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Stabilization of sunflower oil by garlic extract during accelerated storage

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Abstract

Efficacy of garlic extract in stabilizing sunflower oil during accelerated storage has been studied. Extracts of garlic were prepared in different solvents; extract yield was in the range of 6.24–23.2% and antioxidant activity range in the linoleic acid system was 14.1–93.2%. Being highest in yield and antioxidant potential, methanolic extract was thermally evaluated by heating the extract at 185 °C for different intervals, i.e. 0–80 min and evaluating antioxidant activity of the heated extract in the linoleic acid system (71.6% inhibition). Methanolic extract of garlic at three different concentrations, i.e. 250 (SFO-250), 500 (SFO-500) and 1000 ppm (SFO-1000) were added to preheated RBD sunflower oil. BHA (SFO-BHA) and BHT (SFO-BHT) at 200 ppm served as standards besides the control. Weight gain (WG), antioxidant activity index (AAI), free fatty acid (FFA) content, peroxide value (PV), conjugated dienes (CD), conjugated trienes (CT) and thiobarbituric acid-reactive substances (TBARS) were taken as parameters for evaluation of effectiveness of garlic in stabilization of sunflower oil. Results from different parameters were in agreement with each other, suggesting the highest efficiency of SFO-1000, followed by SFO-BHT, SFO-BHA, SFO-500, SFO-250 and Ctrl. Results reveal garlic to be a potent antioxidant for stabilization of sunflower oil.

Keywords: Garlic; Sunflower oil; Antioxidant activity; Thermal stability

1. Introduction

Vegetable oils and fats are recognized as important components of our diet. They provide essential fatty acids, which are precursors of important hormones, such as prostaglandins, and control many physiological factors such as blood pressure, cholesterol level, and the reproductive system (Walisiewicz-Niekbalska, Kosmacinska, & Chmielarz, 1997). Lipid peroxidation is responsible for the quality deterioration of vegetable oils, fats and other food systems (Che Man & Tan, 1999). It results in the losses of nutritional value of food as well as changes in colour, texture, sensory and other physiological properties (Kazuhisa, 2001). Due to these changes, consumers do not accept oxidized products and industries suffer from economic losses. The oil industry has to pay special attention in this context, as oils, fats and fatty foods suffer stability problems (Wu & Nawar, 1986). The oils with higher contents of unsaturated fatty acids, especially polyunsaturated FA, are more susceptible to oxidation. In order to overcome the stability problems of oils and fats, synthetic antioxidants, such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), *ter*-butyl hydroquinone (TBHQ) have been used as food additives. But recent reports reveal that these compounds may be implicated in many health risks, including cancer and carcinogenesis (Hou, 2003; Prior, 2004). Therefore, the most powerful synthetic antioxidant (TBHQ) is not allowed for food application in Japan, Canada and Europe. Similarly, BHA has also been removed from the generally recognized as safe (GRAS) list of compounds (Farag, Badei, & El Baroty, 1989).

Due to these safety concerns, there is an increasing trend among food scientists to replace these synthetic antioxidants with natural ones, which, in general, are supposed

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to be safer. The effectiveness of different natural sources in stabilizing vegetable oils has been previously studied (Anwar, Bhanger, & Yasmeen, 2003; Ito et al., 1986). Jung, Lee, Hun, Kyung, and Chung (2001) evaluated the effect of natural lecithin on the stability of borage oil. Shahidi and Wanasundara (1992) investigated the stabilization of canola oil with canola meal. Fruits, vegetables, nuts, seeds and barks are being investigated for their antioxidant potential (Pratt & Hudson, 1990).

Garlic is indigenous to Asia and is cultivated worldwide for the fleshy segments of its bulbs, which are used as a condiment, especially in Asian cuisine (Dorant, Vanden, & Goldbolm, 1993). Antioxidant potential of garlic in vivo and in vitro has been proved (Jackson et al., 2002). In addition to its antioxidant activity, it has antimicrobial, antibacterial, antiviral, antifungal, antiprotozoal properties and beneficial effects on the cardiovascular and immune systems (Harris, Cottrell, Plummer, & Lloyd, 2001). Garlic is rich in selenium and organosulphur compounds, which have pronounced antioxidant activity (Yin, Hwang, & Chan, 2002; Li, 2000).

Refined, bleached, and deodorized (RBD) sunflower oil was used to evaluate antioxidant efficacy of garlic extracts because it is used in nutrition and is highly appreciated as a source of the essential linoleic acid. Furthermore, due to its higher content of polyunsaturated fatty acids, the stabilization effect is more pronounced in sunflower oil (Shahidi, Janitha, & Wanasundara, 1992).

