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Phenolics, Selenium, Vitamin C, Amino Acids and Pungency Levels and Antioxidant Activities of Two Egyptian Onion Varieties

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Abstract: Selenium, vitamin C, pungency, amino acids, phenolics content and antioxidant activities of two Egyptian onion varieties, namely white (Giza-6) and red (Beheri) onions have been studied. Data analysis showed that the red variety presents higher values for selenium, vitamin C and sulphur-containing amino acids. Concerning pungency, white onion can be classified as intermediate pungency (8.24 μmol of Pyruvic acid/100 g fresh wt.) and red as pungent (11.37 μmol of pyruvic acid/100 g fresh wt.). The phenolic acids, flavonols, anthocyanins and total phenolics content in red variety (81.59, 70.38, 7.56 and 187.17 mg/100 g fresh wt., respectively) were higher than for white variety (72.47, 32.49, 4.90 and 131.65 mg/100 g fresh wt., respectively). Consequently, antioxidant activity was higher for the red variety. Correlation analysis indicates that phenolic compounds beside other factors including Se and sulphur-containing amino acid contents play the major role in the antioxidant activity of onion bulbs. The antioxidant capacity of freeze dried powder from both onion varieties was also tested in sunflower oil-in-water emulsions and hydroperoxide formation was monitored during storage at 40°C. In accordance with differences in Se, sulphur-containing amino acid and phenolics content, Egyptian red onions had better antioxidant activity, while white onions was only effective in the early stages of the oxidation process. These data indicates that red variety has higher potential health benefits related to the presence of antioxidant compounds.

Key words: White onion, red onion, methanolic extract, emulsion, peroxide value

INTRODUCTION

Onions (*Allium cepa* L.), have world-wide importance, ranking second among all vegetables in economic importance after tomatoes (Griffiths *et al.*, 2002). The average intake in the world is 7 kg capita⁻¹ year⁻¹, being Libya (32 kg capita⁻¹ year⁻¹) and Turkey (27 kg capita⁻¹ year⁻¹) the main consumers (FAOSTAT, 2005). In Egypt, onion is the third vegetable more consumed (15 kg capita⁻¹ year⁻¹), after potato and tomatoes and it is cultivated all over the country concentration in delta area and Upper Egypt (84.3% of total area) and new land areas (15.7%), being white (Giza-6) and red (Beheri) onions the most produced varieties. The current production area is being around 122,552 Feddan with total production 1.3 million ton. According to the physical and chemical properties, the red onion variety is predominant in the Egyptian diet while the white onion directed to

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dehydration process. Dehydrated onion production has increased by at least 40% over the past ten years with current production being around 10,000 metric ton year⁻¹.

Beside the nutritional value and unique flavour, onion shows a variety of pharmacological and nutritional effects such as growth-inhibition of tumor and microbial cells, immunostimulatory properties, enhancing reproduction, improving the growth performance (body weight gain, feed consumption and feed conversion), reduction of cancer risk and protection against cardiovascular diseases, diabetes as well as ageing, which are attributed to phenolic compounds (flavonoids, antocyanins, phenolic acids and flavonols), organosulphur compounds, vitamins and some minerals (Teyssier *et al.*, 2001; Furusawa *et al.*, 2003; Kamal and Daoud, 2003; Campos *et al.*, 2003; Gabler *et al.*, 2003; Ismail *et al.*, 2003; Wang *et al.*, 2005). Also, the ability of these compounds to acts as antioxidants has been demonstrated in the literature. Several researchers have investigated the antioxidant activity of flavonoid compounds and have attempted to define the structural characteristics of flavonoids that contribute to their activity (Nieto *et al.*, 1993; Foti *et al.*, 1996; Santas *et al.*, 2008). Phenolic acids, such as caffeic, chlorogenic, ferulic, sinapic, p-coumaric acids, vanillic, syringic and p-hydroxybenzoic appear to be active antioxidants (Larson, 1988; Ibrahim *et al.*, 2004). Vitamin C has a protective function against oxidative damage and a powerful quencher of singlet oxygen (1O_2), hydroxyl (OH) and peroxy (RO_2) radicals (Niki, 1991). Antioxidant activity is fundamental property important for life. Many of the biological functions, such as antimutagenicity, anticarcinogenicity and antiaging, among others, originate from this property (Hung and Ferrao, 1992; Cook and Samman, 1996).

The aim of this study is to quantify the selenium, vitamin C, pungency, sulphur-containing amino acids, phenolic compounds and antioxidant activity of two Egyptian onion varieties. Also, the antioxidant capacity of the onion samples was determined by measurement of hydroperoxide formation in stored sunflower oil-in-water emulsions, in order to study effects in a model food system.

MATERIALS AND METHODS

Materials

Onion samples were obtained from the most widespread local cultivar in the typical area of production, red onion (Beheri) from Tala City, Minufiya Governorate and white onion (Giza-6) from Bani Mazar city, Minia Governorate, Egypt.

Chemicals and Reagents

Phenolic compounds, sodium pyruvate standards and alumina column were purchased from Fluka Chemical Co., Switzerland, while vitamin C, amino acids, α -tocopherol, butyhydroxy anisitol (BHA) and butylhydroxy toluene (BHT) standards from Sigma Chemical Co., St. Louis, Mo. All other reagents and solvent were of analytical or HPLC grade were purchased from (Fisher, UK). De-ionized water (Milli-Q 18.2 M Ω) was used in the preparation of the mobile phases, reagent solutions and standards.

