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## Influence of Adding Essential Oils as Natural Antioxidants on Thermal Stability of Sunflower Oil

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### Abstract

This study was designed to evaluate the effect of adding the essential oils (EOs) extracted from marjoram, peppermint, anise and fennel compared with synthetic antioxidants (BHT and BHA) to sunflower oil (SFO) on the oxidative stability during heat treatments ( $180\pm 5^{\circ}\text{C}$  for 18 h). Results showed that the aromatic plants contained of phenolic substances (26.52 - 45.26 mg) can be used as natural antioxidants. Using of antioxidants (EOs and BHT, BHA) with SFO increased their oxidative stability compared with untreated SFO sample (control). Data demonstrated that the values of acid, peroxide, thiobarbituric acid (TBA value), conjugated diene and triene increased to the highest rates in SFO control (without antioxidant) compared to SFO + antioxidant, while the iodine value was significantly decreased in SFO control compared with SFO + antioxidant during heating. The data also showed that the thermal stability (Rancimat value) of SFO was enhanced by adding EOs. Generally, the adding of EOs as natural antioxidants can definitely create a significant impact in the market as there is no adverse health effect on the usage of EOs as a natural compounds compare with synthetic antioxidant in food.

**Keywords:** *Essential oils, Sunflower oil, , Natural antioxidants, Oxidative stability.*

### Introduction

Oxidative stability of Edible oils is one of the key factors in determining its use in foods and their applicability in industrial. Various methods have been developed to improve stability of oils including genetic modifications, composition changes by chemical means, addition of synthetic antioxidants such as TBHQ, BHT and BHA. But synthetic antioxidants are reported to be carcinogenic, so BHT has been removed from the GRAS list and TBHQ has been banned in many countries because of its health risk. The natural antioxidants that can replace synthetic antioxidants have always been an interesting research area among food scientists. EOs from spices and herbs have attracted lot of attention in this regard (Tugba and Medeni, 2012). The addition of EOs as a natural antioxidant to vegetable oils can impart a combined effect to extend shelf life of oils (Sadeghi *et al.*, 2016).

The plants contains chemical compounds that are source of natural antioxidants used for health promotion, food preservation and food flavoring since they are safer to consumption and more environmentally friendly than their synthetic counterparts (Stevenson and Lowe, 2009, Aberoumand, 2011 and Hussain *et al.*, 2011). The most widely used synthetic antioxidants in food, namely BHT, BHA, PG and TBHQ have been suspected of causing many diseases to humans (Suhaj, 2006). Spices and EOs include a polyphenolic components, mainly flavonoids, phenolic acids, also, ascorbic acid and carotenoids which possess, antioxidant activity against the reactive oxygen species so they are known for their protective effect for health (Williams *et al.*, 2004 and Soobrattee *et al.*, 2005). This damage causes the onset of many diseases such as rheumatoid, cirrhosis, arteriosclerosis, diabetes and cancer (Ebadi, 2006). Currently, there is growing interest in evaluating the potential of natural plant extracts as an alternative of synthetic antioxidants are commonly used in food industries and produced some toxicity in the human body. Hence, search for newer natural antioxidants has ever since increased (Kenari *et al.*, 2020 and Kumar *et al.*, 2018).

Antioxidants are recognized for their potential in promoting health and lowering the risk for cancer, hypertension and heart disease (Valko *et al.*, 2007). The antioxidant properties of many herbs and spices are reported to be effective in retarding the process of lipid peroxidation in oils and fatty acids and have gained interest of many research groups (Huda-Faujan *et al.*, 2009) and (Nanasombat and Teckchuen, 2009). Among the herbs and spices extensively studied, the plants and EOs obtained from the lamiaceae family possess a significant antioxidant activity; for example, those of oregano (Kulisic *et al.*, 2004) and (Hossain *et al.*, 2008)

Al-Dalain *et al.* (2011) stated that phenolic compounds which are found in herbs and spices and other plant materials are of increasing interest in the food industry because they reduce the oxidative degradation of lipids and improve the quality and nutritional value of food, on the other hand they showed that EOs inhibited the formation of primary and secondary oxidation products during thermal treatment and storage of SFO at room temperature. It could be concluded that, EOs extracted from aromatic plants are promising as natural antioxidants.

Sunflower oil (SFO) is one of the most frequently consumed oils which are susceptible to lipid oxidation. It contains a higher amount of polyunsaturated fatty acids, like linoleic acid and the use of antioxidants is the main strategy to protect the oil from oxidation through heating processing (Mezza *et al.*, 2018).

The study aimed to evaluate the effect of adding EOs extracted from marjoram, peppermint, anise and fennel on the oxidative stability of SFO during heating at  $180\pm 5^{\circ}\text{C}$  for 18 hours.

## Materials and Methods

### Materials

Sunflower oil (SFO): fresh refined SFO without adding of any synthetic antioxidant was obtained from El Nile for oils and Detergents Company, El-Minia, Egypt.

