Changes in Total Phenolic Content and Antioxidant Activity of Grapefruit and Mandarin Peels Extracted with Different Solvents

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Abstract

In this research, different solvents were used for the extraction of grapefruit and mandarin peels in order to determine the effects of solvents on the total phenolic content (TPC) and antioxidant activity of peels. According to the results, the higher TPC and antioxidant activity values were determined in the ethanol extract of grapefruit peels as 666.55 mg GAE/g and 428.60 μ mol trolox/g, respectively. Acetone extract of peels showed the lowest values both in the mandarin and grapefruit peels. Total phenolic content of mandarin and grapefruit peels were reported as 32.05 and 50.26 mg GAE/g in the acetone extraction. To conclude the results, TPC and antioxidant activity of mandarin and grapefruit peels showed differences with different solvent extraction.

Keywords: Ethanol, methanol, acetone, peel, phenolic compounds, antioxidant activity

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INTRODUCTION

Citrus belongs to the Rutaceae family which is a shrub cultivated in tropical, sub-tropical and temperate regions of the world. It consists of fruits such as oranges, tangerines, lemons, grapefruits and other citrus varieties. It is found all round the year although oranges and grapefruit, reach to mature stage between mid-December and April in the Northern Hemisphere (Abobatta, 2019). Global citrus production is estimated at 80 million tons per year (Spiegel-Roy et al., 1996; Bocco et al., 1998). Citrus fruit has components that are beneficial to the health and it is considered to be one of the most important fruits in the world. Some of these components include vitamins C, carotenoids, flavonoids, pectin, calcium and potassium. It also contains soluble and insoluble fiber and can also aid in the removal of toxins from the body (Pragasam et al., 2013). The yield of juice obtained from citrus (mainly orange and grapefruit) is less half of the fruit weight and large quantities of citrus by-product (peels) which constitutes waste are gathered every year (Manthey et al., 2001). On the other hand, about 25% to 30% of non-edible fruit yield is peels and seeds (Ajila, 2010). In most cases these non-edible fruit yield by-products contain high contents of antioxidant and antimicrobial compounds that can be successfully utilized as a source of phytochemicals, antioxidant, antimicrobial, antifungal, antibacterial and antivirus agents (Avala-Zavala et al., 2004). Agricultural and industrial by-products have been used recently and many studies have been conducted on the usage of these by-products in the maintenance of food quality (Ucak, 2019; Ucak et al., 2019; Ucak et al., 2018; Ucak, 2020).

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The major advantages of using citrus peels industrial left-over or waste are that it is readily obtainable and provide inexpensive source of biomass which can be used in the health, nutrition and cosmetic industries (Chavan et al., 2018). They are rich in natural flavonoids such as flavanone glycosides, polymethoxylated flavones and flavanones (Cheigh et al., 2012). A considerable amount of valuable by-products are produced during the processing of citrus fruits (Ucak et al., 2021). In addition, citrus peels are abundantly available, cheap and economical wastes of plant origin which can be used to treat lifestyle diseases. Hence, citrus peels can be used in food and food additives as a useful ingredient for potential health properties or as a substitute for chemical stabilizers (Singh et al., 2020).

Citrus peel is including two parts, flavedo and albedo (flavedo) is the external part which is mainly rich in carotenoids and essential oils and the internal spongy portion (albedo) which is rich in phenol and pectin (Espiard, 2002; Ramful et al., 2010; Bejar et al., 2011). Hence, with these outstanding features, a number of studies recommended that citrus left-over or waste could be used as natural additive or natural source of antioxidants to take advantage of these wastes (Bocco et al., 1998; Llorach et al., 2003; Manthey et al., 2001; Wolfe, 2003; Yerlikaya et al., 2015; Yerlikaya et al., 2017; Irkin et al., 2015). In future, for estimation of antioxidant capacity of the citrus fruit, wasted part is required, which is used to explore the potential of their usage in food industries. Therefore, the purpose of this study is to evaluate the capacity of antioxidant activity and phenolic content in citrus peels with different solvent extraction.

MATERIALS AND METHODS

Extraction of peels

Mandarin and grapefruit were obtained from a local market in Niğde province. Peels were provided by squeezing of the fruits. Then the peels were carefully washed, oven-dried for 24-26 hours at 50°C until constant weight was obtained and grounded into powder. Extraction process was conducted with different solvents such as ethanol, methanol and acetone. 10 g of mandarin and grapefruit peels powder dissolved in 100 ml of 70% acetone, ethanol and methanol. The mixture was stirred by an ultrasonic water bath for 30 min and then filtered. Ethanol was evaporated at 50°C, methanol was evaporated at 55°C, and acetone was evaporated at 45°C with a rotary evaporator under vacuum.

