Comparative antioxidant study of onion and garlic waste and bulbs

E A Kotenkova¹ and N V Kupaeva¹

¹ V. M. Gorbatov Federal Research Center for Food Systems of RAS, Tallalikhina 26
Moscow, Russia

E-mail: lazovlena92@yandex.ru

Abstract. Among vegetables, onion and garlic production occupies a leading position worldwide due to their wide usage in various sectors of the food industry. Husk is the main waste from onion and garlic processing. The biological properties of onion and garlic bulbs are well studied, but the husks are not well investigated to date. The total antioxidant capacities of aqueous and ethanol extracts of onion and garlic husks and bulbs were determined by the ORAC method and expressed in μmol equiv. Trolox/g of sample. The husks demonstrated the greatest total antioxidant capacities and significantly exceeded those of the bulbs. Onion husk was the most active, and its total antioxidant capacity was 521.24±11.23 μmol equiv. Trolox/g of sample for aqueous extract and 1206.93±8.37 23 μmol equiv. Trolox/g of sample for ethanol extract. Antioxidant capacity depended on extractant type.

1. Introduction

The biological properties of fruit and vegetable wastes are intensively studied due to the need to reduce environmental pollution [1], as well as to search for new sources of natural antioxidants. To date, it has been determined that the peel of many plants contains large numbers of antioxidants, including polyphenols [1-3]. Therefore, agricultural and industrial wastes are attractive sources of natural antioxidants and dietary fibers [1].

Onions (*Allium cepa*) and garlic (*Allium sativum L.*) are well known vegetables, traditionally used in food processing and medicine [4,5]. Onion and garlic are the most commonly cultivated vegetables, worldwide. According to the Food and Agriculture Organization (FAO), onion is grown in 126 countries on 3.6 million hectares, producing 73.20 million tons per year [4]. Garlic is the second most widely cultivated vegetable after onion. The FAO estimates 1.217 million hectares are used worldwide to cultivate garlic, producing 16.41 million tons per year [5].

Fresh, fried, sautéed, boiled, salted and marinated onion and garlic are used in the food industry in recipes for canned meat, spicy sauces, side dishes, as well as in fish, sausage and pickled cheese processing [4]. Dried onion is also widely produced and used alone or as part of vegetable mixes as flavoring additives in snacks, soups, sauces, gravies, minced meat and fish semi-finished products [6].

In addition to food purposes, onion and garlic are used in other areas, including medicine, due to their biological properties, such as antibacterial, anticancer, hypoglycemic, hypolipidemic, antiplatelet aggregation, and antioxidant activities [4,7,5,8].

Husk is the main waste in *Allioideae* spp. processing. Thus, the amount of waste from peeling onions is from 5.0-9.0% to 21.6-29.9% of feedstock weight depending on the size of the bulbs and the
method of peeling [9], which is approximately 3.66-21.9 million tons per year. The amount of waste from peeling garlic is 16-20% of feedstock weight [9], which is approximately 2.3-2.9 million tons per year.

The aim of this study was to examine and compare the total antioxidant capacity (TAC) of aqueous and ethanol extracts of onion, garlic and their husks, as well as to assess the competitiveness of the most active extracts in comparison with popular spices and herbs from the OracDataBase.

2. Materials and methods

Onion (Allium cepa) and garlic (Allium sativum L.) bulbs and husks were studied. Aqueous and ethanol extracts of bulbs and husks were prepared for the TAC study. The raw materials were ground to less than 5 mm in size and mixed with distilled water at 95°C for aqueous extracts, or with 75% ethanol at room temperature for ethanol extracts, then infused for 15 minutes and 24 hours, respectively, and filtered through a paper filter. Aqueous extracts were prepared directly on the day of the experiment, and alcohol extracts were stored at 4°C for 3 days. Table 1 presents the ratios of extractant and vegetable material used.

| Type of extractant | Husk | Bulb |
|--------------------|------|------|
| Distilled water    | 1:100| 1:25 |
| Ethanol            | 1:25 | 1:5  |

