to be the inhibitor of oxidative enzymes;

(4) to formulate the recommendation for hypothesis-testing research.

Discussion

Fruit phenolic compounds as participants of oxidative changes in food products

Principal possibility for phenolic compounds to have redox properties

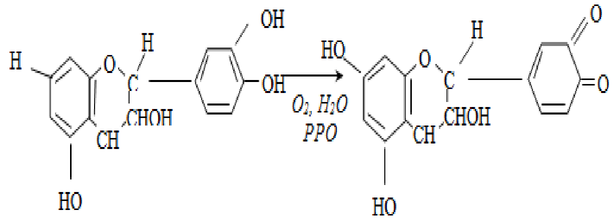

Figure 1. Transformation of catechins into quinone forms

Fruit phenolic compounds can have conjugated bonds with oxygen atoms. It is possible to establish the reversible redox potentials in organic systems, in which there are molecules with conjugated bonds with oxygen atoms or amino groups (Vetter, 1967). It was shown that section of substances can be converted into during the reduction process.

Similar redox-reactions have been determined for phenolic substances of fruits (Zaprometov, 1964). The first product of oxidation of catechin is quinone (Zaprometov, 1964; Martinez and Whitaker, 1995; Araji *et al*., 2014). Therefore, oxidation can lead to quinones formation in fruit products (Figure 1).

The phenolic compounds with low standard redox-potential as possible reducing agents for some components of food system

The oxidation-reduction reactions must be in accordance with the thermodynamic abilities of the processes (Housecroft and Constable, 2006). The spontaneous processes in a system with different redox couples, are the oxidation of reduced forms of substance of redox-couple with more negative standard reduction potential (Eh_0), while oxidized forms of substance of redox-couple with more positive Eh_0 are reduced (Housecroft and Constable, 2006).

It was demonstrated in our previous work (Bocharova, 2008), that the polarisation curves of citrus juice redox-systems are situated in more negative region of potential in comparison with that of the ascorbic acid/dehydroascorbic acid couple. This explains the long stability of vitamin C in orange juice (Tressler and Jocelyn, 1957; Hui, 2006) and proves the idea about the possibility of diatomic phenols to be the inhibitors in the processes of liquid-phase oxidation of carbohydrates (Nikolaevskiy *et al*., 1978).

To prove ours hypothesis it is necessary to study the standard redox-potentials of different flavonoids, such as hesperidin, naringenin, eriodictiol etc.

Phenolic compounds with high standard redox-potential as substances that need antioxidants

On the contrary, the high Eh_0 of catechins

Table 1. Normal redox potentials in aqueous solutions (Kishkovsky and Skurihin,1988)

The electrode	Eh_0 (mV) at pH	
	3	7
Glutathione reduced/ glutathione oxidized	—	40
SO_2 / SO_4^{2-}	200	—
Ascorbic acid/dehydroascorbic acid	210	—
Anthocyans reduced/ anthocyans oxidized	270	—
Tartaric acid/ dihydroxyfumaric acid	220	—
Dihydroxyfumaric acid/ diketosuccinic acid	—	300
Catechins reduced/ Catechins oxidized	430	—

(Table 1) shows the necessity of using antioxidants to prevent their conversion into an oxidized form. Such a preventer could be ascorbic acid (Table 1) or other redox-couples with more negative Eh0. The reducing of oxidized forms of catechins while ascorbic acid is converting into dehydroascorbic acid is thermodynamically favourable reaction (Table 1) and can explain the antioxidant effect of ascorbic acid on catechins. Indeed, we can see from Table 1 (Kishkovsky and Skurihin, 1988), that Eh_0 of ascorbic acid/dehydroascorbic acid couple is less positive than that for catechins reduced/catechins oxidized couple. Therefore, the process of converting quinones into their reduced forms by using ascorbic acid is spontaneous, and this effect results in the inhibition of browning processes in fruit products (Scoriciva, 1973).

As can be seen from above, when food system enzymes are inactivated, the product quality will be mainly affected by the direction of redox-reactions. The role of phenolic compounds in fruit products, with respect to its redox-properties, is caused by redox-potentials. Actually, certain fruit phenolic compounds can provide vitamin C stability, and have an antioxidant effect, but some need antioxidants added to prevent their oxidation conversions into quinones, the polymerisation process, and deterioration of the colour of fruit products.