2. Materials and methods

2.1. Materials

Refined, bleached, deodorized (RBD) sunflower oil was obtained from Wazir Ali Oil Industries Ltd., Hyderabad. Garlic was purchased from local market. All the chemicals and reagents used were of analytical reagent grade and were purchased from Fluka, or E. Merck. BHA and BHT were purchased from Sigma Chemical Co (St. Louis, MO, USA).

2.2. Extraction

Garlic was peeled and dried in an oven at 55 °C for 3 h. The dried garlic was ground to pass through a 1 mm sieve. About 5.0 g of garlic was extracted into 150 ml of methanol, ethanol, diethyl ether, acetone, hexane and ethyl acetate; extracts were subjected to shaking at room temperature overnight at a speed of 1000 vib/min. The extracts were filtered and residue was again extracted with 100 ml of each solvent. This procedure was repeated thrice to ensure the complete extraction of phenolic compounds. Then, the filtrate was subjected to rotary evaporation at 40 °C under reduced pressure for the removal of solvent. The extracts were weighed to calculate the yield and were stored under nitrogen prior to further analyses.

2.3. Evaluation of antioxidant activity

Antioxidant activity was determined in the linoleic acid system. Linoleic acid emulsion (0.02 M) was prepared with linoleic acid (0.2804 g) and Tween 20 (0.2804 g) in potassium phosphate buffer (50 ml, 0.05 M, pH 7.4). A reaction solution containing extracts (0.2 ml, 5.0 mg/ml), linoleic acid emulsion (2.5 ml), and potassium phosphate buffer (2.3 ml, 0.2 M, pH 7.0) was mixed with a homogenizer. The reaction mixture was incubated at 37 °C in the dark, and the degree of oxidation was measured by the thiocyanate method (Misuda, Yasumoto, & Iwami, 1966), by sequentially adding ethanol (4.7 ml, 75%), ammonium thiocyanate (0.1 ml, 30%), sample solution (0.1 ml), and ferrous chloride (0.1 ml, 0.02 M). After the mixture had been stirred for 3 min, the peroxide value was determined by reading the absorbance at 500 nm, and the percent inhibition of linoleic acid peroxidation was calculated as (%) inhibition = 100 − [(absorbance increase of sample/absorbance increase of control) × 100]. All analyses were conducted in triplicate and results were averaged.

2.4. Evaluation of thermal stability of garlic extract

Methanolic extract, being rich in antioxidant activity, was used for further studies. Thermal stability of methanolic extracts was evaluated by heating at 185 °C in an oven for a period of 0, 10, 20, 30, 40, 50, 60, 70, and 80 min in separate crucibles. After each interval, a crucible was removed from the oven, cooled to room temperature and stored at 4 °C before antioxidant activity evaluation in linoleic acid system following the above-cited method.

2.5. Sample preparation

Methanolic extracts of garlic were added to preheated RBD sunflower oil (at 50 °C for 3 h) at concentrations of 250, 500, and 1000 ppm. Synthetic antioxidants (BHA and BHT) were employed at their legal limit of 200 ppm (Duh & Yen, 1997) to compare the efficacy of natural antioxidants. All the samples (120 ml) were placed in dark brown coloured reagent bottles with narrow necks, without stoppers and stored in an oven at a fixed temperature of 65 °C. Control samples were also placed under the same storage conditions. Analyses were carried out after regular intervals of 4 days (96 h). At least three samples of each category were analyzed.

2.6. Weight gain analysis

For weight gain analyses, 2.0 g of each sample (in triplicate) were placed in glass Petri dishes, which were kept in a vacuum oven overnight at 35 °C to remove any traces of moisture. The samples were reweighed and stored in the oven at 65 °C, along with other samples. The rate of oxidation, in terms of weight increase, was recorded at 24 h

intervals upto 14 days. The time required for a 0.5% weight increase for oil was taken as the index of stability.

2.7. Measurement of peroxide value (PV), free fatty acid (FFA) content, conjugated dienes (CD), conjugated trienes (CT) and thiobarbituric acid reactive substances (TBARS)

Measurement of PV, FFA, CD and CT were made at regular intervals following IUPAC methods (Paquot & Hautfenne, 1987), and the percent inhibition of TBARS formation was measured following the AOCS official method, as given in the following equation:

$$\%\ \text{inhibition of TBARS formation} = \left(1 - \frac{\text{TBARS content of treated sample}}{\text{TBARS content of control}}\right) \times 100.$$

2.8. Antioxidant activity index (AAI)

Antioxidant activity index was calculated by the procedure of Metrohm Application Bulletin No. 204/1e (1993). An automated Metrohm Rancimat model 679 was used for the determination of induction periods of treated and control oil samples before storage.