Aromatic plant samples: marjoram leave, peppermint leaves, anise seeds and fennel seeds were obtained from a National Research Centre, Cairo, Egypt

The essential oils (EOs) of four selected aromatic plants (marjoram leave, peppermint leaves, anise seeds and fennel seeds) were extracted by extracted by hydro steam distillation using the Clevenger apparatus according to the method described in the British Pharmacopeia (1988). EOs was collected after 4 hours. The separated EOs was dried over Na<sub>2</sub>SO<sub>4</sub> (anhydrous) before hold in dark glass bottles at 4°C until analysis.

Chemicals All chemicals used (analytical grades) were purchased from Sigma (St. Louis, USA) and from EL-Gamhouria for Trading Chemicals and Drugs Company, Assiut, Egypt.

Antioxidants: Food grade antioxidant of Butylated hydroxyl toluene (BHT) and Butylated hydroxyl anisole (BHA). The food additive regulation in USA had a limitation of 200 ppm synthetic antioxidant, while others of natural antioxidant had 400 ppm as recommended usage level.

### Analytical methods

#### Physicochemical properties of oils

Acid value, peroxide value and iodine number were estimated according to AOCS (1998). Thiobarbituric acid (TBA value) was estimated spectrophotometry at 532 nm according to Guzman-Chozas *et al.* (1997).

#### Conjugated dienes and triene

A Shimadzu UV-1601 PC, UV-Visible spectrophotometer, with the UVPC Personal spectroscopy software version 3.91, was used to determine absorptivity at the UV spectrum. The ultraviolet absorbance at 232-234 nm for conjugated dienes formation and at 268-270 nm for conjugated triene formation as mentioned by Gray, 1978; Chiou, 1992 and Vieira and Regitano-Darce, 1999.

#### Total phenolic

Total phenolic content in aromatic plant extracts were determined spectrophotometrically according to the Folin-Ciocalteu method of Kang *et al.* (2010). The absorbance was measured at 765 nm. The results were expressed as mg Gallic acid / g dry weight.

#### Oxidative stability by Rancimat method

Oxidative stability of the studied oils were determined with a Rancimat apparatus (Metrohm, Herisau, Switzerland) by measuring the induction period of

oils containing the antioxidant, according to the method described by Farahmandfar *et al.* (2018). Antioxidant activities of the studied oil samples were determined by measuring the induction period of oils (Rancimat value) containing the antioxidant

$$\text{Antioxidant index} = \frac{\text{Induction period of oil with extract}}{\text{Induction period of oil alone}}$$

### Thermal treatments of sunflower oil (SFO)

The natural and synthetic antioxidants used were within the recommended usage levels as previously mentioned. Antioxidants were dissolved in SFO and kept in brown glass bottles for the following:

SFO samples were heated at  $180 \pm 5^\circ\text{C}$  for 18 hours at intervals of 3 h heating daily for 6 consecutive days (electric hot plate device, stirring manually with a glass rod). The heated oils were sampled every day after heating and kept in brown bottles at  $5^\circ\text{C}$  for analytical experiments. The remainder of oil samples were heated the next day for another 3 h and then sampled as previously until the sixth day and the total of 18 h heating.

The heated oil samples without antioxidant (control) and with the added antioxidants were used for determination of acid value, peroxide value, iodine number, TBA value, conjugated diene and triene to follow the effect of adding essential oils (natural antioxidant) and synthetic antioxidants (BHT and BHA) at high temperature ( $180 \pm 5^\circ\text{C}$ ) compared to SFO control (without antioxidant).

## Results and Discussion

### Essential oils (EOs) contents

Data presented in Table (1) showed that the EOs contents extracted by hydro steam distillation of aromatic plants (marjoram leaves, peppermint leaves, anise seeds and fennel seeds).

**Table 1. Essential oils content of dry aromatic plants**

Aromatic plant	% Essential oil on dry weight basis
Marjoram leaves	0.94
Peppermint leaves	0.72
Anise seeds	2.86
Fennel seeds	3.21

The percentage of EOs extracted from marjoram leaves, peppermint leaves, anise seeds and fennel seeds were 0.94, 0.72, 2.86 and 3.21%; respectively on dry weight basis. These results are in agreement with that of Lis *et al.* (2007), Verma *et al.* (2010), Shojaii and Abdollahi (2012) and Khammassi *et al.* (2018).

### Content of total phenolic

The amount of total phenolic estimated by Folin-Ciocalteu method in the studied aromatic plant samples are presented in Table (2). Tabulated data showed

that, the amount of total phenolics varied widely in the studied selected aromatic plants, and ranged from 26.52 to 45.26 mg Gallic acid/g of dry weight.

**Table 2. Total phenolic (mg Gallic acid /g) content in aromatic plants (Dry weight)**

Aromatic plants	Total phenolic content (mg/g)
Marjoram leaves	45.26
Peppermint leaves	39.15
Anise seeds	30.22
Fennel seeds	26.52

The highest amount of total phenolic content was found in marjoram leaves (45.26mg/g), while the lowest was in fennel seeds (26.52mg/g). The obtained results in Table (2) showed that the spices were relatively high in total phenolic contents of the studied spices were decreased in the following order: marjoram > peppermint > anise > fennel. Such results are in accordance with those reported by Olgun, *et al.* (2017), Sun *et al.* (2019) and Ahmed *et al.* (2019). The differences between the results were likely due to environmental differences within species and genotypic, time of taking samples and choice of parts tested (kim and Lee, 2004 and Shan *et al.*, 2005).