O-phathaldehyde 2-mercaptoethanol (OPA-2ME) reagent was prepared according to Lindroth and Mopper (1979) with minor modification. Briefly, 27 mg amount of OPA was dissolved in 0.5 mL of methanol and 5 mL of 0.1 M sodium tetraborate (pH 9.65) are added, followed by 20 μ L of 2-ME. The reagent is kept overnight before use and the strength was maintained by addition of 10 mL 2-ME every week.

Equipment's

In the present study, a SP Thermo Separation Products Liquid Chromatograph (Thermo Separation products, San Jose, CA, USA) was used with a pump Consta Metvic 4100, a Spectra Series AS100, Spectra System UV 1000 UV/Visible Spectrophotometer Detector, Spectra System FL 3000 and a PC 1000 system software. The columns used were reversed-phase water Spherosorb ODC-2 (3 μ M; 150 \times 4.6 mm I.d., Alltech USA) for phenolics; a guard column 7.5 \times 3.2 mm containing 5 μ m, C-18 reversed phase Econosphere was attached directly to a reversed-phase C-18 column (3 μ m; 150 \times 4.6 mm I.d. (Alltech, Carnforth Lancashire, UK) for amino acids and a reversed-phase water Adsorbosil C₁₈ (5 μ M, 100 \times 4.6 mm I.d., Alltech USA) for vitamin C analysis.

Experimental Design

This research project was conducted in Nutrition and Food Science Department, Minufiya University, Shebin El-Kom, Egypt from the year 2006 to 2008. After harvesting (mid of March, 2007), the onion samples were stored with skins for three months at an average temperature of 25 \pm 2°C. When bulbs were ready for sale (Mid of June), twenty bulbs for each sample were selected to obtain the representative samples. Analysis were carried out on the edible portion (only the internal part of bulbs) and the results are represented as the mean value of five samples (fresh weight \pm SD). Other samples were prepared for antioxidant evaluation in oil-in-water emulsion as follow: onions were skinned, chopped, blended and finally freeze-dried. The freeze-dried onions were ground in a mortar, in order to obtain a fine powder and were stored at 4°C in the dark and dry atmosphere until used.

Analytical Methods

Selenium

Bulbs defatted samples are digested as described by Singh *et al.* (1991), selenium analyzed in ICP-MS, using a PerkinElmer, Inc., Model D-6355A in the Central Lab., SEOES, Plymouth University, UK.

Vitamin C

Vitamin C was extracted according to the methods of Moeslinger *et al.* (1994). The chromatographic conditions were flow rate, 1 mL min⁻¹; detection, UV absorption at 254 nm, volume of injection, 20 μ L; temperature, room temperature and mobile phase composition was an isocratic system of 100% methanol.

Amino Acids

Amino acids were analyzed in HPLC according to the method of Lindroth and Mopper (1979) with some modifications. For OPA-2-ME derivatives, a 200 μ L of onion sample hydrolysates or standard mixture of amino acids was mixed with 20 μ L of iodoacetic acid (0.8 M in 0.1 M sodium borate buffer, pH 10.5) and 150 μ L of 0.1 M sodium borate buffer (pH 11.5). After incubation for 30 sec at room temperature 20 μ L of OPA-2-ME reagent was added and after 30 sec 40 μ L of the reaction mixture was injected onto the HPLC system. A gradient elution using methanol was performed for better analytes separation and column cleansing prior to subsequent injections. The elution profile was : 0-2 min, 5-10% B; 2-11 min, 10-35% B; 11-20 min, 35-65% B; 20-22 min, 65-100% B; 22-24 min, isocratic 100% B; 24-30 min, 100-5% B. Separations were performed at ambient temperature using a flow rate 1.5 mL min⁻¹. The fluorescence detector was set to operating at 340 nm in the excitation and 455 nm in the emission mode.

Phenolic Acids

Fresh onion bulbs were cut into small cubes, which were placed into freeze-drying jars and then frozen in liquid nitrogen. The frozen samples were lyophilized (Birchover Ltd., Letchworth, Herts) for 72 h then grounded in a wily mill (Tecator, Boulder, Co., USA) fitted with 60-mesh screen sieve. The obtained samples powder were packed in opaque air tied bags and stored at -20°C until HPLC analysis. The phenolic acid extracts were prepared according to the method of Onyenko and Hettiarachchy (1993). The chromatographic conditions were as following: Flow rate, 1 mL min⁻¹; detection, UV absorption at 265 nm, fluorescence Ex: 250 nm - Emλ: 400 nm; volume of injection, 20 μL and temperature, room temperature. The mobile phase composition was an isocratic system of methanol and ammonium acetate buffer, pH 5.4 (12 : 88, v/v).

Flavonols

Flavonols were extracted and analyzed in HPLC according to the method of Hertog *et al.* (1992). Sample peaks were quantified with the external standard method.

Anthocyanins

The anthocyanins were extracted from onion tissues by suspending 1.5 g of homogenized tissue in 5 mL of methanol (0.1% HCl) at room temperature for 10 min. The extract was filtered and used for HPLC analysis as described by Fossen *et al.* (1996) with some modifications described by Gennaro *et al.* (2002).

