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PHENOLIC COMPOUNDS, SWEETNESS AND AMINO ACIDS CONTENT OF ONION CULTIVARS DISTRIBUTED IN EGYPTIAN LOCAL MARKETS AND THEIR RELATIONSHIP WITH ANTIOXIDANT ACTIVITIES

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ABSTRACT

Phenolic compounds, sweetness and amino acids content of two onion (Allium cepa L.) cultivars, white (Giza-6) and red (Giza-20) onions and their relationship with antioxidant activities were assessed. Data analysis showed that the white onion variety has higher values for protein, ash, fiber, total carbohydrates and total energy while red once has the lowest dry matter content (12.61%). Regarding mineral and vitamins levels, the white onion variety represents higher levels of K, Ca, Mg, P, Zn, Cu and Mn while Fe, S, Se and vitamin C were higher in red variety. A white variety shows higher value of total amino acids (1460 mg/100g FW) than red once [1345 mg/100g FW) and the opposite was observed for sulphur-containing amino acid (cysteic, S-carboxymethyl cystein (S-CM cystein), cystine and methionine].

The total single sugars detected in red onion (4.78 g/100g FW) are superior to in white (3.91 g/100g FW). Glucose and fructose levels are higher in the red onion than the white once and the opposite with sucrose. Concerning pungency, white variety can be classified as very sweet (6.24 µmol pyruvic acid/g FW) and red as sweet (8.37 µmol pyruvic acid/g FW). A negative correlation in sucrose and glucose and a positive correlation in fructose, sulphur, vitamin C, sulphur-containing amino acids and phenolics content with pungency were also observed. The phenolic acids, flavonols, anthocyanins and total phenolics content in red variety (81.59, 70.38, 7.56 and 187.17 mg/100g FW, respectively) were higher than for white once (72.47, 32.49, 4.90 and 131.65 mg/100g FW, respectively). Consequently, antioxidant activity was higher for the red variety. Statistical analysis indicates that total phenolic compounds beside other factors including Se and sulphur-containing amino acid contents play the major role in the antioxidant activity of onion bulbs.

Conclusively, *the present data indicates that white onion variety shows higher nutritional value while the potential health benefits related to the presence of antioxidant compounds and other factors were higher in onion red variety.*

Key word: Allium cepa L.; sulphur-containing amino acids; sweetness; phenolics; Antioxidants

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 per capita^{-1}. year^{-1}, being Libya (32 kg per capita^{-1}. year^{-1}) and Turkey (27 kg per capita^{-1}.year^{-1}) the main consumers (FAOSTAT, 2002). In Egypt, onion is the third vegetable more consumed (15 kg per 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 (Giza-20) 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 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 per 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; and 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 and Foti *et al*., 1996). Phenolic acids, such as caffeic, chlorogenic, ferulic, sinapic, *p*-coumaric acids, vanillic, syringic and p-hydroxybenzoic appear to be active antioxidants (Larson, 1988 and El-Sadany, 2001). Vitamin C has a protective function against oxidative damage and a powerfull quencher of singlet oxygen (1 O_2), hydroxyl ($OH^{\cdot}$) and peroxyl (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 (Huang *et al*., 1992 and Cook and Samman, 1996).

The antioxidant activity of several plant materials including onion bulbs has recently been reported (Velioglu *et al*., 1998 and Rodrigues *et al*., 2003); however, information on the relationship between antioxidant activity and phenolics content and composition of onion bulbs is not available.

Therefore, the objective of this study was to determine the phenolic compounds, sweetness amino acids contents and minerals in different onion varieties distributed in Egyptian local markets and to explore relationship(s) between these components and antioxidant activity.

MATERIALS AND METHODS

MATERIALS

Onion samples were obtained from the most widespread local cultivar in the typical area of production, red onion (Giza-20) from Tala city, Minufiya Governorate and white onion (Giza-6) from Bani Mazar city, Minia Governorate, Egypt. After harvesting (mid of March), the onions were stored with skins, for three months at an average temperature of 25±2 ^{0}C. When bulbs were ready for sale (Mid of June), Twenty bulbs for each sample were selected to obtain the representative samples. Analyses 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, FW) ±SD.

CHEMICALS

Phenolic compounds, sugars and sodium pyruvate standards were purchased from Fluka Chemical Co., Switzerland, while vitamin C and amino acids standards from Sigma Chemical Co., St. Louis, Mo.

