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EFFECT OF OLIVE LEAF EXTRACTS (OLEs) AS ANTIOXIDANTS ON THE BIOCHEMICAL CHANGES IN CANOLA OIL DURING HEATING

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ABSTRACT

The present study was undertaken to evaluate and compare the potential of antioxidant activities of olive leaf extracts(OLEs) with other natural or synthetic antioxidants. So, the aim of this study was to assess the effectiveness of methanolic- ,ethanolic- ,and water- olive leave extracts (OLEs) and compare it with other antioxidants such as green tea extract , tert-butylhydroxyquinone (TBHQ) , citric acid on the oxidative stability of virgin canola oil during storage at an oven at 63±1°C temperature for 0,5,10,15,20 days. To follow the relative of oxidative deterioration of canola oil , oils were analyzed periodically for their peroxide value (PV) , iodine value (IV) , acid value (AV) and Thiobarbituric acid (T.B.A.) . Analysis of heated canola oils demonstrated significant increases in PV and AV and T.B.A . However , IV of the oils were markedly decreased . Results also showed that olive leaf extracts (i.e.,methanolic- ,ethanolic- ,and water- olive leave extracts) secured protective effect against oxidation of canola oil and can serve as substitutes for synthetic antioxidants .

Keywords: Antioxidants, canola oil , olive leaf extracts. heat treatment

INTRODUCTION

Antioxidants are used as food additives in order to extend life time of oils and fatty foods during storage and processing. Bitar *et al*., (2008). reported that antioxidants contribute to food preservation, prevent changes in flavor, and slown rancidity and discoloration processes. Litwinienko *et al.,* (1999) reported that some foods like fats and oils, when heated, suffer thermal oxidation and produce compounds such as peroxides. The peroxides turn into aldehydes, ketones, epoxides, dimers and polymers, diminishing the quality of food. In order to minimize such effects, the food industry makes use the antioxidants of the oils treated with natural ingredients was in many cases equivalent or superior to that with added commonly used synthetic antioxidants.

Gazzani *et al*., (1998) reported that the use of synthetic antioxidants are restricted in several countries, because of their undesirable long-term toxicological effects, including carcinogenicity .As a result, there is a great interest in finding antioxidants from natural sources which may provide nutritional and therapeutic effects. (Frankel, 1995 and Decker, 1998).

Synthetic antioxidants as tert-butylhydroxyquinone (TBHQ) is known to be a very effective antioxidant for vegeTable oils, and it is stable at high temperatures . TBHQ is more effective in vegetable oils than burylatedhydroxyanisole (BHA) and burylaredhydroxytoluene (BHT). Allam and Mohamed (2002) reported that TBHQ showed excellent synergism with

other antioxidants such as citric acid. Pokorny*et al*., (2001) reported that in spite of high effectiveness of synthetic antioxidants such as tert-butylhydroquinon (TBHQ), their application is restricted in several countries because of their possible toxicity and carcinogenic effects.

The extraction of natural substances with antioxidant activity, to replace synthetic food preservatives has gained great importance , (Skerget *et al*., 2005). However, several studies analyzed the antioxidant potential of plant extracts concerning the stability of vegetable oils .Shahidi and Wanasundara (1994) studied the stabilization of of canola oil by natural antioxidants. The leaves of olive tree *Oleaeuropaea* ,contain secoiridoids (oleuropein, ligstroside ,dimethyloleuropein, and oleoside), flavonoids (apigenin, kaempferol, luteolin), as well as phenolic compounds (caffeic acid, tyrosol, hydroxytyrosol). The leaves carry the highest content of these compounds among other different plant organs of the tree.

Lee and Lee (2010) reported that OLE is known to be an antioxidant and contain some of powerful known antioxidants . Lujan *et al*.,(2006) reported that percentage of oleuropein (as an olive biophenol model) in olive leaves ranges between 1-14%. Bouaziz *et al*.,(2008) showed that hydrolysate and chemlali olive leaf extracts are excellent antioxidants and can serve as substitutes for synthetic antioxidants in refined olive and in husk oils.

