Stabilization studies of sunflower oil with antioxidants extracted from green and black cardamom

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Abstract: Extracts from green and black cardamom have been used to evaluate their antioxidant potential for sunflower oil samples for a period of 45 days. Synthetic antioxidants BHA/ BHT were also used parallel over a period of 45 days for comparison. Antioxidant potential of natural and synthetic antioxidants were evaluated by measuring free fatty acids (FFA), peroxide value (PV) and iodine value (IV) values by ambient storage of sunflower oil. The results showed that green cardamom extracts were more effective compared to black cardamom extracts. However compared to BHA and BHT (200ppm), these were found to be effective at higher concentrations.

Keywords: Sunflower oil, antioxidant activity, green cardamom, black cardamom.

INTRODUCTION

Vegetable oils are being widely consumed now a day as a source of saturated/unsaturated fatty acids. This is because of the consumer demand and interest in essential fatty acids particularly polyunsaturated fatty acids. These fatty acids reduce both total and HDL cholesterol thereby exhibiting a preventive role in heart diseases. However, unfortunately as reviewed in literature, their shelf life is decreased and the color also changes due to lipid per oxidation, (Tsuda *et al.,* 1994, Shahidi, 1997, Pezzuto and Park, 2002). Lipid oxidation is a serious concern of oil industries to avoid any economic loss because such oxidized products are rejected by the consumers (Iqbal and Bhanger, 2007). Butyl-hydroxyanisole (BHA) and butyl-hydroxytoluene (BHT) are the two common synthetic antioxidants used to control the associated problems, however are disadvantageous because of their expensive and carcinogenic nature (Prior, 2004). The search of alternatives for synthetic antioxidants in the form of natural antioxidants is a growing and continuous effort of the last few years. Some notable contributions appeared in literature are; Badei *et al.,* (2000) described the effect of baking and storage on the essential oils components of anise and cumin biscuits; Jaswir *et al.,* (2000) reported the use of oleoresin rosemary extract, sage extract *etc* for stabilization of palm olein; Jinyoung *et al.,* (2008) described the effects of lignan compounds extracted from roasted sesame oil; Ozcan, (2003) reported the antioxidant potential of rosemary, sage and sumac extracts for stabilization of peanut oil; Gulcin *et al.,* (2004) reported the antioxidant potential of clove buds and lavender extracts; Lesage-Meessen *et al.,* (2001) found that olive oil residues were good source of natural phenolic antioxidants; Nedyalka *et al.,* (2006) in a review described antioxidative efficacy of several natural herbs such as sage, black pepper, cumin, garlic *etc.*

In the present work, antioxidative potential from Green and Black cardamom spices and their efficiency in stabilization of sunflower oil under ambient storage has been investigated by peroxide value (PV), iodine value (IV), free fatty acid value (FFA). The results were compared with the antioxidative potential of commonly used well known synthetic antioxidants BHA and BHT.

MATERIALS AND METHODS

Chemicals and reagents

BHA, BHT, acetic acid, sodium thiosulfate, potassium iodide, chloroform and carbon tetrachloride were obtained from BDH Chemical Laboratory and Fluka Chemicals. Ethanol, HCl and phenolphthalein were obtained from Merck, Germany. Iodine monochloride was obtained from Radiel Datten. Refined, bleached and deodorized (RBD) sunflower oil was obtained from local industry. The glass apparatus used during analysis was immersed in EDTA 0.5% W/V overnight, rinsed with deionized water and finally dried at 150°C (Bhanger *et al.,* 2008).

Black and green cardamom

These are cheap and easily obtainable spices that are used in many Pakistani dishes. Black and Green cardamom are locally named as Bari elaichi and Choti elaichi in Urdu and were obtained from local market of Lahore.

Preparation of black and green cardamom extracts

The extracts of Green and Black cardamom were collected at room temperature following the same method as used in our previous paper (Bhanger *et al.,* 2008). Finely ground Green and Black cardamom were separately extracted in 80% methanol. The extracts were evaporated to dryness under reduced pressure at 40-45°C by rotary evaporator and stored at -18°C for further analyses (Bhanger *et al.,* 2008).

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Stabilization of sunflower oil and antioxidant activity testing

Four samples (5g each) of the sunflower oil were taken as control in four 250mL glass stoppered flasks. Antioxidant potential of one sample was evaluated immediately on the same while rest of the samples was evaluated after an interval of 15, 30 and 45 days. To these flasks synthetic antioxidant (200ppm) BHA was added and evaluated for their antioxidant potential as described on above mentioned timings. The same procedure was followed for the 200ppm BHT, 500 and 1000ppm Green cardamom and 500 and 1000ppm solution of Black cardamom extracts.