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 (Alltech, Baltimore, USA) were The column used was a reversed-phase water Spherosorb ODC-2 (3µM; 150 × 4.6mm I.d., Alltech USA) for phenolics; a guard column 7.5 x 3.2 mm containing 5 µm, C-18 reversed phase Econosphere was attached directly to a reversed-phase C-18 column (3 µm; 150 x 4.6 mm I.d. (Alltech, Carnforth Lancashire, UK) for amino acids; a normal Econosphere NH2 (5 µM, 250 × 4.6 mm I.d., Alltech USA) for sugars; and a reversed-phase water Adsorbosil C_{18} (5 µM, 100 mm × 4.6 mm I.d., Alltech USA) for vitamin C analysis.

ANALYTICAL METHODS

Gross chemical composition: Moisture, protein (T.N. × 6.25, micro - kjeldahl method using semiautomatic apparatus, Velp Scientifica company, Italy), fat (Soxhelt semiautomatic apparatus, Velp Scientifica Company, model SER 148/3 ,Italy, petroleum ether solvent), fiber (automatic extractor, Velp Scientifica Company, model FIWE 6,Italy) and ash contents were determined using the methods described in the A.O.A.C. (1995). Total carbohydrates calculated by differences:

Carbohydrates (%) = 100 - (% moisture + % protein + % fat + % Ash + % fiber)

Minerals: Bulbs defatted samples are digested as described by Singh *et al.*, (1991), the different minerals (K, Ca, Mg, Fe, Zn, Cu, Mn and Se) were analyzed in atomic absorption spectrophotometer, using a Perkin - Elmer, Model 2380. Sulphur was determined with a turbidimetry method and P determined by colorimetric method as described by APHA, (1999).

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

Sugars: To determine fructose, glucose and sucrose, 1 g of fresh onions was added to CH_3CN/H_2O (4:1) up to 10 mL and homogenized in an Ultra Moulinex blender. After, the samples were centrifuged, filtered and analysed in HPLC according to Gennaro *et al*. (2002). The chromatographic conditions were flow rate, 4 ml/min; detection, RI, volume of injection, 20 µl; temperature, room temperature, and mobile phase composition was an isocratic system of acetonitril : water (75:25).

Amino acids: Amino acids were analyzed in HPLC according to the method of Lindroth and Mopper (1979). Chromatographic separations were carried out with a 150 x 4.6 mm stainless-steel Econosphere C-18 reversed-phase column containing 3 µm packing (Alltech, Carnforth Lancashire, UK). A guard column 7.5 x 3.2 mm containing 5 µm, C-18 reversed phase packing (Alltech, Carnforth Lancashire, UK) was attached directly to analytical column. 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%, 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 acid: 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 ^{0}C until HPLC analysis. The phenolic acid extracts were prepared according to the method of Onyencho and Hettiarachchy (1993). The chromatographic conditions were as following: Flow rate, 1ml/min; 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 analyses as described by Fossen *et al.* (1996) with some modification 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 ^{0}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; Sigma Chemical Co., St. Louis, Mo) 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-Saikhan *et al*., 1995).

$AA = [(R_{control} - R_{sample}) / R_{control}] \times 100$

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:

$ORR = R_{sample} / R_{control}$

Where $R_{control}$ and R_{sample} are the same in the previous equation.

In the fourth method, the antioxidant activity coefficient (AAC) was calculated as described by Mallet *et al*., (1994).

$(AAC) = [(Abs_{S\,120} - Abs_{C\,120}) / Abs_{C\,0} - Abs_{C\,120})] \times 1000$

where: $Abs_{S\,120}$ was the absorbance of the antioxidant mixture at time 120 min, $Abs_{C\,120}$ was the absorbance of the control at time 120 min and $Abs_{C\,0}$ was 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 1000g 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.

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

Chemical composition, mineral, vitamin C and amino acids levels. The white onion has higher levels of protein, ash, fiber, total carbohydrates and total energy respect to the white once (Table 1). However, red onion has higher water content that can interfere negatively with storage capacity and using in dehydration process. In the present study, one kg of dehydrated onion is produced from 6.19 kg of fresh white onion compared to 7.42 kg of red once.

Table 1. Gross chemical composition (g/100g of edible portion) and total energy (Kcal / 100 gm) of onion varieties.