Lafka *et al*.,(2013) used several solvents,i.e., methanol, ethanol, ethanol:water 1:1(v:v), n-propanol, isopropanol and ethyl acetate to extract olive leaf,the most effective solvent was ethanol withoptimum phenol extraction conditions 180 min, solvent to sample ratio 5:1 v/w and pH 2. Ethanol extract exhibited the highest antiradical activity among solvents and showed the highest antioxidant capacity compared to synthetic and natural food antioxidants such as BHT, ascorbylpalmitate and vitamin E. Bouaziz and Sayadi (2005) demonstrated that olive leaf extracts exercise a considerable scavenging activity on 2,2-diphenyl-1-picryl-hydrazyl(DPPH). Salta *et al*.,(2009) reported that some oils (olive oil,sunflower oil, palm oil, as well as a vegetable shortening) with polyphenols of olive leaf extract secured protective effect against oxidation.

For many years, citric acid (CA) has been used as synergist of antioxidants for edible oils and fats. Mahoney and Graft, (1986) reported that citric acid has been used for its metal sequestering chelating activity . It can chelate metal ions by forming bonds between the metal and the carboxyl or hydroxyl groups of the citric acid molecule. Citric acid is very effective in retarding the oxidative deterioration of lipids in foods and is commonly added to vegetable oils after deodorization. Brekke,(1980) reported that citric acid is administered during processing to edible oils at levels of 0.005 to 0.01% and helps to protect oils from oxidation .Jaswir *et al*.,(2000) reported that citric acid relates to the inhibition of lipid oxidation. CA has been shown to play a synergist role with primary antioxidants and oxygen scavengers during vegetable oil storage. Chander *et al*., (2005) reported that green tea leaves (*Camellia sinensis L*.)contain other strong well known antioxidant components,in that, catechins have been shown to minimize the oxidation ability of fatty acids by chelating iron and copper which cause the disruption

of metal-catalyzed free radical formation. Ou *et al*.,(2001). reported that green tea has been detected that natural antioxidant compounds such as caffeic acid, cherogenic acid, quercetin, rutin and catechins are stronger scavengers as compared to vitamins C and E.

Considering that the extractability depends mainly on solvent type and the extraction method , the aim of this study was to assess the effectiveness of methanolic- ,ethanolic- ,and water- olive leave extracts (OLEs) and compare it with other antioxidants such as green tea extract , TBHQ and citric acid on the oxidative stability of canola oil during storage at an oven at 63±1°C temperature for 0,5,10,15,20 days,.

MATERIALS AND METHODS

Olive Leaf Extract Preparation

Olive leaves were collected and put in plastic bags. The plant material was then dried at room temperature and powdered (20 mesh).Ground powdered leaves were extracted in distilled water , ethanol (70% v/v) and methanol (70% v/v) as 20 g sample per 100 ml solvent. The mixtures were mixed on ashaker for three hours and filtered through whatman no. 4. To obtaine the solid residues of the olive leaf extracts, the extracts were dried in rotary evaporator under lower temperature

Sample preparation

Olive leaf extracts (300 ppm) ,green tea extract , citric acid and synthetic antioxidants TBHQ (at 300 ppm level ,for each) were added to virgin canola oil before being subjected to oven test to evaluate their capability in retarding the oxidation processes. Control samples bearing no antioxidants were also placed under the same storage conditions.

Oven test

Samples of oil (10 g) were placed in a separate 50 mL open beakers and held in an oven at 63±1°C for up to 0,5,10, 15,20 days. After each storage period, oil samples were immediately analyzed.The temperature of 63°C was used as a rapid method to simulate the storage in real conditions (Besbes *et al*., 2004)

Chemical Analysis

Determination of peroxide value

The method reported by A.O.A.C (1984) was used. 2g each of the oil samples were weighed into different conical flasks and 15ml of the mixture of CH_3COOH and $CHCl_3$ in the ratio of 3:2 were added to the oil samples respectively. 0.5ml of saturated potassium iodide was added to each conical flask and allowed to stand for 5 minutes, thereafter, 15ml of distilled water was added and titrated with 0.1N $Na_2S_2O_3$ until a yellowish colour almost disappeared, then 0.5 ml of starch indicator was added and the titration continued to a colourless end-point. The peroxide value was calculated from the equation:

$PV = 1000 (v_2 - v_1) T/M$

where M = mass of oil taken (2g), V_2 = volume of $Na_2S_2O_3$, V_1 = volume of blank and T = normality of $Na_2S_2O_3$.