The TAC of extracts was determined by the oxygen radical absorbance capacity (ORAC) fluorescent method [10] with the author’s modification on a Fluoroscan Ascent FL system (TermoLaborystems, Finland) using black 96-well plates. Volumes of 30 µL of sample or standard and 200 µL of 0.5 µM of sodium fluorescein (Sigma-Aldrich, USA) were added to the wells, microplates were covered with film (SSIbio, USA) and placed into the Fluoroscan Ascent FL (TermoLaborystems, Finland) for 30 min at 37°C. Then, 30 µL of 153 µM AAPH (Aldrich Chemistry, USA) was added to each well, and fluorescence was measured at 37°C for 60 min at 5 min intervals. Excitation wavelength was 485 nm, emission wavelength was 535 nm. The TAC of each sample was determined four times.

TAC was determined according to a standard curve using (±)-6-Hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox) (Sigma-Aldrich, Switzerland) in the concentration range of 5-75 µM. Depending on their activity, the extracts were diluted with 75 mM phosphate buffer (pH = 7.4). TAC was expressed in µmol equiv. Trolox/g of sample.

STATISTICA 10.0 software was used for statistical analyses. The results were calculated as mean ± standard error (M ± SE). Significant differences were tested by one-way ANOVA, followed by Tukey’s test. Differences with P-values less than 0.05 were considered as statistically significant.

3. Results and discussion

Results are presented in Table 2. The husks demonstrated higher TACs than did the bulbs. Onion husk displayed the greatest TAC, 521.24 ± 11.23 µmol equiv. Trolox/g of sample for aqueous extract and 1206.93 ± 8.37 µmol equiv. Trolox/g of sample for ethanol extract, and these exceeded the TACs of garlic husk by 503.08-fold (P<0.05) and 1060.29-fold (P<0.05), respectively.

| Sample        | TAC of aqueous extract (mean ± SE; µmol equiv. Trolox/g) | TAC of ethanol extract (mean ± SE; µmol equiv. Trolox/g) |
|---------------|--------------------------------------------------------|---------------------------------------------------------|
| Onion husk    | 521.24 ± 11.23                                         | 1206.93 ± 8.37                                          |
| Garlic husk   |                                                        |                                                         |

The husks demonstrated higher TACs than did the bulbs. Onion husk displayed the greatest TAC, 521.24 ± 11.23 µmol equiv. Trolox/g of sample for aqueous extract and 1206.93 ± 8.37 µmol equiv. Trolox/g of sample for ethanol extract, and these exceeded the TACs of garlic husk by 503.08-fold (P<0.05) and 1060.29-fold (P<0.05), respectively.
Substances having antioxidant activity are mainly organic compounds; therefore, yields from raw material should be higher in the case of organic solvent extraction due to the chemical affinity. Casagrande et al [11] compared the antioxidant activity of plant samples depending on solvent used. The results of their study [11] showed the efficiency of solvents increases in following order: water < ethanol < acetone. Smetanska et al [12] studied five different organic solvents: acetone, methanol, ethanol, hexane and diethyl ether. The results of their study [12] showed the antioxidant yield significantly depends on the polarity of organic solvents; methanol and ethanol produced better yields of phenolic compounds [12]. In addition, ethanol is the most suitable solvent for extracting compounds with biological activity that can be included in food, pharmaceutical or cosmetic products, since ethanol possess the lowest toxicity among the organic solvents and produces high yields [11].

In the current study, both aqueous and alcoholic extracts of the bulbs displayed smaller TACs than did the corresponding husk extracts.