Chemical composition	Onion variety		Significance
	White	Red	
Moisture	84.92 ± 3.31	87.39 ± 2.29	***
Total protein (T.N × 6.25)	1.77 ± 0.24	1.53 ± 0.17	*
Crude fat (Pet. ether extract)	0.12 ± 0.03	0.15 ± 0.04	NS
Ash	0.78 ± 0.09	0.62 ± 0.11	***
Fiber	1.17 ± 0.32	0.98 ± 0.15	**
Carbohydrate	11.24 ± 1.15	9.33 ± 1.21	**
Total Energy (Kcal / 100 gm)	53.12 ± 3.21	44.79 ± 4.78	*

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

Regarding mineral and vitamins levels, the white onion has higher levels of K, Ca, Mg, P, Zn, Cu and Mn respect to the red once (Table 2). However, red onion has higher Fe, S, Se and ascorbic acid.

The present data are not in accordance with that obtained by Rodrigues *et al*., (2003) who found that Povoa red onion in Northwest Portugal has higher level in all minerals determined than the white once. This variation explained that the effect of regional varieties, environment beside 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 6.67 and 4.17 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 (reviewed by Linder, 1991 and Packer, 1992).

Table 2. Mineral and vitamin levels of onion varieties (mg/100g of edible portion).

Minerals and vitamins	Onion vVariety		Significance
	White	Red	
Minerals:			
K	214 ± 21	183 ± 17	**
Ca	31 ± 6.2	22.5 ± 4.8	*
Mg	21 ± 3.4	14.43 ± 2.1	*
P	39 ± 5.6	28.54 ± 4.2	**
Fe	1.61 ± 0.43	2.01 ± 0.58	***
Zn	0.81 ± 0.26	0.56 ± 0.09	**
Cu	0.14 ± 0.05	0.09 ± 0.03	*
Mn	0.41 ± 0.08	0.40 ± 0.09	NS
S	48.23 ± 6.9	75.22 ± 8.34	***
Se	1.05 ± 0.11	1.68 ± 0.09	***
Vitamins:			
Vitamin C (Ascorbic acid)	13.84 ± 2.9	14.63 ± 4.7	*

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

The total amino acids levels in white onion (1460 mg/100g FW) is superior than in red (1345 mg/100g FW) (Table 3). The studying of amino acid profiles indicated that the white onion has higher levels of almost amino acids except sulphur-containing amino acid (cysteic, S-CM cystein, cystine and methionine), tryptophan and phenylalanine than the red once. Sulphur-containing amino acids with other organo-sulphur compounds are known to be very important for onion flavour biosynthesis (Randle, 1997).

Sweetness (sugars and pungency):

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 (1-4µmol pyruvic acid/g FW); sweet (5-7µmol pyruvic acid/g FW); intermediate pungency (8-10µmol pyruvic acid/g FW); pungent (11-15µmol pyruvic acid/g FW) very pungent (>15µmol pyruvic acid/g FW). In this work, red variety is classified as sweet and white as very sweet (Table 4). 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).

Table 3. Amino acids composition of onion varieties (mg/100g of edible portion).

Amino acids	Onion variety		Significance
	White	Red	
Aspartic acid	110 ± 2.3	81 ± 1.5	***
Glutamic acid	301 ± 11.0	249 ± 10.6	***
Asparagin	41 ± 4.6	37 ± 2.1	NS
Serine	50 ± 2.7	43 ± 3.8	*
Proline	42 ± 5.3	26 ± 1.9	**
Glutamine	22 ± 0.9	23 ± 0.9	NS
Glycine	57 ± 2.5	46 ± 0.8	*
Histidine	43 ± 3.5	44 ± 2.1	NS
Threonine	56 ± 4.1	42 ± 3.5	*
Alanine	61 ± 2.8	58 ± 1.3	NS
Arginine	75 ± 5.1	69 ± 2.8	*
Tyrosine	48 ± 0.8	44 ± 1.2	*
Ornithine	21 ± 0.3	23 ± 1.7	NS
Tryptophan	17 ± 1.5	49 ± 1.3	***
Valine	57 ± 4.9	28 ± 0.5	**
Phenylalanine	59 ± 3.2	63 ± 6.8	*
Isoleucine	53 ± 1.2	37 ± 0.5	**
Leucine	108 ± 3.9	88 ± 5.2	**
Lysine	81 ± 4.0	69 ± 2.4	**
Sulphur-containing amino acids (SAA)			
Cysteic	41 ± 1.7	63 ± 3.4	**
S-CM cystein (S-carboxy methyl cystein)	58 ± 4.2	65 ± 6.2	**
Cystine	26 ± 1.4	47 ± 1.7	**
Methionine	33 ± 2.0	51 ± 3.4	***
Total	**1460 ± 25.7**	**1345 ± 19.6**	****

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

The total single sugars detected in red onion (4.78 g/100g FW) are superior to in white (3.91 g/100g FW) (Table 4). Glucose and fructose levels are higher in the red onion than the white once and the opposite with sucrose. Sugars are known to be very important for anthocyanin biosynthesis, and they can act as substrate for the synthetic pathways (Gennaro *et al*., 2002).