Determination of Acid value

Each oil sample (1.0 g) was weighed and dissolved with 50 ml of ethanol in a conical flask. Two drops of phenolphthalein indicator were added and titrated to pink end point (which persisted for 15 minutes) with 0.1 N potassium hydroxide solution (KOH). Acid value was calculated according to the method described by Okpuzor *et al*., (2009):

$$\text{Acid value} = 56.1 \times V \times C / m$$

Where 56.1 is equivalent weight of KOH, V is the volume in ml of standard volumetric KOH solution used, C is the exact concentration in KOH solution used (0.1 N); m is the mass in grams of the test portion (1 g).

Determination of iodine value

The iodine value (IV) of an oil is a measure of its level of unsaturation. It is defined as the number of grams of iodine that is added to 100 gram of oil (Allen, 1955).

The iodine value was calculated from the equation,

$1cm^3$ of 0.1N $Na_2S_2O_3 \equiv$ 0.01269 g of iodine

$$IV = 1.26 (a-b)/w$$

where, w = weight of the sample., b = volume of 0.1N $Na_2S_2O_3$ for the sample and a = volume of 0.1N $Na_2S_2O_3$ for the blank

Determination of Thiobarbituric acid (T.B.A.)

The TBA value was determined as outlined in the AOCS Official method Cd , 19-90 (1998). The TBA value calculated as mg malonaldehyde / kg sample (Girgis, (1999).

Statistical Analysis

Statistical analysis were performed in triplicate, values are the mean of six determinations ± SD (Kenney and Keeping, 1962) and the ANOVA analysis using the MASTATC program vergion 3 and means were compared using L.S.D.-rang according to (Gomez and Gomez,1984).

RESULTS AND DISCUSSION

Peroxide value

Peroxide value (PV) is a common method used to measure lipid oxidation, and is suitable for measuring the peroxide formation in early stages of oxidation. The effects of antioxidants on PV of canola oil during oven test for 0- 20 day storage were shown in Table (1). Result showed that PV of the oils increased during storage. All canola oil samples (control and that added with antioxidants) showed a gradual increase in PV.

The PV of control sample which contained no antioxidant was at the highest level for all the days as compared with other treatments .Samples treated with TBHQ, citric acid (CA) ,Green tea extract (GTE) .ethanolic-OLE, methanolic-OLE and water-OLE, significantly decreased

the PV values after 20 day-storage at 63°C than control samples. No significant difference was found in PVs for oil treated with antioxidants used i. e. GTE and CA ,while TBHQ showed the lowest antioxidant activity. CA is often added to oil in order to reduce its oxidation during storage beforebeing processed (Choe and Min, 2006).

Olive leaf - ethanolic extract exhibited the highest antiradeical activity, followed by the methanolic extract, followed by water extract Table (1). Generally, these results may be mainly due to the antioxidant activity of OLEs which correlated with total polyphenol contents (oleuropein as an olive biophenol model in olive leaves ranges between 1-14%.) as reported by Lujan *et al*.,(2006) . It is worth to note that ,in the final or terminating stage of glyceride oxidation , following induction period , hydroperoxides that form inever increasing quantity split or decompose into short chain organic compounds (mainly aldhydes , ketones , alcohols , and acids), which actually cause the rancidity condition that ultimately destroys acceptability and usefulness of oils (Sherwin , 1978) .