The inhibition of non-enzymatic oxidative processes with antioxidant agents in fruit products

As can be seen from the above, the non-enzymatic browning, which is connected with phenolic compound oxidation, includes:

1) oxidation of phenolic compounds to quinones (Martinez and John, 1995);

2) further transformation of quinones, including the polymerization process.

The presence of a reducer, such as ascorbic acid, or glutathione, in food systems due to their redox-properties leads to the opposite process of converting quinones into reduced forms. The authors reported about non-enzymatic browning inhibition with glutathione (El Hosry *et al*., 2009; Wu, 2014). To prove the mechanism of the inhibition of browning in fruit products with glutathione, the standard redox-potential of glutathione should be lower than the standard redox potential of fruit phenolic compounds. As can be seen from Table 1, the value of the standard redox-potential of glutathione is significantly lower than that for catechins. Therefore, the antioxidant effect of glutathione is not in doubt.

Analysing the effect of an antioxidant agent on redox-reactions in fruit systems containing PPO

The rate of oxidative processes can be enhanced with catalysts (Nelson and Cox, 2008). Such a catalyst for oxidative changes of phenolic compounds in fruit products is PPO. The class name of this enzyme is oxidoreductases. Enzymes of this class catalyse the transfer of electrons (Nelson and Cox, 2008), and provide for the conversion of phenolic compounds into quinones (Araji *et al*., 2014). PPOs are found in different higher plants, including fruits (Siddiq and Cash, 2000; Jang and Moon, 2011; Kasikci and Bagdatlioglu, 2016), vegetables (Vamos, 1981; Hunt *et al*., 1993; Vitti *et al*., 2011; Hui and Evranuz, 2015), tea (Martinez and Whitaker, 1995).

The effect of substrate concentration on the velocity of an enzyme-catalysed reaction is a fundamental truth in classical biochemistry (Nelson and Cox, 2008). Therefore, the velocity of enzyme-catalysed reactions increase when antioxidant agents, such as ascorbic acid or glutathione increase the amounts of substrate for PPO, because of reducing the quinones forms of diphenols into its reduced forms (Hutchings, 1994). The velocity of reduction oxidized forms of polyphenols, with an antioxidant agent, can be so significant that this reaction prevails under the reaction of enzymatic oxidation. Such an effect can be illustrated by the popular method of adding ascorbic acid before juicing. In this process, the predominance of the non-enzymatic reduction of quinones over the enzymatic oxidation of diphenols was demonstrated. The velocities of both processes are reflected in the overall direction of the reaction. Such a predominance is possible due to the saturation effect of enzymatic reactions (Nelson and Cox, 2008). Therefore, it is possible to note the effect of decreasing the oxidized forms of substrate in the presence of both an antioxidant agent, and PPO. Such an effect was observed in grape juice (Wu, 2014). The PPO effect on the oxidizing process could be temporary eliminated in such a way. Antioxidant properties of glutathione (Kishkovsky and Scurihin, 1988) allow us to suggest that the anti-browning effect of this agent is due to its reduction action on the oxidized form of phenolic compounds.

The enzyme inhibitor must interfere with catalysis, and as a result, to slow or halt the enzymatic reaction. The data, gained by the scientists show that the same agent, such as glutathione, can be credited with having the properties of an inhibitor of oxidative enzyme activity in fruit products, as well as in meat (Gacche *et al*., 2004; Wu, 2014). These data call attention to the lack of specific activity of the agent, which is not well correlated with the classical theory of enzyme inhibition (Nelson and Cox, 2008). Biochemists use kinetic reaction studies to prove this. There are approaches for the control of PPO activity based on antisense techniques (Biord, 1991). X-ray crystallography and site-directed mutagenesis have been used to control PPO activity (Wagner and Benkovic, 1990). Classical methods based on analysing the Mixaelis-Menten equation can be used for investigating the activity of an agent as the enzyme inhibitor (Nelson and Cox, 2008). It was reported on high reproducibility of results of studying the enzymatic oxidative process with using the Mixaelis-Menten equation, and obtaining in such a way the data for offering the mechanism of reaction (Rogozhin and Peretolchin, 2010). The velocity of oxidized form conversion into reduced form with an antioxidant agent, credited with having PPO activity inhibition, should be checked, and compared with data from kinetic studies. The indirect methods in respect of using the antioxidant agents would not allow to obtain unambiguous results.