When comparing aqueous extracts of garlic husk and bulb, there were no statistically significant differences (P>0.05), but the TAC of onion husk extract exceeded the TAC of onion bulb by 54.3-fold (P<0.05). The TAC of garlic husk ethanol extract was higher than the TAC of garlic bulb ethanol extract by 3.2-fold (P<0.05), while the TAC of onion bulb extract was 29.1-fold greater than that of onion husk ethanol extract (P<0.05). There was no statistically significant difference (P>0.05) between the TACs of garlic and onion bulb ethanol extracts, while the TAC of garlic bulb aqueous extract exceeded the TAC of onion bulb aqueous extract by 1.7-fold (P<0.05). The obtained TACs of garlic bulb extract were consistent with the data described by Deng et al [13]; TACs of our onion and garlic bulbs also coincided with the results of Morales-Soto et al [14]. However, there are few works devoted to the study of onion and garlic husk antioxidant capacity.

The obtained TACs of all extracts were compared with data from the international OracDataBase, created in 2007 by the USDA (United States Department of Agriculture) [15]. Hydrophilic-ORAC-Means for onion and garlic bulbs were 16.94 and 55.41 µmol equiv. Trolox/g of sample, respectively, and were slightly different from the TACs obtained in the current study.

As a result of our research, the most promising raw material was onion husk, but this is not listed in the OracDataBase; therefore TAC of onion husk was compared with various herbs and spices rich in antioxidants [16,17] and traditionally used in the food industry as natural preservatives [18,19].

Parsley (dried), sage, basil (dried) possessed the highest Hydrophilic-ORAC-Means, while cloves (ground) and rosemary (dried) had the highest Lipophilic -ORAC-Mean. Comparison of some spices and herbs with onion husk is presented in Figures 1 and 2. The TAC of onion husk aqueous extract is about half the Hydrophilic-ORAC-Mean of sage, but has about the same TAC as parsley and basil. The TAC of onion husk ethanol extract exceeded by 2.8-fold the Lipophilic-ORAC-Mean of the well known source of natural antioxidants, dried rosemary, but at the same time, it was 32.5% less than the Lipophilic-ORAC-Mean of cloves.

| Substance       | TAC (µmol equiv. Trolox/g) |
|-----------------|----------------------------|
| Onion husk      | 521.24 ± 11.23             |
| Onion bulb      | 9.60 ± 0.78                |
| Garlic husk     | 18.16 ± 0.92               |
| Garlic bulb     | 16.64 ± 0.73               |

- *a, b, c, d, e, f, g, h, i, j, k, l, m, n* significant differences between the samples (P<0.05)
The biological properties of onion and garlic bulbs, including their antioxidant potentials, have been intensively studied for a long time [4-6]. However, our study revealed that husks demonstrated higher TACs than bulbs; onion husk was the most promising raw material. Moreover, the affinity of the solvent significantly affected the yield of compounds with antioxidant activity.

4. Conclusions
This study confirmed onion husk to be a good source of antioxidants, as its TAC was 521.24 ± 11.23 µmol equiv. Trolox/g of sample for aqueous extract and 1206.93 ± 8.37 µmol equiv. Trolox/g of sample for ethanol extract, which exceeded the TAC of onion bulb aqueous and ethanol extracts by 54.3- and 62.2-fold, respectively.

The TAC of onion husk was approximately equivalent to the TACs of well-studied herbs and spices such as sage, parsley, basil and rosemary that are used in the food industry. Therefore, onion husk could compete with them and be used as alternative source of antioxidants instead of synthetic antioxidants. It is also worth noting that the onion husk is a waste of the vegetable industry, so its use would be ecologically sound.

However, it is necessary to study the composition of onion husk in order to explain the different TACs of aqueous and ethanol extracts. Rationalization and selection of suitable extraction parameters, including type of extractant, sample-solvent ratio and temperature, among others, is required.

Acknowledgement
This work was supported by the Russian Science Foundation (project No. 17-76-10033).