Pungency

Pyruvic acid concentration was determined using the Schwimmer and Weston (1961) method. A representative sample (15 quarters, one from each bulb) of each cultivar was crushed in an electric mincer, incubated with 2, 4-dinitrophenylhydrazine and read the absorbance at 420 nm on a spectrophotometer for total pyruvic acid concentration, that were determined against a sodium pyruvate standard curve.

Antioxidant Activity

Minced bulbs (5 g) were extracted with 80% aqueous methanol (100 mL) on an orbital shaker for 120 min at 25°C. The mixture was subsequently filtered (Whatman No. 5) on a Buchner funnel and the filtrate was assayed for antioxidant activity. Antioxidant activity of onion extracts and standards (α-tocopherol, BHA and BHT) was determined according to the β-carotene bleaching method following a modification of the procedure described by Marco (1968). Antioxidant activity was calculated in four different ways. In the first, absorbance was plotted against time, as a knit curve and the absolute value of slope was expressed as antioxidant value (AOX). Antioxidant Activity (AA) was all calculated as percent inhibition relative to control using the following equation (Al-Salkhan *et al.*, 1995).

$$AA = \frac{R_{\text{control}} - R_{\text{sample}}}{R_{\text{control}}} \times 100$$

where, R_{control} and R_{sample} were the bleaching rates of β-carotene in reactant mixture without antioxidant and with plant extract, respectively.

The third method of expression based on the Oxidation Rate Ratio (ORR) was calculated according to the method of Marinova *et al.* (1994) using the Equation:

$$ORR = \frac{R_{\text{sample}}}{R_{\text{control}}}$$

where, R_{control} and R_{sample} are the same in the earlier equation.

In the fourth method, the Antioxidant Activity Coefficient (AAC) was calculated as described by Mallett *et al.* (1994).

$$AAC = \frac{Abs_{S_{120}} - Abs_{C_{120}}}{Abs_{C_0} - Abs_{C_{120}}} \times 1000$$

Where:

$Abs_{S_{120}}$ = The absorbance of the antioxidant mixture at time 120 min

$Abs_{C_{120}}$ = The absorbance of the control at time 120 min

Abs_{C_0} = The absorbance of the control at zero time

Total Phenolics

Two grams of the minced bulb was extracted for 2 h with 20 mL of 80% MeOH containing 1% hydrochloric acid at room temperature on an orbital shaker set at 200 rpm. The mixture was centrifuged at 1000 g for 15 min and the supernatant decanted into 4 mL vials. The pellets were combined and used for total phenolics assay. Total phenolics were determined using Folin-Ciocalteu reagent (Singleton and Rossi, 1965). Results are expressed as ferulic and equivalents.

Antioxidant Evaluation in Oil-In-Water Emulsion

Oil in water emulsions were prepared with 1% of Tween 20 emulsifier and 10% of sunflower oil, previously filtered through alumina column, as described by Yoshida (1993), in order to remove the tocopherols. The oil was added dropwise to the aqueous samples containing emulsifier cooled in an ice-bath, while sonicating for 5 min in total. Freeze-dried powder of both kinds of samples were added directly to the emulsion and homogenized, obtaining final concentration of 10, 20 and 30 mg mL⁻¹. For control, no sample was added. All emulsions were stored in triplicate in 25 mL amber bottles in the dark and allowed to oxidize at 40°C. Peroxide Value (PV) was measured periodically using aliquots of 0.005-0.1 g of each sample and determined by the ferric thiocyanate method (Frankel, 1998) after calibrating the procedure with a series of oxidized oil samples analysed by the AOCS Official Method Cd 8-53.

Statistical Analysis

An analysis of variance was performed to compare differences between varieties using Student t-test. The correlation studies were performed by using MINITAB 12 computer program (Minitab Inc., State College, PA).

RESULTS AND DISCUSSION

Selenium, Vitamin C, Pungency and Amino Acids Levels

The red onion has higher levels of Se and ascorbic acid respect to the white onion (Table 1). The present data are in accordance with that obtained by Rodrigues *et al.* (2003) who found that Povoá red onion in Northwest Portugal has higher level in minerals than the white one. This variation explained that the effect of regional varieties, environment beside

Table 1: Selenium, vitamin C, pungency and sulphur-containing amino acids levels of onion varieties per 100 g of edible portion

Components	Variety		Significant
	White	Red	
Se (mg)	1.05±0.11	1.68±0.09	**
Vitamin C (mg of ascorbic acid)	13.84±2.90	14.63±4.70	NS
Pungency (µmol of pyruvic acid)	8.24±1.28	11.37±2.04	**
Sulphur-containing amino acids (SAA)			
Cysteic	41.00±1.70	63.00±3.40	***
S-CM cystein (S-carboxy methyl cystein)	58.00±4.20	65.00±6.20	*
Cystine	26.00±1.40	47.00±1.70	**
Methionine	33.00±2.00	51.00±3.40	***

NS: Non significant. *, **, ***Significant at $p<0.05$, $p<0.01$ and $p<0.0001$, respectively

the genetic factors. A higher level of Se in both white and red onion bulbs varieties could be played a significant role in nutritional point of view as a functional plant food. The amounts of white and red onion bulbs consumed by adultman to cover the daily requirements in Se (70 µg) were 6.6 and 4.1 g, respectively. Selenium (Se) is an essential trace element. Its importance for human and animal metabolism has become apparent more recently, spurred by the discovery of a Se-dependent enzyme, glutathione peroxidase (widely distributed in tissues) and suggestive evidence that selenium plays a role in the prevention of certain forms of cancer (Linder, 1991; Packer, 1992).