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,

Table 4. Sugars and pungency levels in onion varieties.

Sugars and pungency	Onion variety		Significance
	White	Red	
Sugars (g/100g of edible portion):			
Glucose	1.33 ± 0.19	1.61± 0.23	**
Fructose	1.11 ± 0.08	2.08 ± 0.11	***
Sucrose	1.47 ± 0.21	1.09 ± 0.09	*
Pungency :			
Pyruvic acid(μmol /100g of edible portion)	6.24 ± 0.88	8.37 ± 1.02	**

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

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 (reviewed by 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 5). 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 onions. Many of detected phenolic acids in onion exhibits their antioxidative (Deschamps *et al.*, 1991; and Laranjinha *et al*., 1994), anticarcinogenic (Gali *et al*., 1991; and Harttig *et al*., 1996), and antibacterial (Nakane *et al*., 1990 and Nowosielska *et al*., 1991) effects.

Flavonoids are built upon a diphenylpropane skeleton (C_6-C_3-C_6) 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 (5) 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'-gluciside. For anthocyanins, delphinidin derivatives are predominant in both onion varieties as found by Rodrigues *et al*., (2003). Several studies reported that the red

Table 5. Phenolic compounds levels in onion varieties (mg/100g of edible portion).

Phenolic compounds	Onion variety		Significance
	White	Red	
Phenolic acids:			
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:			
Quercitin-4-glucoside	18.68 ± 2.34	41.74 ± 4.09	***
Quercitin-3-4-diglucoside	12.42 ± 1.29	25.80 ± 3.12	***
Kaempferol-3-O-glucoside	0.79 ± 0.15	1.04 ± 0.08	**
Quercitin	0.41 ± 0.07	1.17 ± 0.12	**
Isoquercitin	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.

bulb colour is influenced by anthocyanin contents (Griffiths *et a*l., 2002 and Rodrigues *et al*., 2003).

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 and 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 Sammon, 1996).

Antioxidant activity. The antioxidant activities and total phenolics of white and red onion varieties are shown in Table (6). 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 Figure (1). The antioxidant activity of red onion bulbs methanolic extract is superior to in white when it was calculated by the four different methods used in this study. The relationship between total phenolics content and antioxidant activity of onion bulbs is shown in Tables (8-9). The results indicated that when all onion varieties were included in the statistical analysis, there was a positive significant ($p< 0.05$) relationship between total phenolics including phenolic acids, flavonoids and anthocyanins and antioxidant activity. Also, the same relationship was observed between antioxidant activity and many other factors include Se and sulphur-containing amino acids. This indicates that total phenolic compounds beside other factors including Se and sulphur-containing amino acid can play a major role in the antioxidant activity of onion bulbs. In similar study, 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) reported that phenolic compounds including flavonoids, correlated well with antioxidant activity (r^2=0.86) in 5 cultivars of fresh pepper (*Capsicum annuum*).

Table 6. Antioxidant activity and total phenolics of methanolic extracts of White and Red onion.

Sample name	Antioxidant value AOX (A/h)	Antioxidant activity AA (%)	Oxidation rate ratio (ORR)	Antioxidant activity coefficient (AAC)	Total phenolics (mg/100 g)
White onion	0.182± 0.011	67.83± 2.21	0.321± 0.020	351.51± 23.11	131.65± 19.17
Red onion	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 ± 0.09	0.00	
BHT, 50 mg/L	0.076± 0.012	86.54± 1.89	0.134± 0.018	676.77± 11.98	
BHT, 200 mg/L	0.010± 0.002	98.31± 1.06	0.017± 0.008	881.39± 21.00	
ά-tocopherol, 50 mg/L	0.011± 0.003	98.11± 0.90	0.019± 0.005	877.91± 18.56	