About 2.5 g of each oil sample was weighed in individual reaction vessels of the instrument and vessels were placed in a heating block for 10 min for preheating of sample. After that, air was supplied by a built-in-pump at flow rate of 20 l/h. Temperature was adjusted to 120 °C and absorption vessels were connected with reaction vessels via teflon tubing after being filled with 60 ml deionized water. Measuring electrodes were immersed in water, ensuring that each one was in its correct position and recording the conductivity. Induction period, the time elapsed from the beginning until the oil starts to became rancid, was measured by drawing tangents on both sides of the induction curve, the intercept of which meet the time axis.

All determinations were carried out in triplicate and data is reported as mean ± standard deviation. Significant differences ($p < 0.05$) were calculated using Duncan's multiple range test, following a previously reported method (Steel & Torrie, 1980).

3. Results and discussion

3.1. Extraction

Table 1 shows the percentage yield and antioxidant activity of garlic extracts in different solvents. Range of extract yield was 6.24–23.2%. Highest yield was obtained in methanol and lowest in ethyl acetate. Methanol is usually recommended for extraction of antioxidant compounds (Iqbal, Bhanger, & Anwar, 2005). More than 20 antioxidative compounds have been reported in methanolic extracts of garlic (Dwivedi, John, & Schmidt, 1998).

Table 1
Determination of garlic extract yield in different solvents and evaluation of their antioxidant activities in a linoleic acid system

Solvent	Yield (%)	Antioxidant activity (%)
Methanol	23.15 ± 0.89	93.2 ± 7.0
Ethanol	19.87 ± 0.77	87.2 ± 4.3
Acetone	17.85 ± 0.63	83.2 ± 5.1
Diethyl Ether	16.07 ± 0.51	25.1 ± 3.2
n-Hexane	6.24 ± 3.1	14.1 ± 1.8
Ethyl acetate	11.71 ± 0.84	23.0 ± 1.3

Data are mean ($n = 3$) ± standard deviation ($n = 3$), ($p < 0.05$).

Results reveal that the antioxidant activity of polar solvent extracts is markedly greater than those of less/non-polar solvent extracts.

Of the six solvent extracts, methanolic extracts exhibited the highest yield, and antioxidant activity. Therefore, methanolic extract was used for the stabilization of sunflower oil.

3.2. Thermal stability of garlic extracts

Effect of heating on methanolic extracts of garlic (at 185 °C) for different intervals is shown in Fig. 1. Thermally treated extracts were subjected to antioxidant activity evaluation in the linoleic acid system and by the thiocyanate method. Upto 20 min heating time, extracts were almost stable, but after 25 min a slight gradual decrease in antioxidant activity was observed with the increase in heating period. The decrease in antioxidant activity was not significant ($p < 0.05$) upto 40 min but became pronounced after 50 min heating time. At the 80 min heating interval, extracts exhibited 71.6% inhibition of lipid peroxidation in the linoleic acid system, which is better than BHA, which lost half of its antioxidant potential after 45 min at 185 °C (Hamama & Nawar, 1991). Results are supported by findings of Aguirrezábal, Mateo, Domínguez, and Zumalacárregui (2000), showing long time effectiveness of garlic in increasing shelf life of chicken sausage versus synthetic antioxidants. This loss of antioxidant activity, after longer heating times at high

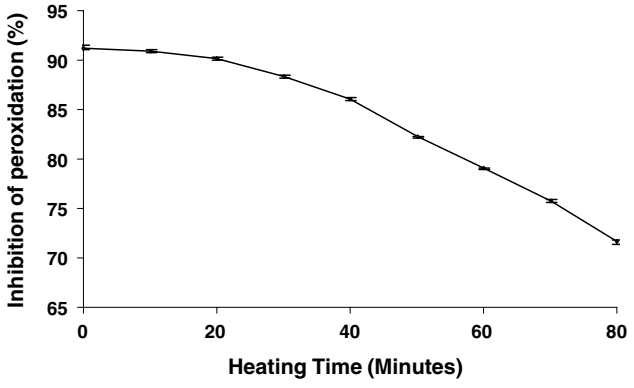

Fig. 1. Antioxidant activity of thermally treated methanolic extracts of garlic as a function of heating time in a linoleic acid system. Data are mean ($n = 3$) ± standard deviation ($n = 3$), ($p < 0.05$).

temperatures, may be due to various chemical reactions occurring during oxidation, leading to the formation of hydroperoxides, hydrolysis, polymerization and chemical decomposition, which lead to deterioration in oils and fats giving rancidity (Warner & Knowlton, 1997). These results reveal garlic to be a potential source of natural antioxidants, which is applicable in food systems even at high processing temperatures.