#### **Oxidative stability of Sunflower oil (SFO) samples by Rancimat method**

The oxidative stability and antioxidant activity (by rancimat) of SFO + EOs, SFO + BHT and BHA compared with SFO control (without antioxidant) are shown in Table (3).

**Table3. Oxidative stability and antioxidant activity of SFO treated with EOs by Rancimat method**

SFO samples	Rancimat value Induction period (hour)	Antioxidant activity
SFO Control	5.52	-
SFO + BHT	10.22	1.851
SFO+ BHA	10.55	1.911
SFO + marjoram oil	12.36	2.239
SFO + peppermint oil	12.02	2.178
SFO + anise oil	11.58	2.098
SFO + fennel oil	10.12	1.833

BHT= Butylated Hydroxyl Toluene, BHA= Butylated Hydroxyl Anisole and SFO= Sunflower oil

The data in Table (3) suggests that EOs have a strong antioxidant activity. The addition of the EOs extracted from marjoram, peppermint, anise and fennel increased the SFO stability up to 12.36, 12.02, 11.58 and 10.12 h; respectively compared with 10.22 and 10.55 hours in SFO with BHT and BHA; respectively. Data showed that the adding of EOs (as a natural antioxidant at 400 ppm concentrations) increases the rancimat value and antioxidant activity of SFO samples compared the control (without antioxidant). This means that all the

added EOs possessed antioxidant effect; it may be due to their phenolic compounds content and the other compounds in EOs which was capable of minimizing oil peroxidation, protecting SFO against autoxidation. These results are in good agreement with those reported by Politeo *et al.* (2006) and El-Kashef *et al.* (2014).

### **Effect of adding essential oils (EOs) as natural antioxidants on characteristics of sunflower oil (SFO) during heating**

The characteristics and quality of SFO during heat treatments ( $180^{\circ}\text{C}\pm 5$ ) are shown in Tables (4-9). The samples were analyzed periodically for acid value, iodine number, TBA, peroxide value, conjugated diene and triene values, since a single reaction criterion is not enough to account for the oxidative changes at various stages of heating (18 h).

#### **Acid value**

Free fatty acids (FFA) are a sign of hydrolytic rancidity, but oxidation of other oils can also produce acids. In addition, free unsaturated fatty acids can be easily broken down into substances with a small molecular weight, which will deteriorate the quality of food. Knowing the composition of the FFA present in the sample can be useful for understanding the cause of their formation or breakdown (Sun *et al.* 2011).

The results in Table (4) revealed that the heat treatments of SFO caused an increase in the acid value. Such increment during heating could be attributed to formation of acidic compounds and FFA. The highest acid value was occurred in SFO samples contained antioxidants up to 18 h in all oil samples. However, the increment in the acid value of the SFO control (without antioxidant) was occurred after 15 h of heating and then decreased. The decrement in acid values of oils can be attributed to the esterification reaction between the FFA and the glycerol in the oil structure leading to the formation of triglyceride. Besides possibility that low molecular weight acids in the oil may be lost through volatilization, hence causing a reduction in FFA (Hau *et al.*, 1987).

At the end of heating periods all SFO samples contained EOs and synthetic antioxidants recorded the lower acid value (1.76-1.96 mg KOH/g) compared the untreated SFO. The SFO+ marjoram oil treatment recorded the lowest acid value (1.76 mg KOH/g) among all treated samples at the end of heat treatment. The amount of FFA that was formed in SFO without antioxidants was higher than SFO contains antioxidants (EOs, BHT and BHA). Thus, as shown in Table (4), EOs are very good antioxidants and this antioxidant ability might be the reason for the lowered FFA formation in SFO + EOs compared to the SFO control (without antioxidant). These results are in agreement with those reported by Saleh *et al.* (2010), Al-Dalain *et al.* (2011), Amorati *et al.* (2013) and Sadeghi *et al.* (2016).

**Table 4. Effect of heating periods at 180°C on acid value (mg KOH/g oil) of SFO treated with EOs**

SFO samples	Heating periods (h)						
	Zero time	3	6	9	12	15	18
<b>SFO (Control)</b>	0.58	0.84	1.02	1.33	1.94	2.62	2.11
<b>SFO + BHT</b>	0.58	0.78	0.96	1.28	1.42	1.64	1.96
<b>SFO + BHA</b>	0.58	0.74	0.98	1.18	1.38	1.52	1.82
<b>SFO + marjoram oil</b>	0.58	0.64	0.80	0.88	1.08	1.36	1.76
<b>SFO + peppermint oil</b>	0.58	0.66	0.82	0.92	1.12	1.38	1.84
<b>SFO + anise oil</b>	0.58	0.69	0.86	0.94	1.16	1.40	1.88
<b>SFO + fennel oil</b>	0.58	0.72	0.90	1.06	1.24	1.48	1.90

BHT= Butylated Hydroxyl Toluene, BHA= Butylated Hydroxyl Anisole and SFO= Sunflower oil

### Peroxide value

The hydroperoxide is the primary product of the autooxidation of unsaturating lipids. The peroxide index directly measures the quantity of hydroperoxides formed in the initial stage of lipid oxidation (Sun *et al.*, 2011). Data in Table (5) showed that the effects of addition antioxidants (EOs, BHT and BHA) on peroxide value of SFO were tested during heating at 180 ±5°C up to 18

Data observed that the peroxide value was gradually increased with increment of heating periods and reaches the highest value after 12 h of all studied samples, and then turns back to decrement during heating up to 18 h. On the other hand, the untreated SFO sample recorded the highest peroxide value during heat treatments up to 18 h compared all SFO contained antioxidants. Besides, the SFO with marjoram oil had the lowest peroxide value among all SFO treatments (Table 5).