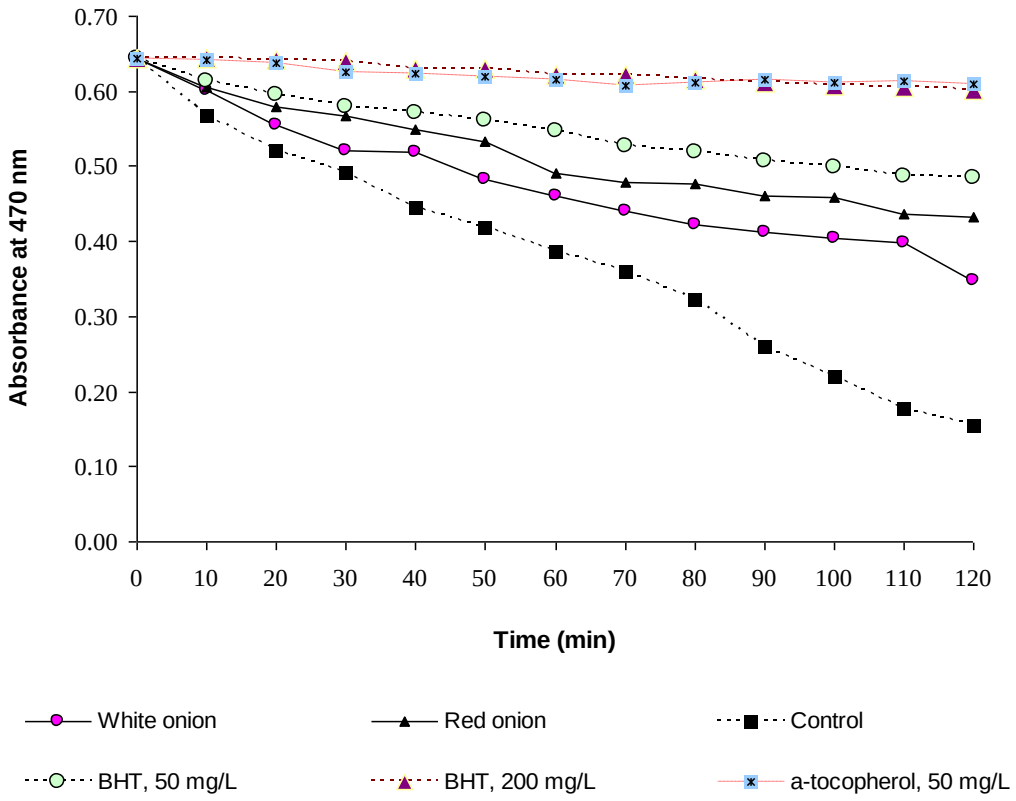

Figure 1. Antioxidant activity (Abs at 470 nm) of methanolic extracts of onion bulbs assayed by the β-carotene bleaching method (BHT at 50 mg/L & 100 mg/L and α–tocopherol at 50 mg/L concentrations were used as references).

In addition, correlation studies indicated that pungency is highly correlated with sulphur content, vitamin C, fructose, sulphur-containing amino acids and phenolics including flavonols and anthocyanins (Table 7) and we found that onions with more sulphur, fructose, sulphur-containing amino acids and phenolics are more pungent. Such data are convenient with that mentioned by Randle *et al*., (1998) mentioned that pungency, measured as pyruvate, vary between genotypes and growing conditions. The genetic system of onion controls sulphur uptake and assimilation of the sulphur and, increased sulphate fertility, higher growing temperatures and dry growing conditions all contribute to increased flavour intensity in onion (Randle, 1997and Ketter and Randle, 1998).

In general, the data of this study with the 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 total phenolic (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 peroxyl radicals resulting in undefined inhibition periods of LDL oxidation and low reactivity with peroxyl radicals. Presumably, 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; and 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 (reviewed by Linder, 1991). Regarding to 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 (Elhassaneen *et al*., 2004).

In conclusion, the Egyptian onion varieties studied evidenced a great variability in chemical composition due mainly to genetic factors and growing conditions. Onions with more sulphur, fructose, sulphur-containing amino acids and phenolic compounds are more pungent. The antioxidant activity of red onion bulbs methanolic extract is superior to in white once. Correlation analysis indicates that total phenolic compounds beside other factors including Se and sulphur-containing amino acid contents play the major role in the antioxidant activity of onion bulbs. Therefore, white variety shows higher nutritional value while the potential health benefits related to the presence of antioxidant compounds and other factors were higher in red variety.

