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Antioxidant potential of cinnamon, ajowan and zataria essential oils in grape seed oil

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Abstract

In order to inhibit the oxidation of lipids, improve the oxidative stability of foods and to minimize the hazard risk to human health, antioxidants are added to food materials in industrial processing. In this work, the antioxidant potential of cinnamon (*Cinnamomum zeylanicum), ajowan (Carum copticum)* and zataria (*Zataria multiflora* Boiss.) essential oils (EOs) at different concentrations (0, 1 and 1.5%) on free fatty acid content (FFA), peroxide value (PV) and thiobarbituric acid reactive substances (TBARS) of grape seed oil stored at 60ºC was evaluated. Ajowan treated samples (1.5%) showed the lowest (1.02%) and zataria treated samples (1%) expressed the highest (1.19%) FFA value among EO-treated samples. Samples treated with 1.5% cinnamon showed the lowest PV (69.5 meq O_2/ kg) at the end of the storage period. Following control, the highest PV was seen in samples treated with zataria (1%). Grape seed oil samples treated with 1 and 1.5% cinnamon showed the lowest TBARS values during the whole storage period (one month). TBARS of zataria treated samples increased slightly toward the end of storage and a similar trend in TBARS was observed for samples treated with ajowan. The antioxidant activity of EOs in grape seed oil followed in descending order was cinnamon, ajowan, and zataria.

Keywords*:* Ajowan, Antioxidant activity, Cinnamon, Grape seed oil, Zataria

Introduction

Antioxidants inhibit the initiation or propagation of oxidizing chain reactions, which involve absorption and neutralization of free radicals, quenching singlet and triplet oxygen, and decomposing peroxides (Velioglu *et al.*, 1998). However, the adverse effects of some synthetic antioxidants such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), which are mostly used in food industry, have already been demonstrated (Reische *et al.*, 1998). Therefore, government agencies authorities and consumers are concerned about the safety of these foodstuffs such as edible oils and fats with synthetic additives.

Essential oils (EOs) are considered as natural antioxidant and antimicrobial substances, obtained from herbs. Main component of herbal EOs and extracts consist of a mixture of terpens, terpenoids, phenolic and other aromatic and aliphatic compounds (Bakkali *et al.*, 2008), however it is clear that their composition can vary extensively depending on the source of origin and growth conditions.

Cinnamon (*Cinnamomum zeylanicum*) is belonging to the family *Lauraceae*. Its EO has shown antioxidant properties and antiradical potential. The main components of cinnamon EO are eugenol and cinnamaldehyde (Ozcan and Arslan, 2011; Perdones *et al.*, 2014).

Carum copticum (ajowan), belonging to the *Apiaceae* family, is an aromatic annual plant. Ajowan grows in Iran, India, Pakistan and Egypt and its fruits have been used extensively in Iranian folk and traditional medicine to treat gastrointestinal, rheumatic and inflammatory disorders. The most important compound of ajowan's EO is thymol (Mahboubi and Kazempour, 2011; Oskuee *et al.*, 2011). *Carum capticum* fruits due to favorite taste, are used by Iranian people from ancient times.

As spice and preservative of foods specially meat

Zataria (*Zataria multiflora* Boiss.) as EO or as an extract is widely used in many food

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products in Iran. The high antioxidant capacity of zataria is due to the phenolic compounds, carvacrol and thymol and also the major non-phenolic compounds, linalool and p-cymene (Akrami e*t al.,* 2015; Basti *et al.*, 2016).

As high levels of unsaturated fatty acids in grape seed oil enhance the formation of oxidized off flavors, food industry has an interest in new approaches that allow edible oil products to be stored with less oxidative deterioration (Jang *et al.*, 2015). The aim of this study was to investigate the antioxidant activity of cinnamon, ajowan and zataria EOs in grape seed oil.

Materials and Methods

Grape seed oil

The red grape seed oil with no antioxidants added was obtained from a local oil extraction shop in Babolsar (Mazandaran, Iran).

Essential oils

The EOs were obtained from Barij Company (Kashan, Iran) and were stored in airtight dark glass vials at 4°C.