3.3. Antioxidant activity index

Induction period (IP) provides direct evidence for trends in resistance to oxidative rancidity of vegetable oils (Rossel, 1989). IPs were determined in all cases at 120 °C. Antioxidant activity index (AAI) is a recommended criterion for evaluation of effectiveness of antioxidants and is determined as the ratio of IP of stabilized sample to that of control (Emmons & Peterson, 1999). AAIs were 2.12, 2.79 and 3.43 h for SFO-250, SFO-500 and SFO-1000, respectively, suggesting an appreciable effectiveness of garlic extracts, at all concentrations, on oxidative stability of sunflower oil. AAI of a garlic stabilized sunflower oil sample, SFO-500, was higher than that of corn oil stabilized with 500 ppm methanolic extract of coffee beans (2.53 h) (Anwar et al., 2003) and that of SFO-1000 was comparable to high oleic corn oil stabilized with 750 ppm rosemary extracts (3.54 h), which has been exploited as a potent natural antioxidant for stabilization of various lipid systems (Dziedzic & Hudson, 1994). Although methanolic extracts of garlic significantly increased the AAI at all the concentrations, revealing an increase in oxidative stability of the treated oil; however, this increase in induction period was not in proportion to concentration. Previous reports (Dziedzic & Hudson, 1994) show that induction period increases with the concentration of primary antioxidant upto a certain optimum level (i.e. the concentration at which maximum stabilizing effect is obtainable for each test antioxidant, beyond which concentration has no significant proportionate effect on stability of foods). However, results determined by the rancimat are not in agreement with those determined by the weight gain method.

3.4. Weight gain

Weight gain (WG) is generally employed for quantitative assessment of the amount of oxygen added to the unsaturated content of lipid molecules and formation of hydroperoxides during oxidation. Weight gain was measured for all the samples (Shahidi & Wanasundara, 1997) regularly at 24 h intervals upto 14 days and results were calculated in percentage (%) (Fig. 2). A significant increase in induction period of all the stabilized samples was observed compared to the control. The time taken to achieve 0.5% increase in weight was 2.57, 4.05, 5.0, 5.86, 7.14, and 9.75 days for Ctrl, SFO-250, SFO-500, SFO-BHA, SFO-BHT, and SFO-1000, respectively. It is reported that each day of storage, in a Schaal-oven test at 65 °C, is equivalent to one month of storage at ambient temperature (Evans, List, Moser, & Cowan, 1973). Initially, WG was not appreciable but it increased very sharply for all the samples reaching a maximum value followed by a sharp decrease, after some time at maximum value, during the last days of storage. Literature reports (Hawrysh, Shand, Tokarska, & Lin, 1988) reveal that percentage weight gain during oxidation parallels the formation of hydroperoxides, as monitored by PV measurements, during the initial stages of oxidation; owing to the breakdown of hydroperoxides to secondary products, this relationship gets changed at later stages. Measurement of the induction period by monitoring changes in WG is therefore possible, and it is also theoretically accepted that the addition of oxygen to form hydroperoxides is quantitative

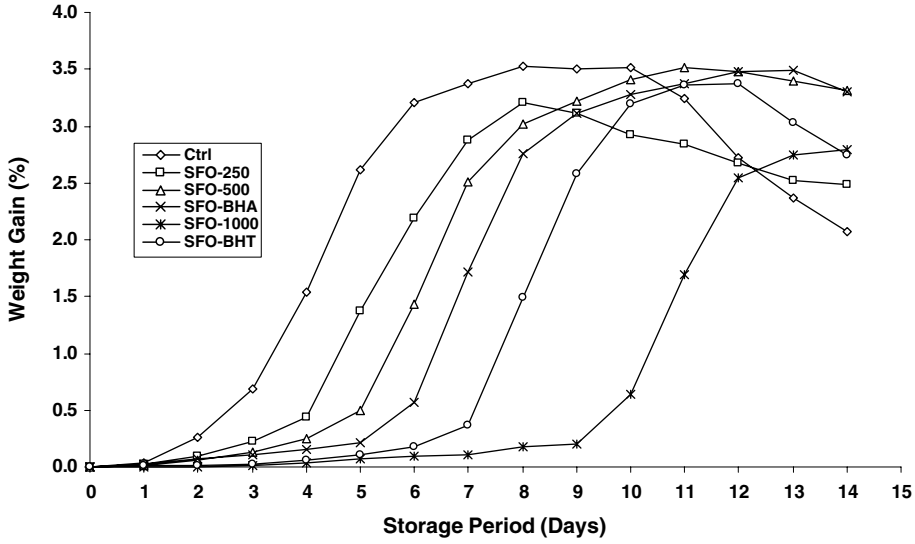

Fig. 2. Increase in weight gain (WG) of control and stabilized sunflower oil samples under accelerated storage. Data are mean ($n = 3$) ± standard deviation ($n = 3$).

during the initial stages of oxidation (Privett & Nickell, 1956). Olcott and Einset (1958) have reported that the weight gain technique is very useful for comparing the effect of antioxidants on the oxidative stability of vegetable oils.