**Table 5. Effect of heating periods at 180°C on peroxide value (meq/kg oil) of SFO treated with EOs**

SFO samples	Heating periods (h)						
	Zero time	3	6	9	12	15	18
<b>SFO (Control)</b>	0.73	2.88	4.92	7.48	9.98	8.32	7.92
<b>SFO + BHT</b>	0.73	2.04	3.87	5.86	8.22	7.84	7.34
<b>SFO + BHA</b>	0.73	2.11	3.16	5.94	8.63	7.66	7.24
<b>SFO + marjoram oil</b>	0.73	1.82	2.18	4.72	7.28	6.96	6.42
<b>SFO + peppermint oil</b>	0.73	1.82	2.86	4.96	7.68	7.12	6.88
<b>SFO + anise oil</b>	0.73	1.96	2.92	5.06	7.82	7.15	6.98
<b>SFO + fennel oil</b>	0.73	2.10	3.12	5.16	7.92	7.42	7.12

BHT= Butylated Hydroxyl Toluene, BHA= Butylated Hydroxyl Anisole and SFO= Sunflower oil

This variation in peroxide values of SFO samples due to use different antioxidants (BHT, BHA and EOs as natural antioxidant). At the beginning of the SFO heating process, peroxide formation was faster than its decomposition.

However, the decrement in peroxide value can be due to the fact that the peroxides formed on heating treatment are unstable compounds towards high temperatures transforming and broken down into smaller compounds as them to ketones, aldehyde and carbonyl compounds (Serjouie *et al.*, 2010). The peroxide formation in SFO without antioxidants (control) was higher than SFO contains antioxidants (natural antioxidant and synthetic antioxidants). Thus, as shown in Table (5), EOs work as natural antioxidants and lowered peroxide formation comparing to SFO without antioxidant during heating, even if peroxide value determination was not a very good measure of oil oxidation during heating (Stevenson *et al.*, 1984). Such results are in accordance with those reported by El-Kashef *et al.* (2014) and Nduka *et al.* (2021).

### Thiobarbituric acid (TBA value)

TBA value expresses lipid oxidation in mg of malonaldehyde equivalents per kg sample of oil (Pikul *et al.*, 1989). Data in Table (6) revealed that the TBA value (mg/kg) of SFO samples went to gradually increasing with the heating period increase for SFO samples. The highest TBA value was found in all samples after 18 h at  $180\pm 5^\circ\text{C}$  were (2.21), (1.72), (1.76), (1.58), (1.66), (1.69) and (1.72) for (SFO control), (SFO +BHT), (SFO +BHA), (SFO + Marjoram oil), (SFO + peppermint oil), (SFO+ anise oil) (SFO +Fennel oil); respectively.

**Table 6. Effect of heating periods at  $180^\circ\text{C}$  on TBA value (mg/kg) of SFO treated with EOs**

SFO samples	Heating periods (h)						
	Zero time	3	6	9	12	15	18
SFO (Control)	0.38	0.52	0.78	0.97	1.41	1.87	2.21
SFO + BHT	0.38	0.48	0.69	0.78	1.11	1.42	1.72
SFO + BHA	0.38	0.45	0.71	0.80	1.14	1.43	1.76
SFO + marjoram oil	0.38	0.42	0.62	0.75	1.06	1.35	1.58
SFO + peppermint oil	0.38	0.42	0.64	0.78	1.10	1.39	1.66
SFO + anise oil	0.38	0.43	0.65	0.80	1.14	1.40	1.69
SFO + fennel oil	0.38	0.45	0.70	0.84	1.16	1.40	1.72

BHT= Butylated Hydroxyl Toluene, BHA= Butylated Hydroxyl Anisole and SFO= Sunflower oil

From The results in Table (6) the addition of EOs as natural antioxidant to SFO was very effective since the TBA values after 18 hours of heating were significantly less than the values of SFO control (without antioxidants). The increment in TBA value indicating to the formation of carbonyl compounds, malonaldehyde, formaldehyde and hydroperoxides. Formation of these substances was due to heating in the presence of air (Sun *et al.* 2011). The extent to which these compounds formed might depend on the nature of oil and the heating procedures adopted, these results are in accordance with those reported by Al-Dalain *et al.* (2011) and Sadeghi *et al.* (2016).