Gas Chromatography/Mass Spectroscopy of EOs

The EOs were analyzed by gas chromatography (GC; Thermo Quest 2000, Finnigan, U.K.). The chromatograph was equipped with a DB5 capillary column (30 m× 0.25 mm ID× 0.25 mm film thickness) and the data were acquired under the following conditions: initial temperature 50°C; program rate 2.5°C, final temperature 265°C and injector temperature 250°C. The carrier gas was helium and the split ratio was 120 ml/min. The EOs were also analyzed by GC mass spectroscopy (MS) (Thermo Quest) using the same capillary column and analytical conditions indicated earlier. The MS was run in the electron ionization mode, using ionization energy of 70 eV. The components were identified based on the comparison of their relative retention time and mass spectra with those of standards (Adams, 2001). In order to calculate the relative retention indices, alkanes were used as the reference points.

DPPH radical-scavenging activity

The 2,2-diphenyl-2-picrylhydrazyl (DPPH) free-radical scavenging assay was used to evaluate the antioxidant potential of the EOs (Shimada *et al.*, 1992). One milliliter of each EO at known concentration (0, 0.1, 0.3, 0.5 and 1% in dimethyl sulfoxide) was added to 0.25 ml of a DPPH methanolic solution. This mixture was then shaken vigorously and left at room temperature for 30 min, in darkness. The absorbance of the solution was measured at 515 nm and corresponded to the ability of the EO to reduce the stable radical DPPH to the yellow colored diphenyl picryl hydrazine. Absorption of a blank sample containing the same amount of methanol and DPPH solution was considered as negative control.

$$\%\text{DPPH scavenging} = [\text{Absorbance}_{\text{control}} - \text{Absorbance}_{\text{sample}}/\text{Absorbance}_{\text{control}}] \times 100 \quad (1)$$

Sample preparation

Two different concentrations of each EO (1.0 and 1.5 %, v/v) were added to grape seed oil and the samples were stored for 30 days at 60°C, in darkness. Experiments were conducted at 5 day intervals.

Free fatty acid (FFA)

FFA content, expressed as percentage of oleic acid in the sample, was measured via the acidimetric titration of the Bligh and Dyer extracts after adding ethanol and using phenolphthalein as an indicator, following AOCS method (AOCS, 1994).

Peroxide value (PV)

To measure the hydro peroxide content of the samples, 5.0± 0.05 g grape seed oil was taken along with 30 ml mixture (2:3, v/v) of chloroform and acetic acid into a 250 ml flask (Mehenbacher *et al.*, 1997). To the above mixture, 0.5 ml fresh saturated aqueous potassium iodide solution was added. The flask was shaken vigorously for about 1 min. Then, 30 ml distilled water was added and mixed thoroughly with the solution and titrated against 0.1 N and 0.01 N sodium thiosulphate solution (in order to accurate titration), 0.5 ml soluble starch solution was used as an

indicator. Also, a blank was prepared with no oil sample. PV was determined according to the following equation:

PV (milliequivalents of peroxide/ Kg oil sample)= $[(V_s-V_b) \times N \times 10^3] / w$ (2)

Where V_s is the volume (ml) of sodium thiosulphate solution used for the sample, V_b that of the blank, N the normality of sodium thiosulphate solution and W the weight of the oil sample in grams.

Determination of thiobarbituric acid reactive substances (TBARS)

Thiobarbituric acid reactive substances are formed as a byproduct of lipid peroxidation which can be detected by the TBARS assay using thiobarbituric acid as a reagent (Kristensen and Skibsted, 1999). The thiobarbituric acid (TBA) reagent was prepared immediately before use by mixing equal volumes of freshly prepared TBA (0.025 M) (preparation into solution by neutralizing with NaOH) and H_3PO_4 (2M) / citric acid (2M). Measurements were performed at 532 nm (red pigment) and 450 nm (yellow pigment) and the results are expressed as absorbance units in one gram of oil sample.

Statistical analysis

The one-way ANOVA was performed to analyze the chemical parameters and significant differences were determined by using Tukey test. The analyses were performed in SPSS 22 and MS Excel programs. All determinations were performed in triplicate.

Results and Discussion

Spices, aromatic plants and culinary herbs are interesting for their high content of bioactive metabolites and compounds that may exert beneficial effects on human health. According to several studies, these compounds exhibit antiradical and antioxidant potential, mainly through hydrogen donating to reactive radicals (Velioglu *et al.*, 1998; Basti *et al.*, 2016). Twenty six compounds were identified for zataria EO; the main constituents were carvacrol (50.53%) and thymol (14.70%). Also, 15 and 31 compounds were detected for cinnamon and ajowan Eos respectively. The main compounds present in cinnamon EO were cinnamaldehyde (71.5%) and eugenol (3.08%), and those in ajowan EO were thymol (62.45%), (Z)- p-cymene (18.01%) and γ-terpinene (15.89%).