The studying of amino acid profiles indicated that the red onion has higher levels of sulphur-containing amino acid than the white once (Table 1). Sulphur-containing amino acids with other organo-sulphur compounds are known to be very important for onion flavour biosynthesis (Randle, 1997).

Although, onions have a significant nutritional and medicinal value to the human diet, they are primarily consumed for their unique flavour and for their ability to enhance the flavour of other foods (Kopsell and Randle, 1997). Flavour intensity in onion is dominated by organosulphur compounds arising from the enzymatic decomposition of S-alk(en)yl-L-cysteine S-oxide flavour precursors and the primary products produced include pyruvate, ammonia and sulphenic acids (Ketter and Randle, 1998). Sweetness in onion is a balance between single sugars and pungency and onions may be classified as to pungency in: very sweet (1-4 µmol pyruvic acid g⁻¹ fresh wt.); sweet (5-7 µmol pyruvic acid g⁻¹ fresh wt.); intermediate pungency (8-10 µmol pyruvic acid g⁻¹ fresh wt.); pungent (11-15 µmol pyruvic acid g⁻¹ fresh wt.) very pungent (>15 µmol pyruvic acid g⁻¹ fresh wt.). In this study, white variety is classified as intermediate pungency and red as pungent (Table 1). Consumption of the more pungent onion variety resulted in a more pronounced reduction in total blood cholesterol, low density lipoprotein and triglycerides, than the milder pungent cultivars (Gabler *et al.*, 2003).

Phenolic Compounds

The term of phenolic compound embraces a wide rang of compound plant substances, which possess in common an aromatic ring bearing one or more hydroxyl substituents. They most frequently occur combined with sugar glycoside and usually located in the cell vacuole. Among the natural phenolic compounds, of which several thousand structures are known, the flavonoids form the largest group but simple monocyclic phenols and phenolic acids, anthocyanins, phenylpropanoids, tannins and phenolic quinones all exist in considerable numbers. Phenolic acids are a group of phenolic compound, which may be identified as hydroxycarboxylic acids with phenolic hydroxyl groups (Harborne, 1998). These acids are

either associated with lignin combined as ester groups or present in the alcohol-insoluble fraction of the leaf, alternatively they may be present in the alcohol-soluble fraction bound as simple glycosides.

The present data indicated that two phenolic acids subgroup are found in onion i.e., benzoic and cinnamics. The red onion contains higher levels of total phenolic acids detected. Chlorogenic acid represents the major phenolic acids predominance (more than 90%) in both varieties (Table 2). All of these data are partially in accordance with that found by others (Emam *et al.*, 2002). No vanillin and caffeic acids were found in these onion varieties. Many of detected phenolic acids in onion exhibits their antioxidative (Deschamps *et al.*, 1991; Laranjinha *et al.*, 1994), anticarcinogenic (Gali *et al.*, 1991; Hartig *et al.*, 1996) and antibacterial (Nakane *et al.*, 1990; Nowosielska *et al.*, 1991) effects.

Flavonoids are built upon a diphenylpropane skeleton (C₆-C₃-C₆) in which the three-carbon bridge between the phenyl groups is usually cyclized with oxygen. They are generally present in plants bound to sugar as glycosides and any one flavonoid aglycone may occur in a single plant in several glycosidic combinations. Flavonoids widely present in vegetables such as onions, are potent antioxidants (Hertog *et al.*, 1993). Two flavonoids subgroup are found in onion, the anthocyanins, which impart a red/purple colour to some varieties and flavonols, such quercetin and kaempferol, responsible for the yellow and brown skins of many varieties (Griffiths *et al.*, 2002). Such as shown in Table 2 the red onion contains higher levels of all flavonoids detected including flavonols and anthocyanins. Major flavonols in both onion varieties are quercetin compounds, quercetin-3, 4'-diglucosides and quercetin-4'-glucoside. For anthocyanins, delphinidin derivatives are predominant in both onion varieties as found by Rodrigues *et al.* (2003). Several studies reported that the red bulb colour is influenced by anthocyanin contents (Griffiths *et al.*, 2002; Rodrigues *et al.*, 2003).