Wanasundara and Shahidi (1994) reported 5.8, 6.0 and 7.0 day times for quercetin-, rutin and (−)-epicatechin-stabilized canola oil samples to achieve 0.5% weight gain, which was 33 and 15 h only for marine oils (seal blubber oil and menhaden oil) stabilized with 200 ppm α-tocopherol (Wanasundara & Shahidi, 1998). Large differences in induction period of marine oils versus sunflower oil may be due to higher contents of polyunsaturated fatty acids in marine oils, besides efficiency of antioxidant material. On the basis of these literature reports, comparing the weight gain data for garlic-stabilized samples with those of flavonoid or α-tocopherol-stabilized oils, the superiority of garlic extract over other antioxidants becomes evident. From the present findings, it is obvious that the synthetic antioxidants i.e. BHA and BHT, have induction time between SFO-500 and SFO-1000. It may be roughly deduced that garlic extract at 700–800 ppm has same stabilizing effect as BHT at 200 ppm.

3.5. Effect on peroxide value (PV)

Peroxide value was in the range 60.71–98.39 meq/kg for stabilized samples after storage upto 24 days, while maximum value of PV for control sample was 170 meq/ kg (Fig. 3). At all stages, highest PV was observed for control sample followed by SFO-250, SFO-500, SFO-BHA, SFO-1000 and SFO-BHT, respectively. Garlic extract, at all the concentrations, controlled peroxide value appreciably; revealing good antioxidant efficacy in stabilization of oil. A regular increase in PV as a function of storage time was observed for all the samples at all intervals. Initially, the difference in peroxide content of control and stabilized oil samples was not noticeable; it became significant ($p > 0.05$) just after heating upto one day. After the 4th day, there was a tremendous rise in PV of control sample, which rose upto 20th day of analysis, followed by a sharp decrease on the 24th day. This may be related to the observation of Shahidi et al. (1992), who suggested that a decrease in PV after long heating times may be due to volatilization of some breakdown products of lipid hydroperoxides, formed in the primary stages of oxidation. Peroxide content for all the stabilized samples also increased but this increase was very slow. PV of SFO-1000 was comparable to that of BHA at all storage periods initially; but decreased after 16th day, suggesting greater stability of garlic extract than BHA. PV of BHT was lower than SFO-1000 initially; but became almost equal at the 20th day of analyses, followed by a gradual increase upto the 24th day. Maximum PV contents for SFO-1000 and SFO-500 were 60.7 and 88.7 meq/kg, which are far less than those of sunflower oil stabilized with ginger extract (He, Li, Guo, & Li, 1999), canola oil stabilized by canola meal extract (Shahidi et al., 1992) and rapeseed oil stabilized by a number of natural antioxidants (Bandoniene, Pukalskas, Venskutomis, & Gruzdiene, 2000).

These data suggest the superiority of garlic extracts over synthetic antioxidants, because of their long term effectiveness and stability. All antioxidants remain effective over a