Measurement of peroxide, free fatty acid and iodine value

IUPAC standard method (IUPAC, 1987) as adopted by us in our previous contribution (Bhanger *et al.,* 2008) was used for the determination of free fatty acids (FFA), peroxide (PV) and iodine (IV) values during ambient storage of sunflower oil.

STATISTICAL ANALYSIS

All the determinations were carried out in triplicate and data is presented as mean ± standard deviation. Significant differences ($P<0.05$) were calculated by using one way ANOVA.

RESULTS

Tables 1, 2 and 3 show the free fatty acid, peroxide and iodine values. These values proved that both black as well as green cardamom extracts possessed appreciable antioxidative potential which is also comparable with synthetic antioxidants (BHA, BHT) at higher concentration. Generally it was observed that green cardamom extracts were more effective compared to black cardamom extracts.

DISCUSSION

Effect of synthetic antioxidants and spices extracts on FFA Value

Oils and fats are deteriorated through oxidative rancidity across double bond in triglyceride molecule as described in literature (Frega *et al.,* 1999). This can be established by measuring an increase in free fatty acid value, an important parameter for the monitoring oil deterioration during such deterioration fatty acids are formed which are easily susceptible of oxidation in the presence of light to produce several organic compounds. It was observed in present study, that FFA contents irregularly increased with the increase in storage period for all samples after addition of BHA, BHT as well as Green and Black cardamom extracts. Highest FFA contents were found in control, while 500ppm and 1000ppm of Green cardamom extracts exhibited least (table1 and fig. 1).

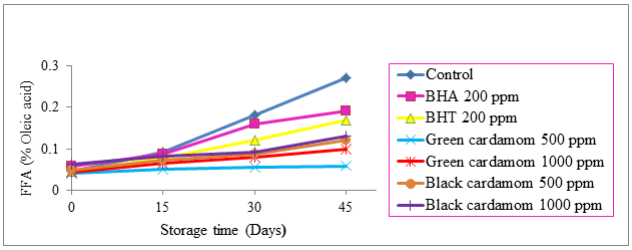

Fig. 1: Comparison of FFA values of synthetic and natural antioxidants with control.

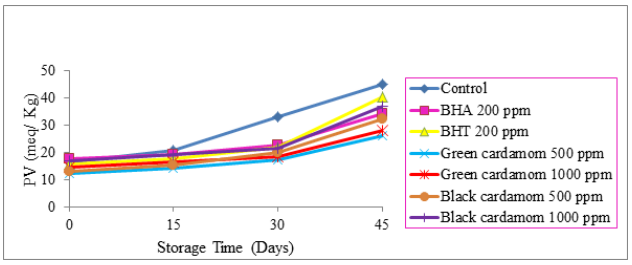

Fig. 2: Comparison of PV of synthetic and natural antioxidants with control.

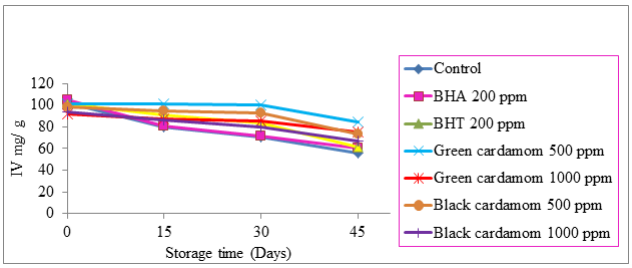

Fig. 3: Comparison of IV's of synthetic and natural antioxidants with control.

Table 1 shows an increase in FFA of stabilized samples after 15 days of storage. Samples added with 500 and 1000ppm of green cardamom had FFA slightly lower than BHA, BHT, control and 500 and 1000ppm of Black cardamom at all stages.

With extract of Green cardamom extracts of 500ppm and 1000ppm concentration, FFA value decreased from 0.27 ±0.04% to 0.059±0.04% and from 0.27±0.04% to 0.1± 0.08% respectively. Similarly with Black extracts of 500 ppm and 1000 ppm concentration, this value decreased from 0.27±0.04% to 0.12±0.05% and from 0.27±0.04% to 0.13±0.02% respectively. This indicates that Green cardamom caused even more significant reduction in FFA value as compared to Black cardamom, whose values are nearly close to BHA and BHT (FFA 0.27±0.04% to 0.19 ±0.03% with BHA and from 0.27±0.04% to 0.17±0.05% with BHT table 1). These results can be compared with the related literature findings (Frega *et al.,* 1999).