Table 2: Phenolic compounds levels in onion varieties (mg/100 g of edible portion)

Phenolic acids	Variety		Significant
	White	Red	
Benzoic			
Gallic	0.84±0.07	1.09±0.10	**
Protocatechuic	1.68±0.11	3.14±0.64	***
p-hydroxybenzoic	0.00	0.90±0.17	---
Vanillin	0.00	0.00	---
Cinnamics			
Chlorogenic	68.45±3.71	74.96±5.32	**
Caffeic	0.00	0.00	---
p-coumaric	0.36±0.05	0.23±0.02	**
Ferulic	1.03±0.12	0.98±0.09	NS
Cinnamic	0.11±0.04	0.29±0.07	***
Total	72.47±4.90	81.59±7.87	**
Flavonols			
Quercetin-4-glucoside	18.68±2.34	41.74±4.09	***
Quercetin-3-4-diglucoside	12.42±1.29	25.80±3.12	***
Kaempferol-3-O-glucoside	0.79±0.15	1.04±0.08	**
Quercetin	0.41±0.07	1.17±0.12	**
Isoquercetin	0.19±0.03	0.63±0.07	***
Total	32.49±4.25	70.38±6.23	***
Anthocyanins			
Delphinidin diglucosylglucoside + petunidin diglucoside	2.44±0.22	4.15±0.44	**
Delphinidin glucosylglucoside	2.03±0.11	2.97±0.23	*
Delphinidin	0.27±0.06	0.31±0.09	NS
Petunidin	0.16±0.03	0.13±0.05	NS
Total	4.90±0.82	7.56±0.98	**

NS: Non significant. *, **, ***Significant at p<0.05, p<0.01 and p<0.0001, respectively

With the nutritional point of view, it has been demonstrated that humans absorb part of the quercetin glucosides accumulating them as quercetin conjugates in the blood plasma (Ioku, 2002). Quercetin prevents oxidation of Low Density Lipoproteins (LDL) *in vitro* by scavenging to free oxygen radicals. Its intake was inversely associated with coronary heart mortality possibly because flavonoids are able to inhibit platelet aggregation *in vitro* (Hollman *et al.*, 1996; Furusawa *et al.*, 2003). Also, many flavonoids exhibit a wide range of biological effects, including antibacterial, antiviral, anti-inflammatory, antiallergic, antithrombotic and vasodilatory actions (Cook and Samman, 1996).

Antioxidant Activity

The antioxidant activity and total phenolics of white and red onion varieties are shown in Table 3. The decrease in absorbance of β -carotene in the presence of different methanolic onion extracts (and well-known antioxidants used as standards) with the oxidation of β -carotene and linoleic acid is shown in Fig. 1. The antioxidant activity of red onion bulbs methanolic extract is superior to in white onion when it was calculated by the four different methods used in this study.

In the correlation analysis, important differences were found between phenolics, Se, vitamin C, pungency and sulphur-containing amino acids levels and antioxidant activity of onion bulbs (Fig. 2a-d, 3a-d). When all onion varieties were included in the statistical analysis, there was a positive significant ($p < 0.05$) relationship between phenolics [phenolic acids ($R^2 = 0.8617$), flavonols ($R^2 = 0.9027$), anthocyanins ($R^2 = 0.89.55$), total phenolics ($R^2 = 0.9254$)], Se ($R^2 = 0.8108$) and sulphur-containing amino acids ($R^2 = 0.8828$) and antioxidant activity. Also, no correlations were observed between the vitamin C and

Table 3: Antioxidant activity and total phenolics of methanolic extracts of onion varieties

Variety	Antioxidant value AOX (A/h)	Antioxidant activity AA (%)	Oxidation rate ratio (ORR)	Antioxidant activity coefficient (AAC)	Total phenolics (mg/100 g of edible portion)
White	0.182±0.011	67.83±2.21	0.321±0.020	351.51±23.11	131.65±19.17
Red	0.155±0.009	72.65±3.09	0.273±0.012	435.30±30.14	187.17±33.89
Control	0.569±0.023	0.00	1.000±0.090	0.00	
BHT (50 mg L ⁻¹)	0.076±0.012	86.54±1.89	0.134±0.018	676.77±11.98	
BHT (200 mg L ⁻¹)	0.010±0.002	98.31±1.06	0.017±0.008	881.39±21.00	
α -tocopherol (50 mg L ⁻¹)	0.011±0.003	98.11±0.90	0.019±0.005	877.91±18.56	