Table(1): Change in peroxide values of canola oil during oven test (as meq O_2/ Kg)

	zero	5 days	10 days	15 days	20 days
Control	2^{P}±0.5	14.3^{H}±1	27.1^{C}±1.1	34.2^{B}±2	55.71^{A}±3
TBHQ	2^{P}±0.5	7.5^{LMN}±0.6	12.5^{I}±0.9	20.1^{F}±1.7	25.1^{D}±1.8
Citric acid	2^{P}±0.5	6.6^{N}±0.4	12.1^{I}±0.2	19.5^{F}±1.4	23.1^{E}±0.6
Green tea ext.	2^{P}±0.5	8.7^{KLM}±1	10.1^{JK}±1.3	18.7^{FG}±1.5	22.3^{E}±1.2
Water-OLE ext.	2^{P}±0.5	6.8^{N}±0.6	11.2^{IJ}±1.0	17.1^{G}±1.2	20.1^{F}±2.1
Methanolic-OLE ext .	2^{P}±0.5	4.6^{O}±0.8	09.1^{KL}±1.0	15.1^{H}±0.9	19.8^{F}±1.7
Ethanolic- OLE ext.	2^{P}±0.5	3.2^{OP}±0.6	07.1^{MN}±0.3	12.5^{I}±1	18.6^{FG}±2.4
LSD 0.05	1.628				

All Values are means± SD of 3sample .Means in a row with superscripts without a common letter differ, P<0.05.

Iodine value

Iodine value (IV) is an index of the unsaturation of oil, which is the most important analytical characteristic of an oil. The effects of antioxidants on IV of virgin canola oil during oven test for 20 days storage are shown in Table (2).

It was observed that iodine value decreased gradually during heat storage .Onyeike and Acheru (2002) reported that the low degree ofunsaturation leads to the high resistance to oxidativerancidity. Decrease in IV refers to some of the double bonds were destroyed during autoxidation (Zhang *et al*., 2010). Oxidation of fats or oils is a degradation process which occurs at the double- bond unsaturation sites in glyceride molecules – the building blocks of oil . Of course, the more unsaturation (i.e. the more double bonds in the molecules) by the types of fatty acids making up the triglyceride structure , the more susceptible oils are to oxidative breakdown . On the other hand, heat greatly accelerate oxidation , especially at higher temperatures (above $60C^{o}$) as reported by Sherwin, (1978).

Results showedthat maximum iodine value was 114.6 units initially in control and other treatment TBHQ, CA ,GTE , ethanolic-OLE, methanolic-OLE and water-OLE which decreased to 50.5, 79.4,78.8,81.5,84.4,85.8 and 89.8 units , respectively by the end of the storage period.

When compared the total decrease of IV in Canola oil , ethanolic -OLE showed higher total decreased of IV compared to that of in extracts (methanolic-OLE and water-OLE). Higher efficacy of ethanolic-OLE to protect the unsaturated bonds of fatty acids in canola oil being oxidized by free radicals, in iodine value of oil may be due to induction period where fat was oxidized slowly showing initiation stage of auto oxidation reaction. Rapid changes in iodine value of oil may be attributed to propagation of auto oxidation process where hydro-peroxides are formed from free radicals in fatty acids generated in initiation stage or auto oxidation reaction. During the end of storage period slight change in iodine value was observed which might be due to termination stage of reaction. (Nasirullah*et al*.,1991).

Table(2): Change in iodine values of canola oil during oven test (g I/100g oil)

	Zero	5 days	10 days	15 days	20 days
Control	114.6^{A}±1	92.7^{JK} ±3.7	79.6^{PQ} ±1	68.7^{R}±1.8	50.5^{S}±2.1
TBHQ	114.6^{A}±1	104.3^{EF}±2.5	90.4^{KL}±2.2	87.5^{MN} ±2.1	79.4^{PQ} ±1
Citric acid	114.6^{A}±1	104.1^{F}±3	91.0^{KL} ±1.6	89.6^{LM} ±0.9	78.8^{Q} ±2
Green tea ext.	114.6^{A}±1	106.7^{CD} ±2.8	96.5^{HI} ±3.1	92.2^{JK}±2.1	81.5^{P} ±3.1
Water-OLE ext.	114.6^{A}±1	106.5^{CDE}±2	97.7^{H} ±2.5	89.3^{LM} ±2.4	84.4^{O} ±1
Methanolic-OLE ext .	114.6^{A}±1	108.7^{BC} ±1.6	100.8^{G} ±1.9	94.2^{IJ} ±2.6	85.8^{NO}±0.9
Ethanolic- OLE ext.	114.6^{A}±1	110.6^{B}±1	106.1^{DEF} ±2	96.8^{H} ±3.1	89.8^{LM} ±2.2
LSD 0.05	2.323				