It seems that high degree of antioxidant and antiradical activities of cinnamon EO found in the present work probably derived from the hydrogen donating potential exhibited by a wide range of its constituents, especially cinnamaldehyde and eugenol (Ozcan and Arslan, 2011; Perdones *et al.*, 2014).

The main compounds of ajowan EO are reported to be terpenes such as thymol, (Z)- *p*-cymene and γ-terpinene, as determined in this work and other studies (Mahboubi and Kazempour 2011; Oskuee *et al.*, 2011). The relative antioxidant activity of ajowan suggests that this plant can have the promising potential to be used as a natural antioxidant and flavoring compound in food industry to avoid food spoilage and oxidation while increasing the safety of the food products during the processing and also during the storages at various conditions.

The major components of zataria EO were carvacrol and thymol. In our results, the amount of carvacrol was less than other studies (Akrami *et al.*, 2015; Basti e*t al.*, 2016) that may explain the lower antioxidant activity of this EO in comparison with the other studies. The different amount of chemical compounds in the EOs might be related to harvest season, geographical situation, grinding conditions and genetic parameters (Peter, 2004).

Antioxidant potential of the EOs was evaluated by DPPH assay (Fig. 1). In the present study it has been found that cinnamon EO at concentration of 1% was able to reduce the stable radical DPPH to 1, 1-diphenyl-2-picrylhydrazine up to 76.51%, followed by ajowan and zataria EOs with 54.20 and 26.35% inhibitory activity, respectively.

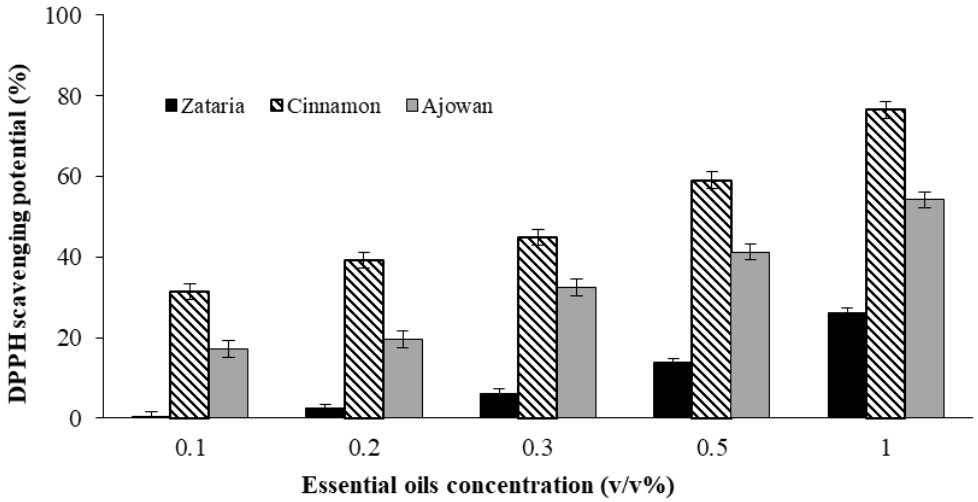

Fig. 1. The effect of different concentrations of EOs (Zataria, cinnamon and ajowan) on free-radical scavenging

The EOs were capable of scavenging DPPH free radicals in a dose-dependent manner through hydrogen-donation converting it to the nonradical hydrazine form. The potential of scavenging DPPH radicals was determined as the cinnamon> ajowan> zataria. The DPPH radical scavenging activities were 76.51%, 54.20 % and 26.35% for cinnamon, ajowan and zataria, respectively, which suggests that the components within cinnamon EO are more efficient radical-scavenging components. The results obtained in this work showed that the antiradical activity may be related to the presence of cinnamaldehyde, carvacrol, thymol and eugenol in essential oils. Cinnamon essential oil had significantly higher persistent antioxidant activity, probably due to considerably high content of cinnamaldehyde (Ozcan and Arslan, 2011).