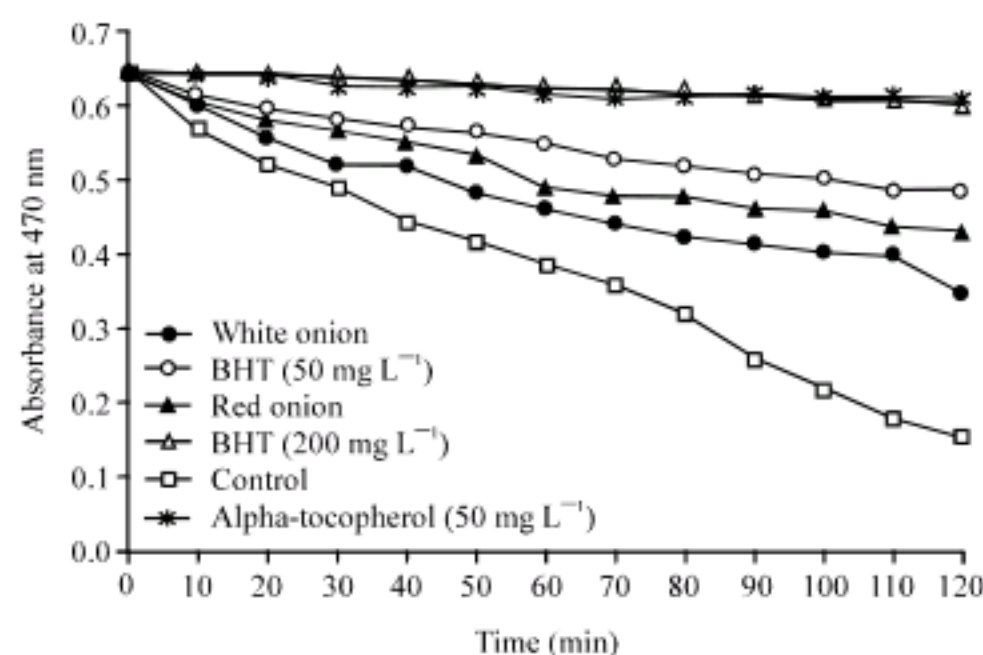


Fig. 1: Antioxidant activity (Abs at 470 nm) of methanolic extracts of onion bulbs assayed by the β -carotene bleaching method (BHT at 50 mg L⁻¹ and 100 mg L⁻¹ and α -tocopherol at 50 mg L⁻¹ concentrations were used as references)

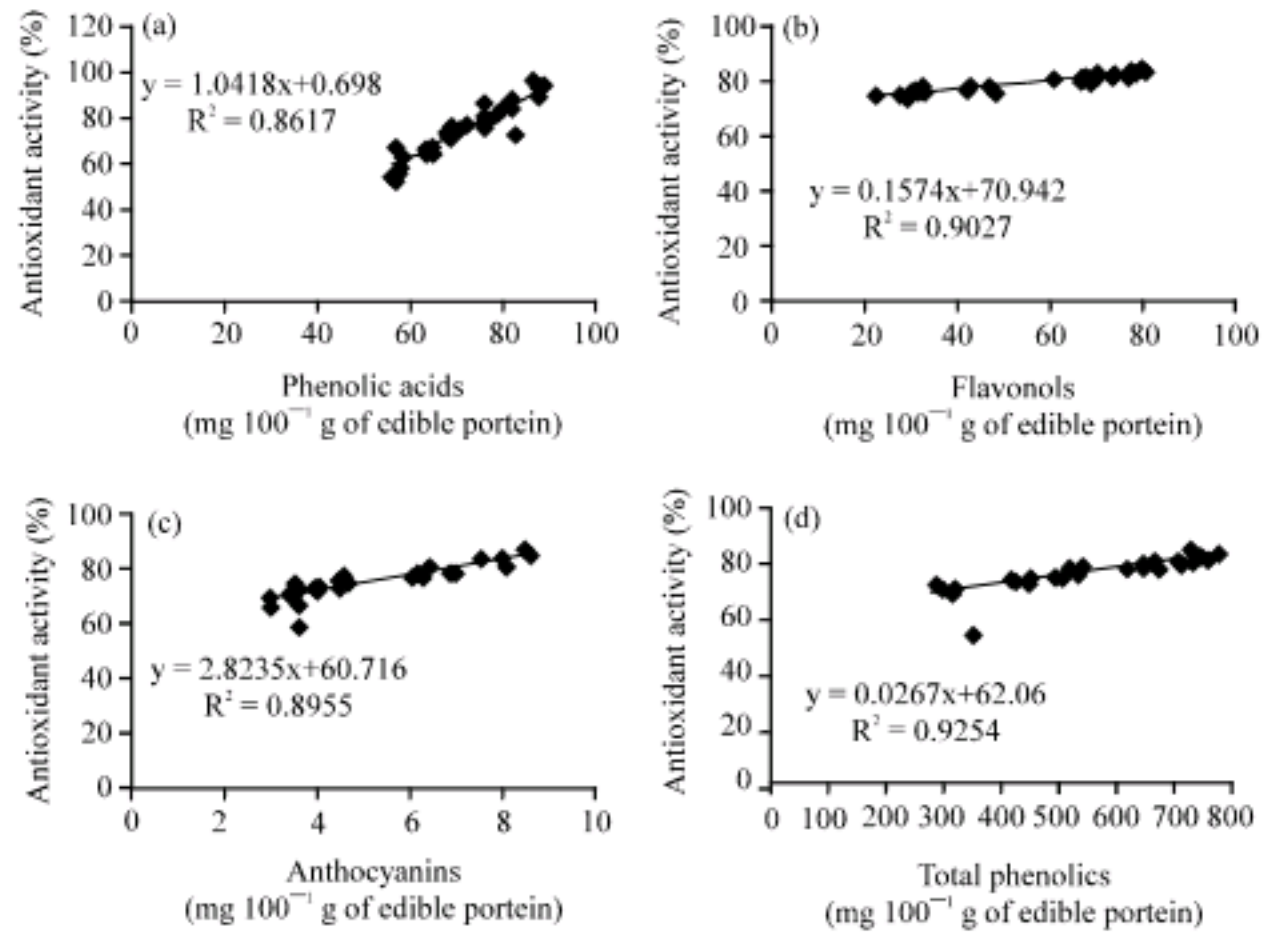


Fig. 2: Correlation between different phenolic components detected and antioxidant activity of both onion varieties: (a) antioxidant activity vs. phenolic acids, (b) antioxidant activity vs. flavonols, (c) antioxidant activity vs. anthocyanins and (d) antioxidant activity vs. total phenolics