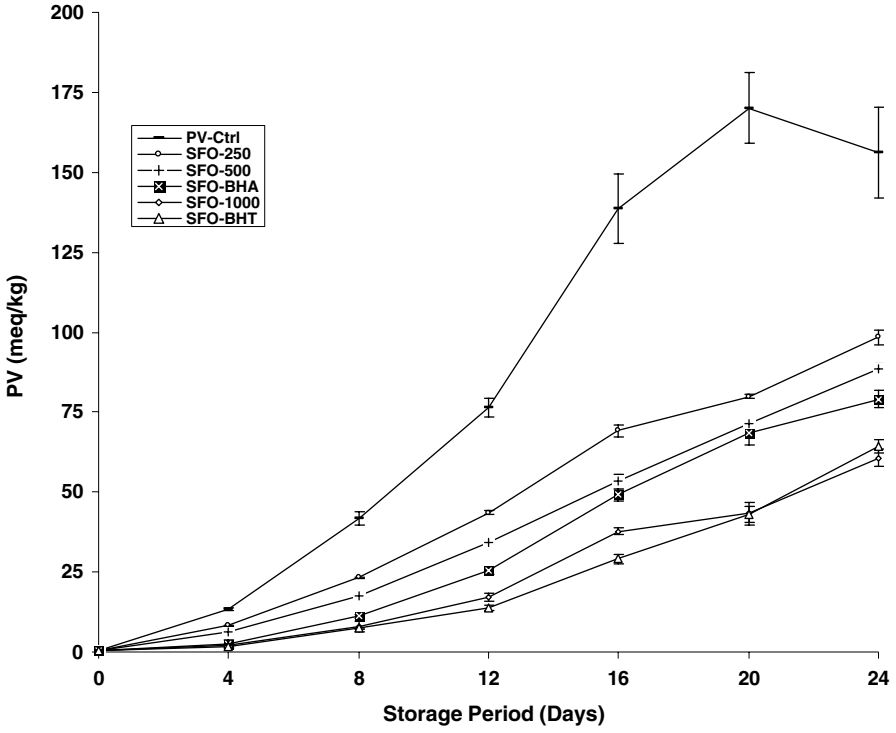

Fig. 3. Relative increase in peroxide value (PV) of treated sunflower oil samples under accelerated storage.

specific period of time, and with the passage of time their effectiveness decreases and they finally become ineffective (Laandrault et al., 2001). Such antioxidants end or at least interrupt oil and fat deterioration in the early stages and thus delay the onset of the reaction and are found to be efficient only upto a specific period. It may be hypothesized that phenolic antioxidants inhibit lipid peroxidation at the cost of their own life and thus decompose and deteriorate themselves with the course of time (Anwar, Bhanger, & Kazi, 2000). With these perspectives, only those antioxidants are to be preferred which have good effectiveness over longer periods and drastic conditions (Shahidi & Wanasundara, 1997). Peroxide value is conventionally used as measure of oxidative deterioration of oil, fat and fatty foods (Gertz, Klostermann, & Kochhar, 2000). The activity of an antioxidant can be estimated by quantitatively determining primary or secondary products of oxidation (Chen & Ahn, 1998). Generally, the delay in hydroperoxides formation or production of secondary products of autoxidation by chemical or sensory methods can be used to evaluate the efficacy of antioxidants.

3.6. Conjugated dienes and trienes

Figs. 4 and 5 show the formation of conjugated dienes (CD) and trienes (CT), respectively, in control and stabilized sunflower oil samples as a function of storage time. Highest contents were observed for control, indicating greater intensity of oxidation, followed by SFO-250, SO-500, SFO-1000, SFO-BHA and SFO-BHT, respectively. The determination of CD and CT is a good measure of the oxidative state of oils (Yoon, Kim, Shin, & Kim, 1991) and thus a good indicator of effectiveness of antioxidants. CD and CT contents went on increasing with the increase in storage time. A regular pattern of rise was observed for all the samples. However, rate of increase in stabilized samples was very slow compared to the control sample. Initially, rate of formation of CD was higher, and went on decreasing with the increase in storage time, while the reverse behaviour was observed for CT content, i.e. initially rate was lower, and went on increasing with the storage time. Formation of high contents of CD may be related to the presence of higher contents of polyunsaturated fatty acids (Liu & White, 1992) in sunflower oil. Conjugated trienes may be produced by dehydration of conjugated diene hydroperoxides (Fishwick & Swoboda, 1977).

3.7. Free fatty acids content (FFA)

Formation of free fatty acids might be an important measure of rancidity of foods. FFAs are formed due to hydrolysis of triglycerides and may get promoted by reaction of oil with moisture (Frega, Mozzon, & Lercker, 1999). FFA content went on increasing with the increase in storage period for all the samples, but no regular pattern of increase could be observed. Control exhibited the highest FFA, while SFO-BHT and SFO-1000 exhibited least (Fig. 6). Initially, there was no increase in FFA of stabilized samples but, after 7–8 days of storage, an increase was observed. SFO-1000 had FFA equal to BHT and slightly lower than BHA at all stages, which decreased after the 20th day of storage. At the 20th day, FFA content of