FFA contents of treated grape seed oil samples are shown in Fig. 2. There was a significant difference between FFA of EO-treated samples with the control ($P<0.05$). Ajowan (1.5%) treated samples showed the lowest (1.02± 0.06 %) and zataria (1%) treated oil samples expressed the highest (1.19± 0.04%) FFA value among EO-treated samples ($P<0.05$).

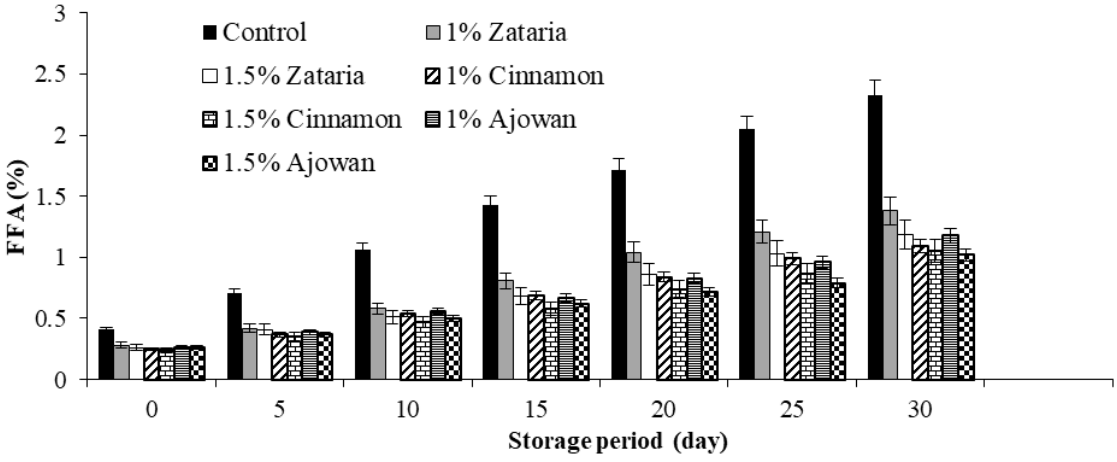

Fig. 2. The effect of type and different concentrations of EOs (Zataria, cinnamon and ajowan) and storage time on the FFA (mg/g oil sample) of grape seed oil

FFAs are produced by the hydrolysis of oils and fats as the result of exposure to various factors such as storage, processing, heating or frying. As FFAs are less stable than triglycerides, they are more prone to start oxidation and to turning rancid. In the present study, the oil samples treated with antioxidants had higher oxidative stability and lower free fatty acid content than the control sample. FFA contents especially in the control and samples treated with 1% zataria EO showed a considerable increase. As it is obvious from the results, cinnamon EO at both concentration of 1 and 1.5% and ajowan EO at 1.5% were more inhibitory against FFA increase, in comparison with other treatments. In a study conducted by Villa-Ruano et al. (2013) anti-lipase effect of 30 medical plants was confirmed.

The effects of type and concentration of EOs and storage time on the PV of grape seed oil at 60°C are illustrated in Fig. 3.