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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محتوى المركبات الفينولية ودرجة الحلاوة والأحماض الأمينية لأصناف البصل المنتشرة بالأسواق المصرية وعلاقتها بالأنشطة المضادة للأكسدة

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تم من خلال هذه الدراسة تقدير محتوى المركبات الفينولية ودرجة الحلاوة والأحماض الأمينية لبعض أصناف البصل الشائعة الانتشار بالأسواق المصرية وهما البصل الأبيض (جيزة-٦) والبصل الأحمر (جيزة-٢٠) وعلاقة تلك المركبات بالأنشطة المضادة للأكسدة. ولقد أوضحت النتائج ارتفاع نسبة البروتين والرماد والألياف والمواد الكربوهيدراتية الكلية ومحتوى الطاقة في البصل الأبيض مقارنة بالبصل الأحمر الذي انخفض محتواه من المواد الصلبة الكلية لتسجل ١٢.٦١%. أما فيما يخص محتوى المعادن والفيتامينات فقد سجل البصل الأبيض مستويات عالية من البوتاسيوم والكالسيوم والماغنيسيوم والفوسفور والزنك والنحاس والمنجنيز في حين سجل البصل الأحمر مستويات عالية لكل من الحديد والكبريت والسيلينيوم وفيتامين جـ. كذلك الحال بالنسبة لمحتوى الأحماض الأمينية الكلية الذى كان مرتفعا في البصل الأبيض (١٤٦٠ ملجم/١٠٠ جرام وزن رطب) مقارنة بالبصل الأحمر (١٣٤٥ ملجم/١٠٠ جرام وزن رطب)، وعلى العكس من ذلك فقد كان مستوى الأحماض الأمينية الكبريتية (السيستيك- اس كربوكسى ميثايل سيستين- اسيستين – الميثيونين) مرتفعا بالبصل الأحمر عنه في البصل الأبيض. كما تميز البصل الأحمر بارتفاع مستوى السكريات حيث بلغ ٤.٧٨ جم/١٠٠ جرام وزن رطب مقارنة بالبصل الأبيض الذي سجل مستوى قدره ٣.٩١ جم/١٠٠ جرام وزن رطب، هذا علاوة على إرتفاع مستوى سكر الجلوكوز والفركتوز وانخفاض سكر السكروز في البصل الأحمر مقارنة بالبصل الأبيض. وفيما يتعلق بالحرافية والتي عبر عنها بمستوى حامض البيروفيك فقد كان محتوى البصل الأبيض ٦.٢٤ ميكرومول/ جرام وزن رطب والبصل الأحمر ٨.٣٧ ميكرمول/ جرام وزن رطب مما وضعهما في أقسام الأبصال عالية الحلاوة والحلوة على التوالي.ولقد أظهرت درجة الحرافية ارتباطا سالبا مع كل من الجلوكوز والسكروز وارتباطا موجبا مع الفركتوز والكبريت وفيتامين جـ والأحماض الأمينية الكبريتية والمركبات الفينولية. أما فيما يتعلق بالأحماض الفينولية والفلافونات والأنثوسيانينات والفينولات الكلية فقد سجلت قيما مرتفعة بالبصل الأحمر بلغت ٨١.٥٩، ٧٠.٣٨ ، ٧.٥٦ ، ١٨٧.١٧ ملجم/١٠٠ جرام وزن رطب على التوالي مقارنة بالبصل الأبيض الذي سجل قيما لتلك المركبات مقدارها ٧٢.٤٧ ، ٣٢.٤٩، ٤.٩٠ ، ١٣١.٦٥ ملجم/١٠٠ جرام وزن رطب على التوالي ، مما ترتب عليه ارتفاع مستوى الأنشطة المضادة للأكسدة بالبصل الأحمر مقارنة بالبصل الأبيض. ولقد أظهرت التحاليل الإحصائية أن المركبات الفينولية الكلية بجانب عناصر أخرى تشتمل على السيلينيوم والأحماض الأمينية الكبريتية هي التي تلعب الدور الأساسي في الأنشطة المضادة للأكسدة التى توجد في البصل . ولقد خلصت الدراسة إلى أن أصناف البصل الأبيض تتميز بارتفاع قيمتها الغذائية في حين أن الفوائد الصحية المحتملة والمميزة للبصل والتي ترجع إلى وجود المركبات المضادة للأكسدة مع بعض العوامل الأخرى كانت مرتفعة في أصناف البصل الأحمر.