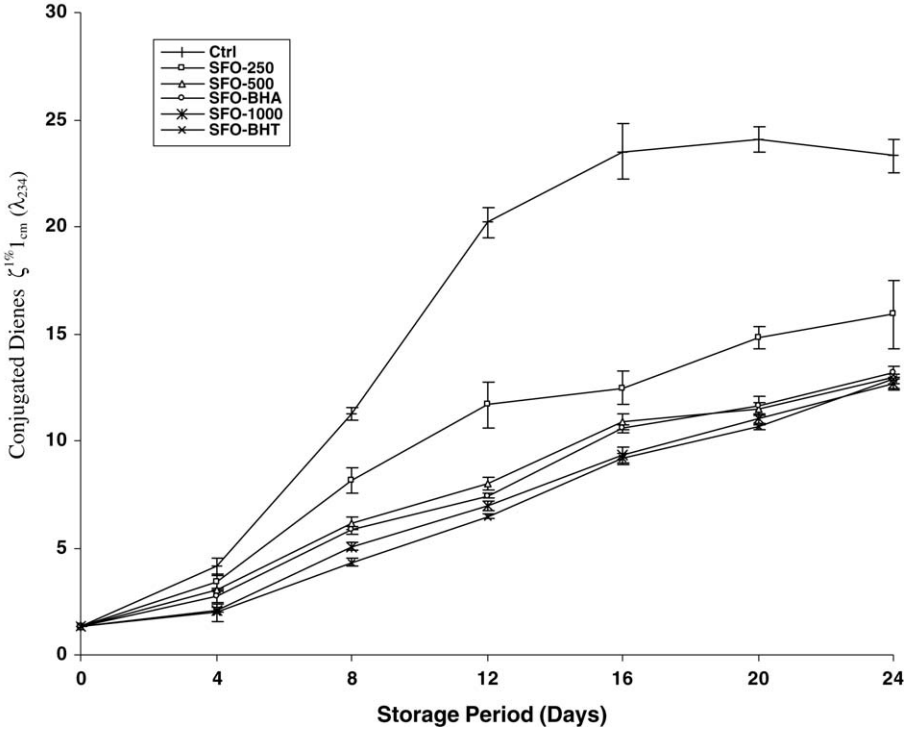

Fig. 4. Relative increase in conjugated dienes content (cd) of treated sunflower oil samples in accelerated storage ($\zeta^{1\%}_{1\,cm(\lambda 234)}$).

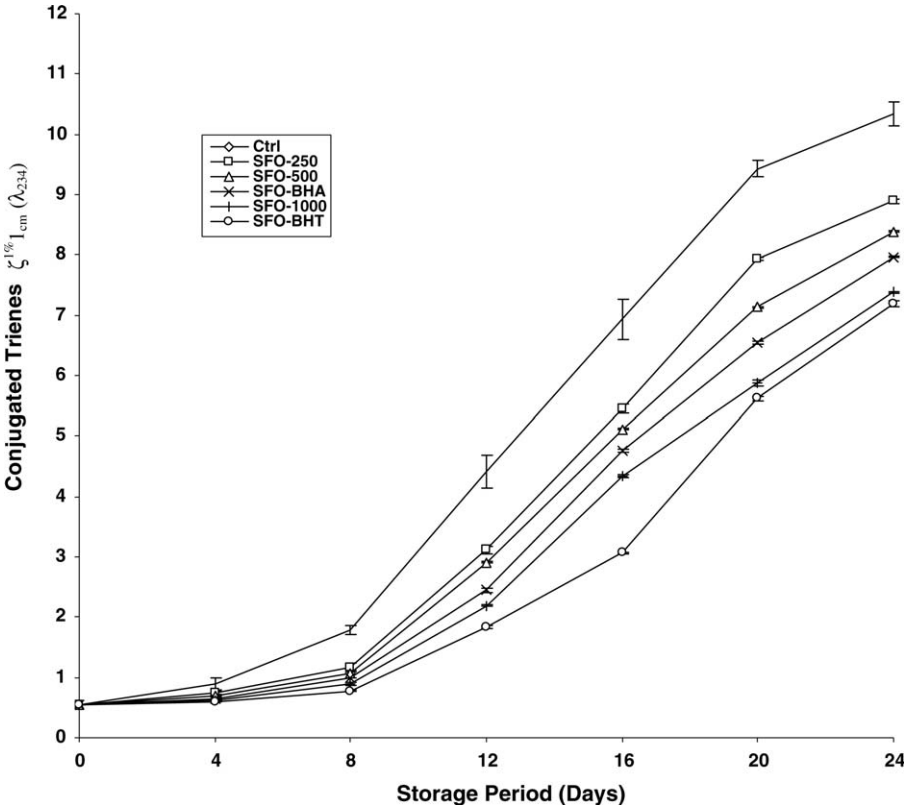

Fig. 5. Relative increase in conjugated trienes content (CT) of treated sunflower oil samples in accelerated storage.