Analyses

Total phenolic content

Folin-Ciocalteu colorimetric method was used for the determination of total phenolic contents (TPC) at 765nm and expressed as gallic acid equivalent (GAE) according to the method described by (Re, R., et al. 1999). The samples were added to Folin-Ciocalteu reagent and Na₂CO₃ solution and placed in a dark place at 24°C for 2h. Results were expressed as mg gallic acid equivalents/ml sample (GAE/g sample). The standard curve was prepared by 160, 140, 120, 100, and 80 mg/ml solutions of gallic acid in ethanol, methanol, and acetone: water with the ratio 70:30 (v/v).

Antioxidant activity

A 7 mM ABTS solution covering 2.45 mM potassium persulfate was prepared and the radical solution (ABTS + •) was made by putting for 16 hours at room temperature in the dark place. 10 μ l of sample was added on 1 ml ABTS + and a decrease in absorbance was observed for 6 minutes. (Re et al., 1999) The standard curve was prepared by 40, 60, 80, 100,120, 160, 170 and 180 mg/ml solutions of 1 mM trolox in ethanol, methanol, and acetone: water by the ratio 70:30 (v/v).

Statistical analysis

All samples were carried out three times and analyzed by using the SPSS software (Statistical Analysis System, Cary, NC, USA). Variance analysis (ANOVA) was used to evaluate the data and significance level of Duncan's test was done to compare the differences between means of parameters.

RESULTS AND DISCUSSION

Antioxidant activity

Total antioxidant activity of mandarin and grapefruit peels extracted with different solvents was given in Table 1.

Table 1. Changes in total antioxidant activity (μ mol trolox/g) of mandarin and grapefruits peels extracted in different solutions

	Ethanol	Methanol	Acetone
Mandarin peel	425.51±32.02 ^{Aa}	256.72±2.87 ^{Bb}	124.45±2.91 ^{Cb}
Grapefruit peel	428.60±50.94 ^{Aa}	349.08±21.53 ^{ABb}	303.72±17.49 ^{Ba}

Different capital letters indicate a significant difference among solvents, and different lower-cases letters indicate a significant difference between groups (P < 0.05).

The antioxidant activity values of mandarin peels extracted in ethanol, methanol, and acetone solutions were found as 425.51, 256.72 and 124.45 μ mol trolox/g, respectively, while this value was higher in grapefruit peels extracts as 428.60, 349.08 and 303.72 μ mol trolox/g, respectively. The highest antioxidant activity value was found in the ethanol group, while the lowest value was observed in the acetone group both in the mandarin and grapefruit peels. Ferreira et al. (2018) reported the values of hydro-ethanolic extract from mandarin orange as 322 μ mol Trolox/100 g. However, the result obtained in this study for mandarin peel was higher as 425.51 μ mol trolox/g. According to (Ghasemi et al., 2009), antioxidant activity of grapefruit peel methanolic extract was 2.1 mg/mL IC50. (Guimarães et al., 2010) reported that the antioxidant activity value of grapefruit peel methanolic extract was 5.15 mg/ml IC50. The reason for these differences might be due to diverse types of extraction, method and solvent used, as well as the different origin of the samples. It was reported that the antioxidant activity of albedo fragments of bitter orange was 0.537± μ M trolox (Yerlikaya et al., 2017).

In another study, it was determined that the total antioxidant activity of grapefruit albedo and flavedo fragments were 0.103 and 0.183 μ M TEAC, respectively.

Total phenolic content

The results of total phenolic content (TPC) of mandarin and grapefruit peels extracted with different solvents are presented in Table 2.

Table 2. Changes in total phenolic content (mg GAE/g) of mandarin and grapefruit peels extracted in different solvents

	Ethanol	Methanol	Acetone
Mandarin peel	387.70 ± 9.14^{Ab}	84.823 ± 0.5832^{Bb}	$32.05 \pm 0.09^{\text{Cb}}$
Grapefruit peel	666.55 ± 1.22^{Aa}	$160.29 \pm 11.66^{\text{Ba}}$	50.26 ± 1.79^{Ca}

Different capital letters indicate a significant difference among solvents, and different lower-cases letters indicate a significant difference between groups (P < 0.05).