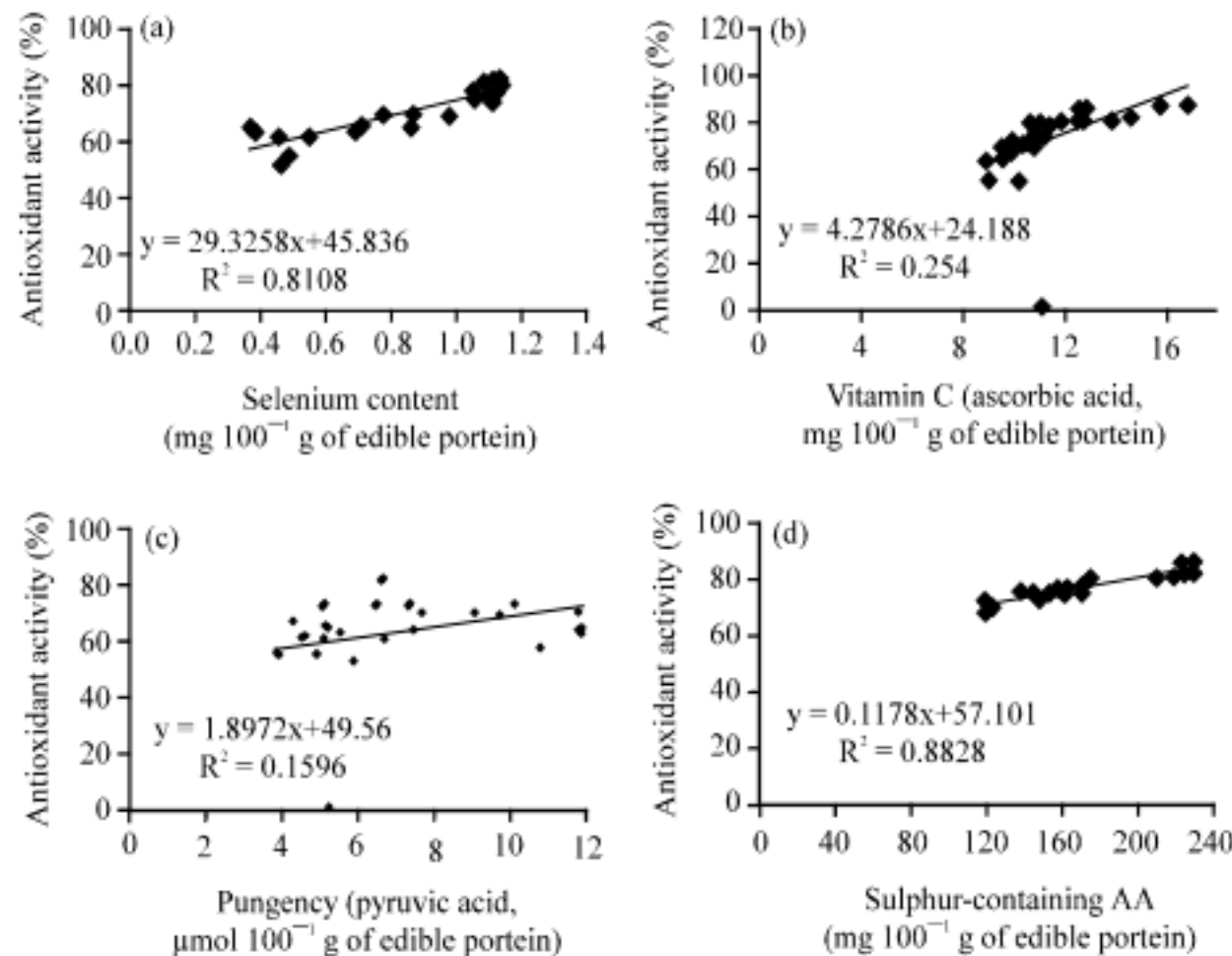


Fig. 3: Correlation between different components detected and antioxidant activity of both onion varieties: (a) antioxidant activity vs. selenium content, (b) antioxidant activity vs. vitamin C content, (c) antioxidant activity vs. pungency and (d) antioxidant activity vs. sulphur-containing amino acids

pungency levels and antioxidant activity of onion bulbs. These correlations confirm that phenolic compounds with others i.e., Se and sulphur-containing amino acid are mainly responsible for the antioxidant activity of onion bulbs. Several studies have reported a good correlation between the phenolics content of plant extracts and antioxidant activity. For example, Velioglu *et al.* (1998) reported that the correlation coefficient between total phenolics and antioxidative activities of 28 plant products, including sunflower seeds, flaxseeds, wheat germ, buckwheat, several fruits, vegetables and medicinal plants was statistically significant. Also, Lee *et al.* (1995) found that phenolic compounds including flavonoids, correlated well with antioxidant activity ($r^2 = 0.86$) in 5 cultivars of fresh pepper (*Capsicum annuum*). Finally, Santos *et al.* (2008) reported that good correlations were observed between phenol content and antioxidant activity of two Spanish onion varieties.