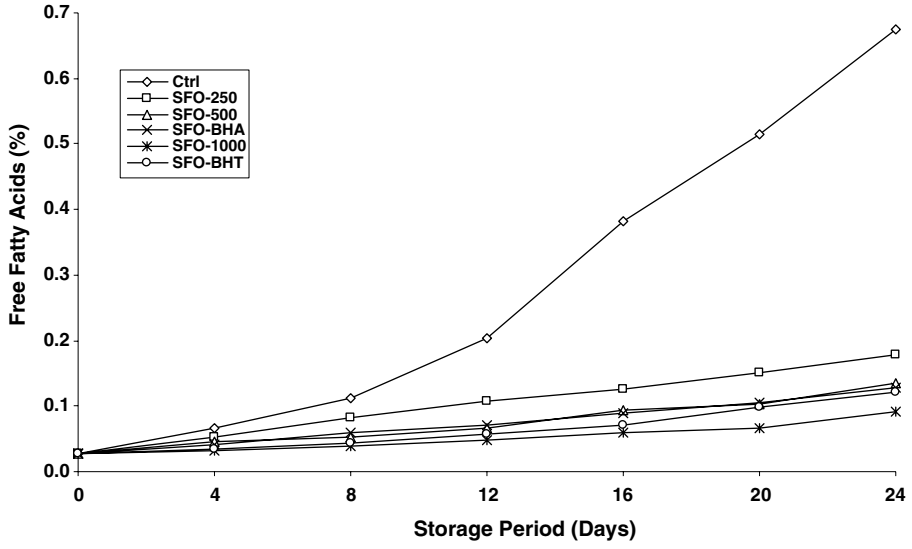

Fig. 6. Relative increase in free fatty acid content (FFA) of treated sunflower oil.

SFO-BHA became equal to SFO-500, revealing less interaction among moisture and garlic extract. From the present results, it may be concluded that garlic at 1000 ppm is more effective over longer storage period than BHT and BHA.

3.8. Thiobarbituric acid reactive substances (TBARS)

TBARS for all the samples were determined upto 24 days of storage under accelerated conditions (Fig. 7). The same order of garlic extract efficiency was observed with TBARS as was observed in the case of other assays. TBARS were in the range of 1.33–2.25 μmol/ g oil for stabilized samples and 3.64 μmol/ g oil for control sample after 24 days of storage. TBARS measures the formation of secondary oxidation products i.e. aldehydes or carbonyls, which may contribute to off-flavour of oxidized oils. Garlic extract inhibited the formation of TBARS at all concentrations.

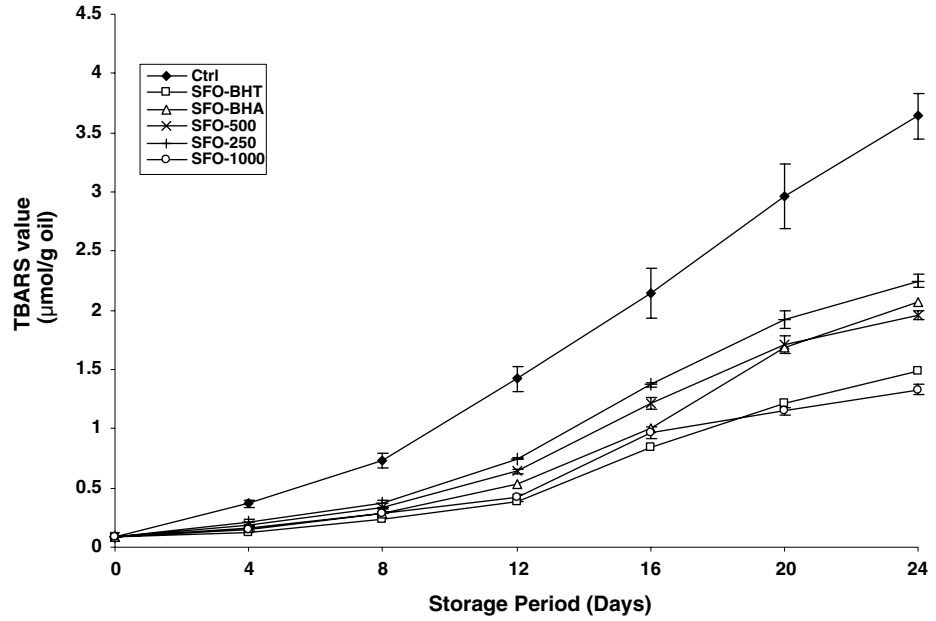

Fig. 7. Increase in (TBARS) of control and stabilized sunflower oil samples under accelerated storage.

4. Conclusion

From the present study, it is concluded that garlic can stabilize sunflower oil upto a greater extent than commonly employed synthetic antioxidants. It inhibits thermal deterioration of oil by improving its hydrolytic stability, inhibiting double bond conjugation and reducing the losses of polyunsaturated fatty acids. Appreciably high thermal stability of garlic extract shows an added advantage at high processing temperatures, contrary to synthetic antioxidants. Therefore, garlic can be considered as a potential antioxidant source of natural origin.

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