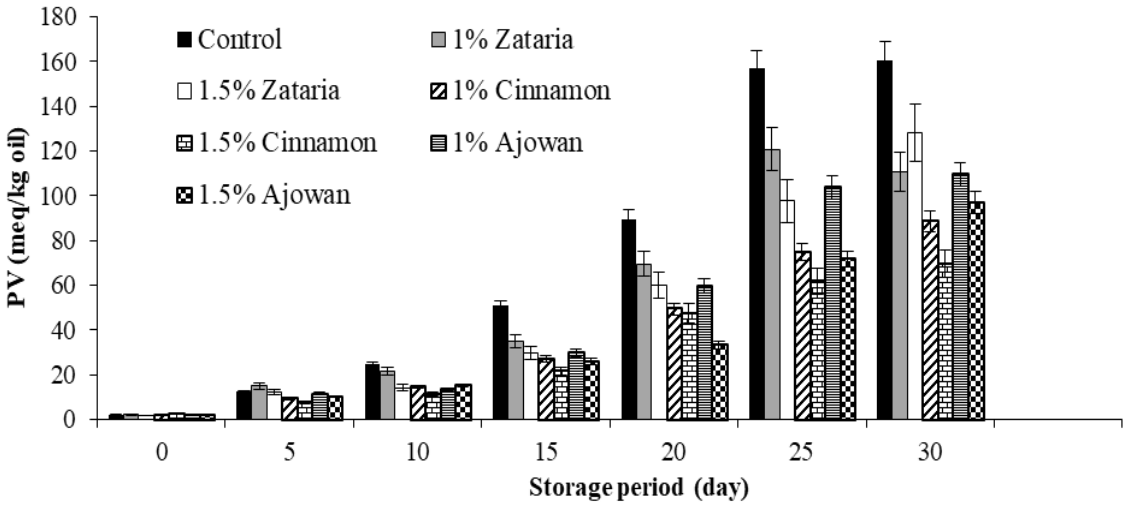

Fig. 3. The effect of type and different concentrations of EOs (Zataria, cinnamon and ajowan) and storage time on the PV (meqO_2/ kg oil) of grape seed oil

After 4 weeks, significant increase in PV was determined in all samples but oil sample treated with 1.5% cinnamon EO showed the lowest PV (69.5 meqO_2/ kg) at the end of the storage period ($p<0.05$). Among EO- treated oil samples, the highest PV was seen in samples treated with 1% of zataria EO ($p<0.05$).The essential oils of cinnamon and ajowan showed more inhibitory effect on PV increase and oxidative deterioration in grape seed oil. Reduction of PV within the last days of storage can be explained by an increase in the rate of hydro peroxide destruction during such period. The same results were obtained by other researchers who observed an increase in PV of soybean oil samples during the first 2 months of storage at 20, 30 and 40ºC and then decrease in PV to the end of the 6-month storage period (Dolati *et al.*, 2016). The PV in control sample was still increasing so the destruction of hydro peroxides didn't result in PV reduction.

Amount of secondary lipid oxidation products were quantified using the TBARS method. The changes of TBARS in the oil samples stored at 60°C are shown in Fig. 4. Grape seed oil samples treated with 1 and 1.5% cinnamon EO, in comparison with other samples, showed the lowest TBARS values during the whole storage period ($p<0.05$). BARS of zataria treated samples increased slightly toward the end of storage and a similar trend in TBARS was observed for samples treated with ajowan EO.

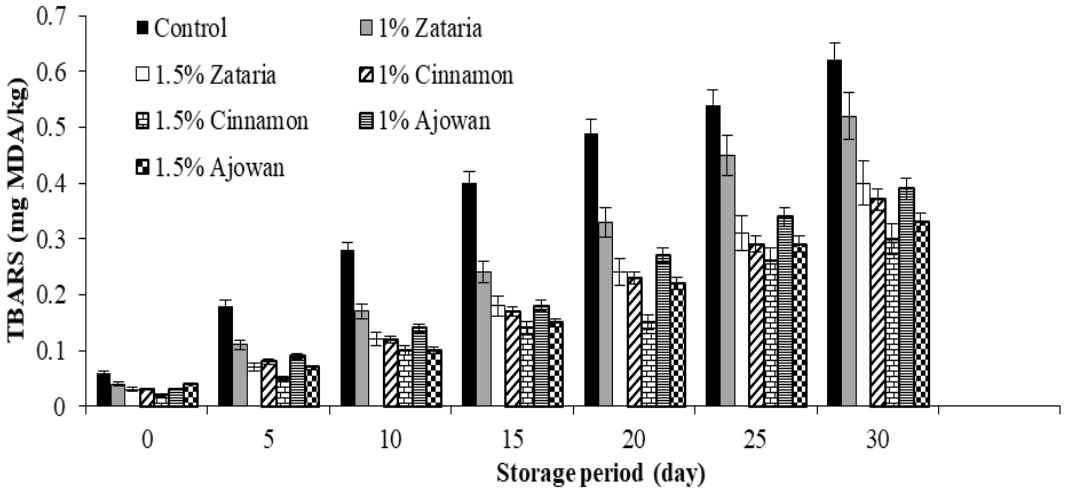

Fig. 4. The effect of type and different concentrations of EOs (Zataria, cinnamon and ajowan) and storage time on the TBARS (mg Malondialdehyde /kg oil) of grape seed oil