## Iodine value

Iodine value is a measure the quantity of unsaturation in fatty acids. The results in Table (7) showed EOs effects on iodine value of SFO samples during heating process at  $180\pm 5^\circ\text{C}$  for 18 h. It was clear that the iodine value decreased during heating for 18 hours at  $180\pm 5^\circ\text{C}$  from (125.24) to (113.22), (117.24), (117.90), (118.42), (118.11), (117.18) and (117.12) for (SFO control), (SFO +BHT), (SFO + BHA), (SFO + Marjoram oil), (SFO + peppermint oil), (SFO + anise oil) and (SFO + Fennel oil); respectively. This decrement in iodine values may be due to the breakdown of unsaturated fatty acids and to the high-temperature oxidation of the oil (Nduka *et al.*, 2021).

**Table 7. Effect of heating periods at  $180^\circ\text{C}$  on Iodine value (g  $\text{I}_2/100\text{g}$  oil) of SFO treated with EOs**

SFO samples	Heating periods (h)						
	Zero time	3	6	9	12	15	18
SFO (Control)	125.24	123.98	121.66	119.24	117.26	115.36	113.22
SFO + BHT	125.24	124.62	122.94	121.58	119.82	118.08	117.24
SFO + BHA	125.24	124.56	122.83	121.69	120.81	119.11	117.90
SFO + marjoram oil	125.24	124.94	123.12	122.96	121.38	120.85	118.42
SFO + peppermint oil	125.24	124.81	123.78	121.98	121.04	120.68	118.11
SFO + anise oil	125.24	124.78	123.27	121.97	120.97	119.76	117.18
SFO + fennel oil	125.24	124.66	122.90	121.96	120.78	118.18	117.12

BHT= Butylated Hydroxyl Toluene, BHA= Butylated Hydroxyl Anisole and SFO= Sunflower oil

EOs extracted from aromatic plants work as natural antioxidants reduced rate in the change in iodine values of SFO during heating at  $180\pm 5^\circ\text{C}$  compared with SFO control (without antioxidants). SFO + marjoram oil had the highest iodine value followed by SFO + peppermint oil sample. However, the untreated SFO sample recorded the lowest value. Such results are in good agreement with those reported by El-Kashef *et al.* (2014) and Nduka *et al.* (2021).

## Conjugated diene and triene value

Conjugated dienes forms during the oxidation of unsaturated fatty acids which exhibit an intense absorption at 232-234 nm (White, 1991). While Conjugated trienes (absorption at 268-270nm) are produced by the linolenate oxidation (Houhoula *et al.*, 2002). The increment in UV absorption reflects the formation of primary oxidation products in oils.

Data in Tables (8 and 9) revealed that conjugated diene and triene formation went to gradually increasing with heating time increasing of SFO samples. The highest conjugated diene value after 18 hours at  $180^\circ\pm 5$  were (6.32), (4.64), (4.56), (4.20), (4.30), (4.48) and (4.62), also the highest conjugated triene value at the same time were (4.96), (3.32), (3.26), (2.98), (3.06), (3.25) and (3.30) for (SFO control), (SFO +BHT), (SFO +BHA), (SFO + Marjoram oil), (SFO + peppermint oil), (SFO+ anise oil) and (SFO +Fennel oil);

respectively. The increment in the diene and triene values agreement with the results of peroxide and TBA values were above mentioned in Tables (5 and 6).

**Table 8. Effect of heating periods at 180°C on conjugated diene value of SFO treated with EOs**

SFO samples	Heating periods (h)						
	Zero time	3	6	9	12	15	18
SFO (Control)	0.72	0.91	1.64	2.82	4.18	5.54	6.32
SFO + BHT	0.72	0.82	1.11	1.64	2.84	3.82	4.64
SFO + BHA	0.72	0.79	1.06	1.60	2.72	3.76	4.56
SFO + marjoram oil	0.72	0.76	0.98	1.48	2.55	3.42	4.20
SFO + peppermint oil	0.72	0.77	1.02	1.56	2.67	3.66	4.30
SFO + anise oil	0.72	0.78	1.10	1.58	2.70	3.74	4.48
SFO + fennel oil	0.72	0.80	1.14	1.66	2.80	3.76	4.62

BHT= Butylated Hydroxyl Toluene, BHA= Butylated Hydroxyl Anisole and SFO= Sunflower oil

**Table 9. Effect of heating periods at 180°C on conjugated triene value of SFO treated with EOs**

SFO samples	Heating periods (h)						
	Zero time	3	6	9	12	15	18
SFO (Control)	0.35	0.78	0.98	1.29	2.16	3.52	4.96
SFO + BHT	0.35	0.66	0.86	1.23	1.92	2.56	3.32
SFO + BHA	0.35	0.62	0.88	1.18	1.96	2.70	3.26
SFO + marjoram oil	0.35	0.58	0.79	1.07	1.72	2.46	2.98
SFO + peppermint oil	0.35	0.64	0.83	1.22	1.76	2.51	3.06
SFO + anise oil	0.35	0.65	0.90	1.24	1.81	2.54	3.25
SFO + fennel oil	0.35	0.70	0.92	1.28	1.74	2.66	3.30

BHT= Butylated Hydroxyl Toluene, BHA= Butylated Hydroxyl Anisole and SFO= Sunflower oil

The highest values of conjugated diene and triene were found in SFO control samples (6.32 and 4.96; respectively) after 18 h of heat treatment. However, SFO contained marjoram oil recorded the lowest conjugated diene (4.20) and triene (2.98) among all treated and untreated SFO samples at the end of the same heat treatments.