Effect of synthetic antioxidants and spice extracts on peroxide value

Peroxide value represents the amount of peroxides formed in fats, oils and fatty food by oxidation process and can

Table 1: Comparative effects of different Antioxidants on free fatty acid value of sunflower oil

Storage (Days)	FFA (Oleic Acid)						
	Control	BHA	BHT	Ctrl− Green cardamom		Ctrl− Black cardamom	
		200 ppm	200 ppm	500 ppm	1000ppm	500 ppm	1000ppm
0	0.047±0.02	0.058±0.04	0.046±0.02	0.04±0.05	0.044±0.03	0.048±0.03	0.064±0.01
15	0.092±0.07	0.086±0.04	0.078±0.04	0.05±0.01	0.066±0.02	0.072±0.06	0.082±0.04
30	0.18±0.05	0.16±0.08	0.12±0.02	0.056±0.01	0.079±0.06	0.088±0.03	0.093±0.06
45	0.27±0.04	0.19±0.03	0.17±0.05	0.059±0.04	0.1±0.08	0.12±0.05	0.13±0.02

Table 2: Comparative effects of different Antioxidants on Peroxide Value of sunflower oil

Storage Time (Days)	PV (meq/kg)						
	Ctrl	Ctrl− BHA	Ctrl −BHT	Ctrl−Green cardamom		Ctrl− Black cardamom	
		200 ppm	200 ppm	500 ppm	1000ppm	500 ppm	1000ppm
0	16.5±0.01	17.8±0.02	15.8±0.06	12.4±0.07	14.4±0.01	13.0±0.04	17.1±0.05
15	20.7±0.01	19.2±0.04	17.6±0.03	14.2±0.02	16.6±0.05	15.2±0.08	19.4±0.06
30	33.2±0.04	22.6±0.05	21.8±0.04	17.2±0.06	18.6±0.02	20.2±0.02	21.6±0.04
45	45.2±0.06	34.4±0.02	40.4±0.07	26.0±0.01	28.0±0.01	32.2±0.03	37.0±0.04

Table 3: Comparative effects of different Antioxidants on Iodine Value of sunflower oil

Storage Time (Days)	IV (mg/g)						
	Ctrl	Ctrl − BHA	Ctrl − BHT	Ctrl−Green cardamom		Ctrl−Black cardamom	
		200 ppm	200 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
0	101.9±0.04	104.6±0.01	101.26±0.04	101.52±0.05	92.0±0.06	98.49±0.01	93.45±0.02
15	79.7±0.03	80.6±0.02	90.7±0.03	101.0± 0.02	87.2±0.08	94.6±0.03	86.2±0.01
30	70.5±0.05	71.06±0.06	83.56±0.07	100.25±0.01	85.02±0.09	92.66±0.05	79.8±0.06
45	55.5±0.07	60.21±0.02	61.39±0.05	84.72±0.02	75.02±0.02	73.3±0.06	66.5±0.07

also be used as a conventional parameter for the monitoring of the extent of oil spoilage (William *et al.,* 2009).

The effect of storage conditions on PV (meq/kg) of sunflower oil has been studied for 45 days and the values are tabulated in table 2. This table and fig. 2 shows that after 45 days of storage, the PV of sunflower oil treated with Green cardamom (500ppm and 1000ppm) reduced from 45.2±0.06meq/ kg (control) to 26.0±0.01meq/kg and 45.2±0.06meq/kg to 28.0±0.01meq/kg respectively. A similar trend was also noted when sunflower oil was stabilized with Black cardamom (500ppm and 1000ppm) peroxide value of control was 45.2±0.06meq/kg after 45 days of storage.

It can be safely concluded that cardamom extracts at all concentrations, controlled PV appreciably, revealing good antioxidant efficacy in stabilization of oil. The data is comparable to the related literature (Shahidi and Wanasundara 1992, Shahidi *et al.,* 1992).

Iodine value (IV)

Iodine value denotes the degree of unsaturation of a given oil sample. Higher iodine value attributes a greater degree of unsaturation. Iodine values measured for the sunflower oil samples in control, in the presence of BHT, BHA and extracts are given in table 3. Fig. 3 indicates that the iodine value initially remained same and then decreased with the passage of time over a period of 45 days. After 15 days, IV decreased rapidly for control compared to the sample having 500ppm of Green cardamom extract. Results show that extracts are effective at concentration of 500 and 1000ppm.

CONCLUSION

The stabilization study for sunflower demonstrated that both black as well as green cardamom extracts possessed appreciable antioxidative potential and hence can be safely employed as an alternative natural antioxidant when compared with synthetic antioxidants (BHT and BHA). Generally it was observed that green cardamom extracts were more effective compared to black cardamom extracts. However compared to BHA and BHT (200ppm), these were found to be effective at relatively higher concentrations.

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