Total phenolic content (TPC) of mandarin and grapefruit peels extracted with ethanol were found as 387.70 and 666.55 mg GAE/g, respectively. The lowest TPC values were observed in the acetone extracts as 32.05 and 50.26 mg GAE/g in mandarin and grapefruit peels, respectively. Grapefruit peels extracts showed higher TPC values than the mandarin peels extracts in all solvents. The highest TPC values were found in the ethanolic extraction of both peels. In a study, (Fejzić., 2014) used percolation with ethanol extract and the highest phenolic content was determined in the mandarin peel (0.334 mg GAE/g), while the lowest content was found in the red grapefruit peel (0.283 mg GAE/g). (Petchlert et al.,2013) reported the TPC value of mandarin as 5.71 mg GAE/ml. The phenolic content determined in albedo fragments of bitter orange was 8.31 g GAE/100g (Yerlikaya et al., 2017). As a reporte the TPC of bitter orange (*C. aurantium* L.) as 0.51 mg GAE/100 g dietary fiber (Garau et al., 2007). Extraction parameters like temperature, time, raw material and solvents have effects on the differences in the TPC and antioxidants activity.

CONCLUSION

This study based on the effects of different solvents on the total phenolic content and antioxidant activity of some citrus peels. According to the results, ethanolic extract of both mandarin and grapefruit peels showed highest total phenolic content and antioxidant activity values, while the lowest values were observed in acetone extraction. Comparing with the mandarin, grapefruit peels showed higher total phenolic content and antioxidant activity in all solvents extraction. It has been concluded that the highest antioxidant and phenolic content of Grapefruit and Mandarin Orange peels, recently started an important area of research with ethanol and acetone extraction use in the health, food, and cosmetics sectors.

REFERENCES

- Abobatta W. F. 2019. Citrus varieties in Egypt: An impression. *International Research Journal* of Applied Sciences, 1, 63-66.
- Ajila C. M., Aalami M., Leelavathi K. & Rao, U. J. S. P. 2010. Mango peel powder: a potential source of antioxidant and dietary fibre in macaroni preparations. *Innovative Food Science* and Emerging Technologies, 11, 219-224.
- Ayala-Zavala J. F., Wang S. Y., Wang C. Y. & Gonzalez-Aguilar G. A. 2004. Effect of temperature on antioxidant capacity and aroma compounds in strawberry fruit. *Lebensmittel-Wissenschaft Technologie*, 37, 2004, 687-695.
- Bejar A. K., Ghanem N., Mihoubi D., Kechaou N. & Mihoubi N. B. 2011. Effect of infrared drying on drying kinetics, color, total phenols and water and oil holding capacities of orange (*Citrus sinensis*) peel and leaves. *International Journal of Food Engineering*, 7(5), 1-25.
- Bocco A., Cuvelier M. E., Richard H. & Berset C. 1998. Antioxidant activity and phenolic composition of citrus peel and seed extracts. *Journal of agricultural and food chemistry*, 46(6), 2123-2129.
- Chavan P., Singh A. K. & Kaur G. 2018. Recent progress in the utilization of industrial waste and by-products of citrus fruits: A review. *Journal of Food Process Engineering*, 41(8), e12895.
- Cheigh C. I., Chung E. Y. & Chung M. S. 2012. Enhanced extraction of flavanones hesperidin and narirutin from *Citrus unshiu* peel using subcritical water. *Journal of Food Engineering*, 110(3), 472-477.
- Espiard E. 2002. Introduction à la transformation industrielle des fruits (Ed) TEC &DOC. France, 259-265.
- Ferreira S. S., Silva A. M. & Nunes F. M. 2018. Citrus reticulata Blanco peels as a source of antioxidant and anti-proliferative phenolic compounds. Industrial Crops and Products, 111, 141–148.
- Fejzić A. & Cavar S. 2014. Phenolic compounds and antioxidant activity of some citruses. Bulletin of the Chemists and Technologists of Bosnia and Herzegovina, 42, 1-4.
- Garau M. C., Simal S., Rossello C. & Femenia A. 2007. Effect of air-drying temperature on physico-chemical properties of dietary fibre and antioxidant capacity of orange (Citrus aurantium v. Canoneta) by-products. *Food chemistry*, *104*(3), 1014-1024.
- Ghasemi K., Ghasemi Y. & Ebrahimzadeh M. A. 2009. Antioxidant activity, phenol and flavonoid contents of 13 citrus species peels and tissues. *Pakistan Journal of Pharmaceutical Sciences*, 22(3), 277–281.
- Guimarães R., Barros L., Barreira J. C., Sousa M. J., Carvalho A. M. & Ferreira I. C. 2010. Targeting excessive free radicals with peels and juices of citrus fruits: Grapefruit, lemon, lime and orange. *Food and Chemical Toxicology*, 48(1), 99–106.
- Irkin R., Dogan S., Degirmencioglu N., Diken M. E. & Guldas M. 2015. Phenolic content, antioxidant activities and stimulatory roles of citrus fruits on some lactic acid bacteria. *Archives of Biological Sciences*, 67(4), 1313-1321.
- Llorach R., Espín J. C., Tomás-Barberán F. A. & Ferreres F. 2003. Valorization of cauliflower (*Brassica oleracea* L. var. botrytis) by-products as a source of antioxidant phenolics. *Journal of agricultural and food chemistry*, 51(8), 2181-2187.