All Values are means± SD of 3sample .Means in a row with superscripts without a common letter differ, P<0.05.

T.B.A value

Results show that the rate of production of primary oxidation products was much higher than that of the decomposition of the primary oxidation products and the antioxidants were still effective in protecting canola oil against oxidative rancidity.T.B.A values in the control were similar to those in the treatment containing theantioxidants almost as same as the samples with antioxidants in zero time , T.B.A was significantly high in the control (13.662 mg malonaldhyde / kg) compared to the samples with TBHQ (7.93 mg malonaldhyde / kg), CA (7.89 mg malonaldhyde / kg), and GTE (7.48 mg malonaldhyde / kg), methanolic-OLE (6.01),ethanolic-OLE(5.791)and water-OLE(7.398) ,(Table ,3) .

Thiobarbituric acid value of control canola oil and the other canola oil – enriched with natural or synthetic antioxidants are shown in Table (3). Significant increase in T.B.A values could be noticed between the initial and final periods of storage in the treated canola oil indicating the development of off -flavour,.The results of the present study are in agreement with that of Semwal*et al*.(1996), and Semwal and Arya (2001) who reported that thiobarbituric acid (values on storage for oils) increases the storage period of oils.

Table(3): Change in T.B.A values of canola oil during oven test (as mg malonaldhyde / kg)

	Zero	5 days	10 days	15 days	20 days
Control	1.8^{M}±0.5	4.23^{HIJK}±0.5	6.618^{CDEF}±1.5	9.598^{B}±1.4	13.662^{A}±1.3
TBHQ	1.8^{M}±0.5	2.099^{LM}±0.8	4.93^{GHIJ}±0.7	5.236^{FGHI}±0.8	7.93^{C}±0.4
Citric acid	1.8^{M}±0.5	2.044^{LM}±0.4	4.89^{GHIJ}±0.7	5.015^{FGHIJ}±0.6	7.89^{C}±0.7
Green tea ext.	1.8^{M}±0.5	2.0^{LM}±0.4	4.48^{GHIJK}±0.3	5.02^{DEFG}±0.4	7.48^{CD}±0.5
Water-OLE ext.	1.8^{M}±0.5	2.0^{LM}±0.3	4.398^{GHIJK}±0.7	5.965^{DEFG}±0.5	7.398^{CDE}±0.3
Methanolic-OLE ext .	1.8^{M}±0.5	2.989^{KLM}±0.5	4.01^{IJK}±0.8	3.89^{IJK}±0.7	6.01^{DEFG}±0.6
Ethanolic-OLE ext.	1.8^{M}±0.5	2.879^{KLM}±0.6	3.791^{IJK}±0.8	3.456^{JKL}±0.5	5.791^{EFGH}±0.4
LSD 0.05	1.628				

All Values are means± SD of 3sample .Means in a row with superscripts without a common letter differ, P<0.05.

Acid value

Acid value is defined by Woollat (1985) as the number of mg of KOH requires to neutralised 1g of free fatty acid in an oil. According to Divine and Williams (1961), the acid value of oil is a measure of the quality of oil. In this study the acid value increased gradually in all oil samples during storage. However, the rate of increase was dependent on the antioxidant used Table (4). Generally, it can be observed from the results that the control oil sample had the highest increase in acid value compared with other oil samples (10.89 KOH/ g). The lowest increase in acid value was found in oil samples treated with ethanolic –OLE , methanolic-OLE, water-OLE, , GTE , CA and TBHQ (5.767 ,6.186 ,6.885 ,6.997 ,6.009, 6.122 in canola oil samples, respectively).