From the results SFO control (without antioxidant) increase in conjugated diene and triene values a high rate compared with SFO contain antioxidant (BHT, BHA and EOs as natural antioxidant). The increase in conjugated diene and triene was proportional to hydroperoxides and hydroperoxide decomposition products, there was not much increase in dienes and trienes in SFO contain antioxidant. The results agreement with Iqbal & Bhanger (2007), Sun *et al.* (2011) and Chandran *et al.* (2017).

In general, it could be observed that exposure of studied oils to thermal treatments induced pronounced changes in chemical characteristics of these oils.

This might be due to the effect of heating on unsaturated fatty acids, which in turn affected the properties of oils. EOs and some of its components have been possessing very good antioxidant activities because of its contents of phenolic compounds. The better thermal stability of oils in the present study may be due to the antioxidant activities of these components.

## Conclusion

The study revealed that EOs extracted from marjoram, peppermint, anise and fennel could be used as a natural antioxidant, to improve the stability of SFO during heat treatments. The addition of EOs to SFO increased its thermal stability in terms of its antioxidant properties as well as its flavor. The study may be extendable to other commonly used edible oils and EOs from other aromatic plants.

## References

- Aberoumand, A.(2011). Survey on some food plants as source of antioxidants. *Innovative Romanian Food Biotech.* 8: 22–25.
- Ahmed, A.F.; Shi, M.; Liu, C. and Kang, W.Y. (2019). Comparative analysis of antioxidant activities of essential oils and extracts of fennel (*Foeniculum vulgare* Mill.) seeds from Egypt and China, *Food Sci. Hum. Wellness* 8: 67–72.
- Al-Dalain, S. Y.; Al-Fraihat, A.H. and Al Kassabeh, E.T. (2011). Effect of aromatic plant essential oils on oxidative stability of SFO during heating and storage. *Pakistan Journal of Nutrition*, 10(9): 864-870.
- Amorati, R.; Foti, C.M. and Valgimigli, L. (2013). Antioxidant activity of essential oils. *J Agric Food Chem* 61:10835–10847
- AOCS (1998). *Official Methods and Recommended Practices of the AOCS*, (5 th Edition) Published by the American Oil Chemists Society 35, East Walker Drive, Chicago, Illinois, U.S.A
- British Pharmacopoeia (1988). HMSO, London, P.2: A137-138.
- Chandran, J.; Nayana, N.; Roshini, N. and Nisha, P. (2017). Oxidative stability, thermal stability and acceptability of coconut oil flavored with essential oils from black pepper and ginger. *Journal of food science and technology*, 54(1): 144-152.
- Chiou, R.Y. (1992). Antioxidative activity in oil prepared from peanut kernels subjected to various treatment and roasting. *J. Agric. Food Chem.*, 40: 1958-1962.
- Ebadi, M.S. (2006). Herbal drug and their high demand in treating diseases. In: *Pharmacodynamic Basis of Herbal Medicine*, CRC Press, London, pp: 125–126.
- El-Kashef, A.H.m.; Rashwan, M.R.A.; Darwish, S.M. and A Khalifa, A.H. (2014). Effects of some Aromatic Plant Oils on Thermo Oxidative Stability of Sun Flower Oil. *Assiut Journal of Agricultural Sciences*, 45(1): 45-57.
- Farahmandfar, R.; Asnaashari, M.; Pourshayegan, M.; Maghsoudi, S. and Moniri, H. (2018). Evaluation of antioxidant properties of lemon verbena (*Lippia citriodora*) essential oil and its capacity in sunflower oil stabilization during storage time. *Food science & nutrition*, 6(4): 983-990.