- Manthey J. A., & Grohmann K. 2001. Phenols in citrus peel byproducts. Concentrations of hydroxycinnamates and polymethoxylated flavones in citrus peel molasses. *Journal of Agricultural and Food Chemistry*, 49(7), 3268-3273.
- Pragasam S. J. & Rasool M. 2013. Dietary component p-coumaric acid suppresses monosodium urate crystal-induced inflammation in rats. *Inflammation Research*, 62(5), 489-498.
- Petchlert C., Kaewnoi R., Siriboot A., & Suriyapan O. 2013. Antioxidant capacity of commercial Citrus juices from supermarket in Thailand. In *Pure and Applied Chemistry International Conference* (pp. 1-4).
- Ramful D., Bahorun T., Bourdon E., Tarnus E. & Aruoma O. I. 2010. Bioactive phenolics and antioxidant propensity of flavedo extracts of Mauritian citrus fruits: Potential prophylactic ingredients for functional foods application. *Toxicology*, 278(1), 75-87.
- Re R., Pellegrini N., Proteggente A., Pannala A., Yang M. & Rice-Evans C. 1999. Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free radical biology and medicine*, 26(9-10), 1231-1237.
- Singh B., Singh J. P., Kaur A. & Singh N. 2020. Phenolic composition, antioxidant potential and health benefits of citrus peel. *Food Research International*, 132, 109-114.
- Spiegel-Roy P. & Goldschmidt E. E. 1996. The biology of citrus. Cambridge university press.
- Ucak I., Abuibaid A. K. M., Aldawoud T. M. S., Galanakis C. M. & Montesano D. 2021. Antioxidant and antimicrobial effects of gelatin films incorporated with citrus seed extract on the shelf life of sea bass (*Dicentrarchus labrax*) fillets. *Journal of Food Processing and Preservation*, 45(4), e15304.
- Ucak I, Khalily R., Abuibaid A. K. M. & Ogunkalu O. 2018. Maintaining the quality of rainbow trout (*Oncorhynchus mykiss*) fillets by treatment of red onion peel extract during refrigerated storage. *Progress in Nutrition*, 20, (4), 672-678.
- Ucak I. 2019. Physicochemical and antimicrobial effects of gelatin-based edible films incorporated with garlic peel extract on the rainbow trout fillets. *Progress in Nutrition*, 21(1), 232-240.
- Ucak I. 2020. Investigation of oxidative, microbial and sensory quality changes of fish burgers enriched with pomegranate seed extract. *Food Health* 6(4), 238-247.
- Ucak I., Yerlikaya P., Khalily R., Abuibaid A. K. M. 2019. Effects of Gelatin Edible Films Containing Onion Peel Extract on the Quality of Rainbow Trout Fillets. *Eurasian Journal* of Food Science and Technology, 3(2), 40-48.
- Wolfe K., Wu X. & Liu R. H. 2003. Antioxidant activity of apple peels. *Journal of agricultural and food chemistry*, *51*(3), 609-614.
- Yerlikaya P., Ucak I. & Gümüş B. 2017. Prolonged Fish Lipid Stability with Albedo Fragments of Bitter Orang. *Turkish Journal of Fisheries and Aquatic Sciences*, 17,1397-1403.
- Yerlikaya P., Ucak I, Gümüş B., Gökoğlu N. 2015. Citrus peel extract incorporated ice cubes to protect the quality of common Pandora. *Journal of Food Science and Technology*, 52(12), 8350–8356.