Antioxidant Evaluation in Oil-Water Emulsion

Lipid oxidation is mainly responsible for off-flavour development in fatty foods, so phenolic antioxidants should be studied in suitable food system. In the present study, peroxide formation has been determined in sunflower oil-in-water emulsions incubated at 40°C. Different amounts of dry onion powder of both Egyptian varieties (10, 20 and 30 mg mL⁻¹ emulsion) were added to test their antioxidant activity. Figure 4 shows hydroperoxide formation during emulsion storage. Samples from white onions showed little antioxidant activity but red onion extracts were more effective. The higher antioxidant activity of red onion powder in emulsions was in good agreement with its higher levels of phenolics, Se and sulphur-containing amino acids.

In general, the data of this study with others proved the importance of using selected onion varieties and/or extracts as natural potent antioxidants in both therapy and food technology. The antioxidant activity of onion bulbs could be attributed mainly to the high levels of phenolics (phenolic acids, flavonols and anthocyanins) beside Se and sulphur-containing amino acids. Many studies indicated that feeding of phenolic acid (ellagic) significantly increased the levels of reduced glutathione and glutathione reductase in liver and lungs of male and female mice as well as increase in inhibition of NADPH-dependent lipid peroxidation (Majid *et al.*, 1991). The antioxidant activity of four phenolic acids like detected in onion bulbs, upon low density lipoprotein peroxidation were studied *in vitro* in a Low Density Lipoprotein (LDL) oxidation model by Laranjinha *et al.* (1994). The addition of these acids exhibits a complex reaction with peroxy radicals resulting in undefined inhibition periods of LDL oxidation and low reactivity with peroxy radicals. Presumably,

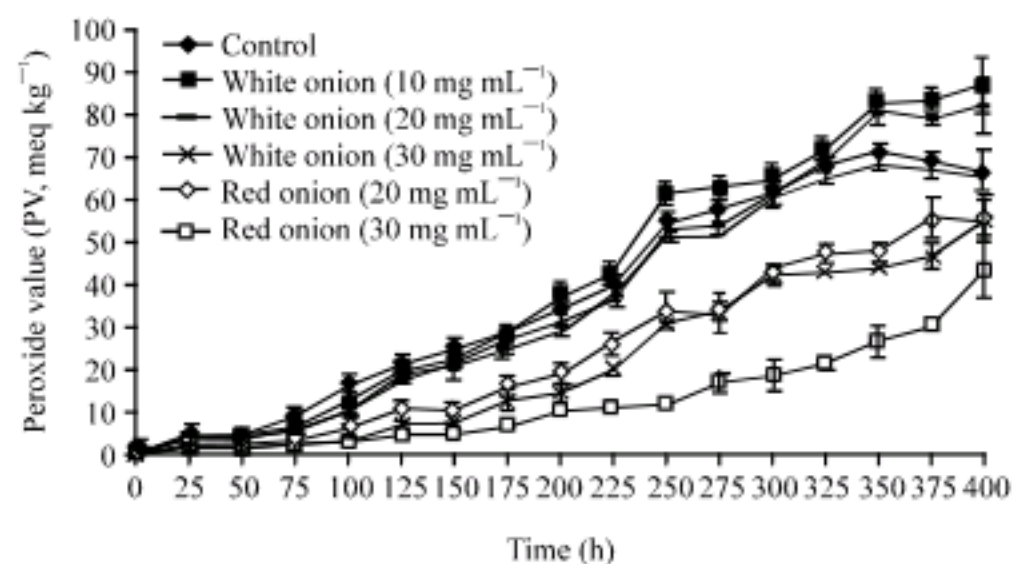


Fig. 4: Effect of onion powder on Peroxide Value (PV) formed in stored emulsions at 40°C

secondary radicals of these compounds are unable to initiate LDL oxidation. Several researchers have investigated the antioxidative activity of flavonoids compounds and have attempted to define the structural characteristics of flavonoids that contribute to their activity (Nieto *et al.*, 1993; Foti *et al.*, 1996). Also, Se is an essential trace element. Its importance for human and animal metabolism has become apparent more recently, spurred by the discovery of a Se-dependent enzyme, glutathione peroxidase (widely distributed in tissues) and suggestive evidence that selenium plays a role in the prevention of certain forms of cancer (Linder, 1991). Regarding food technology applications, there are beneficial effects of onion addition to some foods, like traditional sausage chouriço to maintain oxidative stability. That is due to its flavonoid content, mainly quercetin, because they are potent antioxidants and function by interrupting the free radical chain in the propagation step of the oxidative process (Karastogiannidou, 1999). Also, the adding of phenolic acids including in onion bulbs to vegetable oils leads to significant decrease in the rate of hydrolysis, rancidity and formation of the toxic and carcinogenic substances during the deep frying process (El-Hassaneen, 2004).

In conclusion, the Egyptian onion varieties evidenced a great variability in chemical components due mainly to genetic factors and growing conditions. The antioxidant activity of red onion (Beheri) bulbs methanolic extract is superior to in white onion (Giza 6). Correlation analysis indicates that phenolic compounds with Se and sulphur-containing amino acid contents play the major role in the antioxidant activity of onion bulbs. Dry powder of both onion varieties retarded oxidation in an oil-in-water emulsion system. Red onions were more effective in retarding oxidation than white samples. Further work is in progress in our laboratory to elucidate the possibility of using the highly antioxidant activity of onion bulbs extracts in many nutritional and food technology applications.

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