- Gray, J.I. (1978). Measurement of lipid oxidation: A Review. *J. Am. Oil Chem. Soc.*, 55: 539-546.
- Guzman-Chozas, M.; Vicario, I.M. and Guillen-Sans. (1997). Spectrophotometric profiles of flavor aldehydes by using their reactions with 2-thiobarbituric acid. *J. Agric. Food Chem.*, 45: 2452-2457.
- Hau, L.B.; Hwang, L. and Young, P. (1987). Quality assessment of oils during heating and frying. In *Journal of The American Oil Chemists Society* 1608 BROADMOOR DRIVE, CHAMPAIGN, IL 61821-0489: AMER OIL CHEMISTS SOC 64, (5) : 655-655.
- Hossain, M.B.; Brunton, N.P.; Barry-Ryan, C.; Martin-Diana, A.B. and Wilkinson, M.(2008). Antioxidant activity of spice extracts and phenolics in comparison to synthetic antioxidants. *Rasayan J. Chem.* 1: 751–756.
- Houhoula, D.P.; Oreopoulou, V and Tzai, C. (2002). A kinetic study of oil deterioration during frying and a comparison with heating. *J Am Oil Chem Soc* 79:133–137.
- Huda-Faujan, N.; Noriham, A.; Norrakiah, A.S. and Babji, A.S. (2009). Antioxidant activity of plants methanolic extracts containing phenolic compounds. *Afr. J. Biotech.* 8: 484–489.
- Hussain, A.I.; Anwar, F.; Iqbal, T. and Bhatti, I.A. (2011). Antioxidants attributes of four Lamiaceae essential oils. *Pak. J. Bot.* 43(2): 1315–1321.
- Iqbal, S. and Bhangar, M. I. (2007). Stabilization of sunflower oil by garlic extract during accelerated storage. *Food Chemistry*, 100(1): 246-254.
- Kang, W.Y.; Li, C.F. and Liu, Y.X. (2010). Antioxidant phenolic compounds and flavonoids of *Mitragyna rotundifolia* (Roxb.) Kuntze in vitro. *Medicinal chemistry research*, 19(9): 1222-1232.
- Kenari, R.E.; Amiri, Z.R.; Motamedzadegan, A.; Milani, J.M.; Farmani, J. and Farahmandfar, R. (2020). Optimization of Iranian golpar (*Heracleum persicum*) extract encapsulation using sage (*Salvia macrosiphon*) seed gum: chitosan as a wall materials and its effect on the shelf life of soybean oil during storage. *Journal of Food Measurement and Characterization*, 14(5): 2828-2839.
- Khammassi, M.; Loupassaki, S.; Tazarki, H.; Mezni, F.; Slama, A.; Tlili, N. and Khaldi, A. (2018). Variation in essential oil composition and biological activities of *Foeniculum vulgare* Mill. Populations growing widely in Tunisia. *Journal of Food Biochemistry*, 42(3): e12532.
- Kim, D.O. and Lee, C.Y. (2004). Comprehensive study on vitamin C equivalent antioxidant capacity of various polyphenolics in scavenging a free radical and its structural relationship. *Critical Review. Food Science and Nutrition*, 4: 253-273.
- Kulusic, T.; Radonic, A.; Katalinic, V. and Milos, M. (2004). Use of different methods for testing antioxidative activity of oregano essential oil. *Food Chem.* 85: 633–640.
- Kumar, S.; Kamboj, A. and Sharma, A.K. (2018). Antioxidant evaluation of ethanolic extract of *Fumaria parviflora* Lam. obtained from root, stem, leaf and fruit and measurement of their total phenols and flavonoids. *The Pharma Innovation Journal*, 7(4): 577-579.

- Lis, A.; Piter.S. and Gora J. (2007). A comparative study on the content and chemical composition of essential oils in commercial aromatic seasonings *Herba Polonica*, 53 (1) pp: 21-26.
- Mezza, G.N.; Borgarello, A.V.; Grosso, N.R.; Fernandez, H.; Pramparo, M.C. and Gayol, M.F. (2018). Antioxidant activity of rosemary essential oil fractions obtained by molecular distillation and their effect on oxidative stability of sunflower oil. *Food chemistry*, 242: 9-15.
- Nanasombat, S. and Teckchuen, N. (2009). Antimicrobial, antioxidant and anticancer activities of Thai local vegetables. *J Med. Plants Res.* 3(5): 443–449.
- Nduka, J.K.C.; Omozuwa, P.O. and Imanah, O.E. (2021). Effect of heating time on the physicochemical properties of selected vegetable oils. *Arabian Journal of Chemistry*, 14(4): 103063.
- Olgun, Ç.; Özkan, O.E.; Güney, B.; Pattabanoglu, E.S.; Güney, K. and Gür, M. (2017). Chemical composition and antimicrobial activity in cold press oil of fennel, Anise, white and black mustard seeds. *Indian Journal of Pharmaceutical Educational Research*, 51: S200-S204.
- Pikul, J.; Leszczynski, D.E.; and Kummerow, F.A. (1989). Evaluation of three modified TBA methods for measuring lipid oxidation in chicken meat. *J . Agric. Food Chem.* 37(5): 1309–1313
- Politeo, O.; Jukić, M. and Miloš, M. (2006). Chemical composition and antioxidant activity of essential oils of twelve spice plants. *Croatica chemica acta*, 79(4): 545-552.
- Sadeghi, E.; Mahtabani, A.; Etminan, A. and Karami, F. (2016). Stabilization of soybean oil during accelerated storage by essential oil of *ferulago angulataboiss*. *J Food Sci Technol* 53:1199–1204.
- Saleh, M.A.; Clark, S.; Woodard, B.; Deolu-Sobogun, S.A. (2010). Antioxidant and free radical scavenging activities of essential oils. *Ethnic Dis* 20:78–82.
- Serjouie, A.; Tan, C. P.; Mirhosseini, H. and Che Man, Y. B. (2010). Effect of vegetable-based oil blends on physicochemical properties of oils during deep-fat frying. *American journal of food technology*, 5(5): 310-323.
- Shan, B.; Cai, Y.Z.; Sun, M. and Corke, H. (2005). Antioxidant capacity of 26 spice extracts and characterization of their phenolic constituents. *Journal of the Agriculture and Food Chemistry*, 53: 7749-7759.
- Shojaii, A. and Abdollahi, F.M. (2012). Review of pharmacological properties and chemical constituents of *Pimpinella anisum*. *International Scholarly Research Notices*: 2012.
- Soobrattee; M.A.; Neergheen, V.S.; Luximon-Ramma, A.; Aruoma, O.I. and Bahorun, T. (2005). Phenolic as potential antioxidant therapeutic agents: Mechanism and actions. *Mutation Res.* 579: 200–213
- Stevenson, D.E. and Lowe, T. (2009). Plant-derived compounds as antioxidants for health - Are they all really antioxidants? In: Hancock R.D. (Ed.) *Antioxidant Properties of Crops I. Func. Plant Sci. Biotech.* 3 (Special Issue 1): 1–12.