Although the primary lipid oxidation products are peroxides but they provide little information about the nature of the oxidative processes during storage of the oils and fats. Lipid peroxides are degraded to products of secondary lipid oxidation. TBARS value of all samples increased significantly with the advancement of storage period. High potential of cinnamon EO in inhibiting TBARS increase in food samples is reported in several studies (Schmidt, 2006; Ozcan and Arsalan, 2011). Shahsavari *et al.* (2008) observed good antioxidant activity from zataria EO at concentration of 0.6% in soybean oil. Also Hashemi *et al.* (2014) reported that the antioxidant effect of 0.75% ajowan EO in sunflower oil considerably restrained TBARS value. In this work, in comparison with other studies, the concentration of 1.5% (v/v) of all three EOs had the highest inhibitory effect on the formation of primary and secondary oxidation products. Zataria and ajowan EOs expressed stronger antioxidant activities in comparison with similar EOs in our work. This may be due to difference in the total phenolic and other antioxidant compounds of EOs with different origins in different studies.

Conclusions

The results of our study revealed that the herbal EOs express considerable antioxidative activity in grape seed oil samples. The main components of EOs in present study are phenolic and terpene compounds which can act as antiradicals through free radical scavenging pathways. In the present study, the antioxidant activity of EOs followed by cinnamon> ajowan> zataria pattern. The concentration of 1.5 % (v/v) of cinnamon EO was the most effective in decreasing peroxide and secondary oxidation products formation rate in grape seed oil samples.

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References

Adams R.P. (2001). Identification of essential oil components by gas chromatography/ mass spectroscopy (2nd ed ed.). Illinois: U.S. Allured Publishing Corporation.

Akrami F., Rodríguez-Lafuente A., Bentayeb K., Pezo D., Ghalebi S. R. and Nerín C. (2015). Antioxidant and antimicrobial active paper based on Zataria (*Zataria multiflora*) and two cumin cultivars (*Cuminum cyminum*). *LWT - Food Science and Technology* 60(2), 929-933.

AOCS. (1994). The official methods and recommended practices of the American Oil Chemists' Society (Vol. (Ca 5a-40, Cd 8-53)). Champaign: U.S. *The American Oil Chemists' Society*.

Bakkali F., Averbeck S., Averbeck D. and Idaomar M. (2008). Biological effects of essential oils: a review. Food and Chemical Toxicology 46, 446-475.

Basti A.A., Gandomi H., Noori N. and Khanjari A. (2016). Shirazi thyme (*Zataria multiflora Boiss*) Oils . In Preedy, A. and Victor, R. (Eds). Essential Oils in Food Preservation, Flavor and Safety, p. 731-736. San Diego: Academic Press.

Dolati M, Rezaei K., Piravi Vanak Z. and Movahed S. (2016). Study of the effects of essential oils of cumin, savory and cardamom as natural antioxidants on the flavor and oxidative stability of soybean oil during the storage. *Journal of Essential Oil Bearing Plant*s 19(1), 176-184.

Hashemi M., Niakousari M., Saharkhiz M. and Eskandari M. (2014). Stabilization of sunflower oil with *Carum copticum* Benth and Hook essential oil. *Journal of Food Science and Technology* 51(1), 142–147.

Kristensen D. and Skibsted L. H. (1999). Comparison of three methods based on electron spin resonance spectrometry for evaluation of oxidative stability of processed cheese. Journal of *Agricultural and Food Chemistry* 47, 3099–3104.

Mahboubi M. and Kazempour N. (2011). Chemical composition and antimicrobial activity of *Satureja hortensis* and *Trachyspermum copticum* essential oil. *International Journal of Food Microbiology* 3, 194-200.

Mehenbacher V.C., Sallee E.M., Walker R.O., Hopper T.H., Link W.E., Walker R.C. and Firestone D. (1997). Official Methods and Recommended Practices of the American Oil Chemists' Society. *Illinois*: U.S. AOCS Press.

Oskuee R. K., Behravan J. and Ramezani M. (2011). Chemical composition, antimicrobial activity and antiviral activity of essential oil of *Carum copticum* from Iran. *Avicenna Journal of Phytomedicine* 1, 83-90.

Özcan M.M. and Arslan D. (2011). Antioxidant effect of essential oils of rosemary, clove and cinnamon on hazelnut and poppy oils. Food Chemistry 129(1), 171-174.

Perdones A., Vargas M., Atarés L. and Chiralt A. (2014). Physical, antioxidant and antimicrobial properties of chitosan–cinnamon leaf oil films as affected by oleic acid. *Food Hydrocolloids* 36, 256-264.