Matching the redox properties of fruit phenolic compounds with data according to which polyphenols can inhibit the free-radical processes of the oxidation of substrates

The possibility of phenolic compounds to be the inhibitors of free-radical oxidation of substrates was shown by many scientists (Azatyan *et al.,* 1973; Dinis *et al.*, 1994; Gerebin, 1994; Tang, 2001; Pazos, 2005; Lee *et al.*, 2006; Mielnik, 2006; Celiktar, 2007; Georgieva and Mihaylova, 2015).

The mechanism of the inhibition of free-radical oxidation of substrates in fruit beverages was represented (Gerebin, 1994) by the equation:

$$RO_2^{\bullet} + PhO^{\bullet} \rightarrow \text{products},$$

where $RO_2^{\bullet}$ is a free radical, and $PhO^{\bullet}$ is a phenolic compounds.

$$\begin{cases} Q + H^{+} \leftrightarrow HQ^{+} \text{ — chemical equilibrium;} \\ HQ^{+} + \bar{e} \leftrightarrow HQ \text{ — reaction of the transition} \\ 2HQ \leftrightarrow Q + H_2Q \text{ — chemical equilibrium.} \end{cases}$$

$$\overline{H_2Q \leftrightarrow Q + 2H^{+} + 2\bar{e}},$$

where Q is ortho-quinoid form of cyanidin; H_2Q is ortho-diphenolic form of cyanidin; HQ is semiquinone.

Figure 2. The mechanism of redox conversion of anthocyans

The founding of semiquinone presence in quinone/hydroquinone system (Vetter, 1967), as well as our previous results, according to which there is a presence of semiquinone in the cyanidin reduced/cyanidin oxidized system (Bocharova, 2008), allow us to offer the semiquinone form of diphenols as an inhibitor of free-radical oxidation of substrates in plant food products. Indeed, the mechanism of redox conversion of anthocyans was presented as shown in Figure 2 (Bocharova, 2008).

The mechanism of redox conversions of diphenols helps in understanding their positive role in the inhibition of free-radical processes of oxidation of substrates. Above mentioned do not deny the possibility of diphenols polymerisation. It is clear that reduced forms of diphenols cannot take part in such a process. As can be seen from the above, the presence of semiquinones in the equilibrium systems of plant flavonoids, such as anthocyans etc., and the chemical possibility, as well as the facts of inhibition the free-radical processes of oxidation of substrates with polyphenols, prove the vital role of semiquinones in this process.

Conclusion

(1) The two main theories, according to which the phenolic compounds in fruit products may be initiators of oxidation process, as well as its inhibitor, are the two sides of one redox phenomenon.

The phenolic compounds of redox-system of fruits with high reducing ability could act like antioxidants, and increase the stability of vitamin C; other phenolic compounds, with low reducing ability, like catechins, need to be reduced with such reducing agents as ascorbic acid or glutathione. The redox-potential of polyphenols is the main factor, which effects the direction of non-enzymatic oxidative changes in fruit products. The value of standard redox-potential of polyphenolic substances can be the criterion for predicting the direction of redox - conversions in fruit products.

To prove this, it is advisable to study the standard redox potentials of such polyphenols as hesperidin, tangerine, and eriodictiol, by classical volt-amperometric method (Vetter, 1967). The redox-potentials of the above mentioned flavonoids should be less positive than the redox-potential of ascorbic acid/dehydroascorbic acid couple to prevent browning in fruit products, and than the potential of tartaric acid/dihydroxyfumaric acid couple, as well as of dihydroxyfumaric acid/ diketosuccinic acid couple to prevent the oxidation of tartaric acid.

(2) The functioning of flavonoids as redox-systems are strictly connected with their ability to inhibit the free-radical processes of oxidation of substrates due to the semiquinone presence in the equilibrium system.

To prove this it is advisable to study the process of inhibition of the free-radical processes of oxidation of substrates with:

quinone/ hydroquinone system in which the presence of semiquinones can be neglected;

highly substituted quinones, such as tetra-methyl-benzoquinone, in equilibrium systems of which there are substantial amounts of semiquinones (Vetter,1967).

(3) The glutathione can prevent browning of fruit products because of its low redox-potential, but not as inhibitor of PPO activity.

To prove this hypothesis, and investigate the activity of an agent with antioxidant properties as an enzyme inhibitor, the velocity of oxidized form conversion into reduced form, with such an agent, should be checked, and compared with data of kinetic studies for the resulting process. The classical methods based on analysing the Mixaelis-Menten equation are preferable.

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