- Stevenson, S.G.; M. Vaisey-Genser and N.A.M. (1984). Quality control in the use of deep frying oils. *J. Am. Oil Chem. Soc.*, 61: 1102-1108.
- Suhaj, M. (2006): Spice antioxidants isolation and their antiradical activity: A review. *J. Food Comp. Anal.* 19: 531–537.
- Sun, W.; Shahrajabian, M.H. and Cheng, Q. (2019). Anise (*Pimpinella anisum* L.), a dominant spice and traditional medicinal herb for both food and medicinal purposes. *Cogent Biology*, 5(1):673-688.
- Sun, Y.E.; Wang, W.D.; Chen, H. W. and Li, C. (2011). Autoxidation of unsaturated lipids in food emulsion. *Critical reviews in food science and nutrition*, 51(5): 453-466.
- Tugba, I. and Medeni, M. (2012). The potential application of plant essential oils/extracts as natural preservatives in oils during processing: a review. *J Food Sci Eng* 2:1–9.
- Valko, M.; Leibfritz, D.; Moncola, J.; Cronin, M.T.D.; Mazura, M. and Telser, J. (2007). Free radicals and antioxidants in normal physiological functions and human disease. *Int. J. Biochem. Cell Biol.* 39: 44–84
- Verma, R. S.; Rahman, L.; Verma, R. K.; Chauhan, A.; Yadav, A. K. and Singh, A. (2010). Essential oil composition of menthol mint (*Mentha arvensis*) and peppermint (*Mentha piperita*) cultivars at different stages of plant growth from Kumaon region of Western Himalaya. *Open Access Journal of Medicinal and Aromatic Plants*, 1(1): 13.
- Vieira, T.M.F.S. and Regitano-Darce, M.A.B. (1999). Ultraviolet spectrophotometric evaluation of corn oil oxidative stability during microwave heating and oven test. *J. Agric. Food Chem.*, 47: 2203-2206.
- White, P.J. (1991). Methods for measuring changes in deep-fat frying oils. *Food Technol* 45:75–80.
- Williams, R.J.; Spencer, J.P.E. and Rice-Evans, C. (2004). Flavonoids: Antioxidants or signalling molecules. *Free Rad. Biol. Med.*, 36: 838–849.

## تأثير إضافة الزيوت العطرية كمضادات أكسدة طبيعية على الثبات الحراري لزيت عباد الشمس

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## الملخص

هدفت هذه الدراسة الي تقييم تأثير إضافة الزيوت العطرية المستخلصة من نبات البردقوش والنعناع واليانسون والشمر كمصدر لمضادات الأكسدة الطبيعية مقارنة بمضادات الأكسدة الصناعية المختلفة (BHT و BHA) على الثبات التأكسدي لزيت عباد الشمس أثناء التسخين عند  $180 \pm 5$  درجة مئوية لمدة 18 ساعة. أظهرت النتائج أن هذه النباتات العطرية تحتوي على مركبات فينولية (26.52- 45.26 ملجم) يمكن استخدامها كمضادات أكسدة طبيعية، كما تبين أن زيت عباد الشمس الذي يحتوي على مضادات الأكسدة (BHT، BHA) والزيوت العطرية كمضادات أكسدة طبيعية) أكثر ثباتا مقارنة بالزيت الخالي من مضادات الأكسدة (الكنترول). حيث أظهرت النتائج أن قيمة الحموضة و رقم البيروكسيد و رقم الـ TBA وقيم الـ Diene و Triene المترافقة زادت بمعدل مرتفع في زيت عباد الشمس الخالي من مضادات الأكسدة (الكنترول) مقارنة بزيت عباد الشمس الذي يحتوي علي مضاد أكسدة (BHT، BHA) والزيوت العطرية كمضادات أكسدة طبيعية) ، بينما انخفض الرقم اليودي بشكل ملحوظ في الزيت الخالي من مضادات الأكسدة مقارنة مع زيت عباد الشمس المضاف له مضادات أكسدة ( BHT، BHA) والزيوت العطرية)، ايضا أظهرت النتائج أن قيمة الرانسماث Rancimat والثبات التأكسدي لزيت عباد الشمس ازدادت بإضافة الزيت العطري اليه. بشكل عام يمكن أن تؤدي إضافة الزيت العطري كمصدر طبيعي لمضادات الأكسدة إلى إحداث تأثير كبير في السوق حيث لا يوجد تأثير صحي ضار على استخدام المكونات الطبيعية في الطعام مقارنة بمضادات الأكسدة الاصطناعية.