Peter K.V. (2004). Handbook of Herbs and Spices. 1st ed. Cambridge: Woodhead Publishing Ltd.

Reische D.W., Lillard D.A. and Eintenmiller R.R. (1998). Antioxidants in food lipids. In Ahoh, M.D.B. C C (Ed). Chemistry, Nutrition and Biotechnology, p. 423-448. New York: Marcel Dekker.

Schmidt E. (2006). Composition and antioxidant aActivities of the essential oil of cinnamon (*Cinnamomum zeylanicum* Blume) leaves from Sri Lanka. *Journal of Essential Oil Bearing Plants* 9(2), 170-182.

Shahsavari N., Barzegar M., Sahari M.A. and Naghdibadi H. (2008). Antioxidant activity and chemical characterization of essential oil of *Bunium persicum*. J*ournal of Plant Foods for Human Nutrition* 63, 183-188.

Shimada K., Fujikawa K., Yahara K. and Nakamura T. (1992). Antioxidative properties of xanthan on the autooxidation of soybean oil in cyclodextrin. J*ournal of Agricultural and Food Chemistry* 40, 945-948.

Velioglu Y.S., Mazza G., Gao L. and Oomah B.D. (1998). Antioxidant activity and total phenolics in selected fruits, vegetables, and grain products. *Journal of Agricultural and Food Chemistry* 46(10), 4113-4117.

Villa-Ruano N., Zurita-Vásquez G.G., Pacheco-Hernández Y., Betancourt-Jiménez M.G., Cruz-Durán R., Duque-Bautista H. (2013). Anti-lipase and antioxidant properties of 30 medicinal plants used in Oaxaca, México. *Biological Research* 46(2), 153-160.

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پتانسیل آنتی‌اکسیدانی اسانس‌های دارچین، زنیان و آویشن شیرازی در روغن هسته انگور

مریم عزیزخانی[1*]- فاطمه آدینه‌پور[2]

تاریخ دریافت: 1397/02/30
تاریخ پذیرش: 1398/05/26

چکیده

در فرآیند صنعتی مواد غذایی، به‌منظور ممانعت از اکسیداسیون چربی‌ها، بهبود پایداری اکسیداتیو مواد غذایی و به حداقل رساندن آسیب به سلامت افراد آنتی‌اکسیدان‌ها به مواد غذایی اضافه می‌شوند. در این پژوهش، توانایی آنتی‌اکسیدانی اسانس‌های دارچین (*Cinnamomum zeylanicum*)، زنیان (*Carum copticum*) و آویشن شیرازی (*Zataria multiflora* Boiss.) در غلظت‌های مختلف (صفر، 1 و 1/5%) بر میزان اسیدهای چرب آزاد، عدد پراکسید و ترکیبات واکنش‌دهنده با تیوباربیتوریک اسید در روغن هسته انگور در 60 درجه سانتی‌گراد ارزیابی گردید. نمونه‌های تیمار شده با اسانس زنیان (1/5%) پایین‌ترین (1/02%) و نمونه‌های تیمار شده با اسانس آویشن شیرازی (1%) بالاترین (1/19%) میزان اسید چرب آزاد را در میان نمونه‌های تیمارشده با اسانس نشان دادند. نمونه‌های تیمارشده با 1/5 اسانس دارچین دارای پایین‌ترین اندیس پراکسید (69/5 $meqO_2/kg$) در انتهای دوره نگهداری بودند. پس از نمونه کنترل، بالاترین اندیس پراکسید در نمونه‌های حاوی اسانس آویشن شیرازی (1%) مشاهده گردید. نمونه‌های روغن هسته انگور تیمارشده با 1 و 1/5% اسانس دارچین واجد کمترین اندیس تیوباربیتوریک اسید در کل دوره نگهداری (یک ماه) بودند. اندیس تیوباربیتوریک اسید نمونه‌های دارای اسانس آویشن شیرازی تا انتهای دوره نگهداری با شیب ملایمی افزایش یافت و تغییرات مشابهی نیز در نمونه‌های تیمارشده با زنیان مشاهده شد. فعالیت آنتی‌اکسیدانی اسانس‌ها در روغن هسته انگور به‌ترتیب نزولی دارچین، زنیان، آویشن شیرازی بود.

واژه‌های کلیدی: آویشن شیرازی، دارچین، روغن هسته انگور، زنیان، فعالیت آنتی‌اکسیدانی

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