References
[1] Al-Sayed H M A and Ahmed A R 2013 Utilization of watermelon rinds and sharlyn melon peels as a natural source of dietary fiber and antioxidants in cake Ann. Agr. Sci. 58 83–95
[2] Devatkal S K, Narasiah K and Borah A 2010 Antioxidant effect of extracts of kinnow rind, pomegranate rind and seed powders in cooked goat meat patties Meat Sci. 85 155–9
[3] Elbadrawy E and Sello A 2016 Evaluation of nutritional value and antioxidant activity of tomato peel extracts Arab. J. Chem. 9 S1010–8
[4] Lawande K E 2012 Onion Handbook of Herbs and Spices (Second edition) vol 1, ed K V Peter (Woodhead Publishing Limited) chapter 23 pp 417–29
[5] Pandey U B 2012 Garlic Handbook of Herbs and Spices (Second edition) vol 1, ed K V Peter (Woodhead Publishing Limited) chapter 17 pp 299–318
[6] Byvalets O A, Shpilev A A and Kuksarova V M 2014 Food additives food technology Izvestiya Yugo-zapadnogo gosudarstvennogo universiteta Seriya fizika i khimiya. 1 56–61

[7] Ouyang H, Hou K, Peng W, Liu Z and Deng H 2018 Antioxidant and xanthine oxidase inhibitory activities of total polyphenols from onion Saudi. J. Biol. Sci. 25 1509–13

[8] Horita C N, Farias-Campomanes A M, Barbosa T S, Esmerino E A, da Cruz A G, Bolini H M A and Pollonio M A R 2016 The antimicrobial, antioxidant and sensory properties of garlic and its derivatives in Brazilian low-sodium frankfurters along shelf-life Food Res. Int. 84 1–8

[9] Ochistka plodoobotschnogo syrya pered sushkoy Zoonzhernenyi facultet MSKhA Available from: http://www.activestudy.info/ochistka-plodoovoshhnogo-syrya-pered-sushkoy

[10] SP&A Application Laboratory 2016 Determination of Antioxidant Capacity on the Thermo Scientific Varioskan LUX Multimode Reader Thermo Fisher Scientific Available from: http://www.thermofisher.com/ru/ru/home.html

[11] Casagrande M, Zanela J, Júnior A W, Busso C, Wouk J, Iurckevicz G and Malfatti C R M 2018 Influence of time, temperature and solvent on the extraction of bioactive compounds of Baccharis dracunculifolia: In vitro antioxidant activity, antimicrobial potential, and phenolic compound quantification Ind. Crops. Prod. 125 207–19

[12] Smetanska I Helfert J Appeltauer-Brandl U Voytsekhivskiy V Mohdaly A Shevchenko Y 2016 Antioxidant activity of apple peels Mech & Technol. 52 61–5

[13] Deng G F, Lin X, Xu X R, Gao L L, Xie J F and Li H B 2013 Antioxidant capacities and total phenolic contents of 56 vegetables J. Funct. Foods 5 260–6

[14] Morales-Soto A, García-Salas P, Rodríguez-Pérez C, Jiménez-Sánchez C, de la Luz Cádiz-Gurrea M, Segura-Carretero A and Fernández-Gutiérrez A 2014 Antioxidant capacity of 44 cultivars of fruits and vegetables grown in Andalusia (Spain) Food Res. Int. 58 35–46

[15] OracDataBase Dietary Antioxidants/Bioactives USDA (United States Department of Agriculture) Available from: http://oracdatabase.com

[16] Sokamte T A, Mbougueng P D, Tatsadjieu N L and Sachindra N M 2019 Phenolic compounds characterization and antioxidant activities of selected spices from Cameroon S. Afr. J. Bot. 121 7–15

[17] Embuscado M E 2015 Spices and herbs: Natural sources of antioxidants—a mini review J. Funct. Foods 18 811–9

[18] Nychas G-J E and Tassou C C 2014 Traditional Preservatives – Oils and Spices Encyclopedia of Food Microbiology (Second edition) ed C A Batt and M L Tortorello (Amsterdam : Academic Press, Elsevier, Ltd.) pp 113–8

[19] Cortes-Rojas D F de Souza C R F and Oliveira W P 2014 Clove (Syzygium aromaticum): a precious spice Asian Pac. J. Trop. Biomed. 4 90–6