Results revealed that the oil samples treated with ethanolic -OLE showed a little higher increase in acid value than oil samples treated with methanolic-OLE and water-OLE. The slight gradual increase in the acidity could be attributed to the hydrolysis of some phosphatides and triglycerides into glycerol and free fatty acids. Although the acid value is an index of hydrolytic rancidity, it was measured as acids contribute to the development of off-flavours and off-odours in the product (Noor and Augustin, 1984).

Table (4): Change in acid values of canola oil during oven test (mg KOH/ g)

	Zero	5 days	10 days	15 days	20 days
Control	0.112^{L}±0.1	2.861^{H}±1.5	4.898^{DEFG}±0.7	7.623^{B}±0.9	10.89^{A}±1.1
TBHQ	0.112^{L}±0.1	1.449^{IJK}±0.6	2.785^{H}±0.8	4.981^{DEFG}±0.7	6.122^{CDE}±1.4
Citric acid	0.112^{L}±0.1	1.431^{IJK}±0.6	2.673^{HI}±0.5	4.896^{DEFG}±0.6	6.009^{CDEF}±1.3
Green tea ext.	0.112^{L}±0.1	1.401^{IJKL}±0.4	2.656^{HI}±0.3	4.842^{EFG}±0.4	6.997^{BC}±0.9
Water-OLE ext.	0.112^{L}±0.1	1.397^{IJKL}±0.3	2.541^{HIJ}±0.8	4.761^{FG}±0.6	6.885^{BC}±0.6
Methanolic-OLE ext .	0.112^{L}±0.1	1.306^{JKL}±0.4	2.461^{HIJ}±0.4	3.708^{GH}±0.7	6.186^{CD}±0.4
Ethanolic-OLE ext.	0.112^{L}±0.1	0.928^{KL}±0.2	2.443^{HIJ}±0.2	3.021^{H} ±1	5.767^{CDEF}±1
LSD 0.05	1.302				

All Values are means± SD of 3sample .Means in a row with superscripts without a common letter differ, P<0.05.

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تأثير مستخلصات ورق الزيتون كمضادات اكسدة على التغيرات الكيميائية الحيوية في زيت الكانولا خلال التسخين

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أجريت هذه الدراسة لتقييم ومقارنة إمكانيات النشاط المضاد للأكسدة من مستخلصات أوراق الزيتون (OLEs) مع غيرها من مضادات الأكسدة الطبيعية أو الاصطناعية . لذلك، كان الهدف من هذه الدراسة تقييم فعالية المستخلصات المثيلي ، الايثانول ، و المياه لأوراق الزيتون (OLEs) ومقارنتها مع غيرها من مضادات الأكسدة مثل الشاي الاخضر المقتطف، TBHQ ، وحامض الستريك على درجة الأكسدة فى زيت الكانولا أثناء التخزين في فرن عند ٦٣ ± ١ درجة مئوية لفترات صفر و ٥ و١٠ و١٥ و٢٠ أيام . لمتابعة التدهور النسبى التأكسدي فى زيت الكانولاالخام . أظهرت النتائج، بعد تحليل الزيوت بشكل دوري لقيم كل من بيروكسيد (PV) ، الرقماليودي (IV) ، ورقمالحموضه (AV) وحامضthiobarbituric (T.B.A) . حيث اظهر زيتالكانولا زيادات كبيرة في قيمالPV و AV و T.B.A . ومع ذلك، فقد انخفض الرقماليودي (IV) للزيوت بشكل ملحوظ . وأظهرت النتائج أيضا أن مستخلصات أوراق الزيتون (المستخلص المثيلي و الايثانول و المستخلص المائى لأوراق الزيتون) لهاتأثير وقائي ضد أكسدة زيت الكانولا و يمكن أن تكون بمثابة بدائل آمنةٍ للمضادات الأكسدة الاصطناعية .

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