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Stabilization of sunflower oil with extracts from fenugreek, mint and liquorice

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Stabilization studies of sunflower oil were carried out after adding synthetic antioxidants (Butylated hydroxyanisole BHA and Butylated hydroxyltoluene BHT) as well as methanolic extracts of Fenugreek, mint and Liquorice at ambient storage conditions. The antioxidant potential of these methanolic herb extracts was evaluated by PV (peroxide value), FFA (free fatty acid value), IV (iodine value), CD (conjugated diene) and CT (conjugated triene) value determination. These parameters revealed that an appreciably higher concentration (roughly 5 times that of BHA and BHT) of the herb extracts (Liquorice, Mint and Fenugreek) can safely be used to control the rancidity of sunflower oil.

Keywords: Antioxidants, BHA, Lipid peroxidation, Sunflower oil.

INTRODUCTION

Lipid peroxidation is responsible for the development of rancidity causing an unacceptable color, unbearable odor and flavor. This phenomenon may lead to the reduction of the shelf life of oils and eventual economic losses [1]. BHA (butylated hydroxyl anisol), BHT (butylated hydroxyl toluene) and TBHQ (ter-butyl hydroquinone) are some examples of synthetic antioxidants which are most frequently used as potential inhibitors of lipid peroxidation. The use of these synthetic antioxidants has been restricted because of their bad side effects [1]. The addition of antioxidants also prevents deterioration in some other oxidizable products [2]. The concern about these side effects by the consumers diverted the attention of the researchers from the replacement of synthetic by natural antioxidants that may safely be applied for the storage of oils and fats. Some notable related contributions that appeare in the literature are; Jaswir *et al.*, (2000) [3], Badei *et al.*, (2000) [4], Jinyoung *et al.*, (2008) [5], Nedyalka *et al.*, (2006) [6], Burg *et al.*, (2006) [7].

Fenugreek is scientifically named as *Trigonelle foenum-graecum* [8] while locally known as Methi in Pakistan. It's an annual plant and is cultivated worldwide. As a dried or fresh herb it is used as a spice or sometimes directly as food. Mint is locally called Pudina and scientifically named as *Mentha piperita* [9]. It is also called Peppermint in English and has medicinal importance in many Pakistani, Indian and Bangladeshi dishes. Liquorice is Glycyrrhiza glabra L. [10] and called Mulaithi in Urdu and Sanskrit it is prescribed to treat chronic hepatitis and peptic ulcer. In the present study, we have selected these three locally available herbs (Fenugreek, Mint, Liquorice). The purpose was to evaluate their methanolic extracts for possible antioxidant activities leading to the stabilization of sunflower oil, the most common edible oil.

EXPERIMENTAL

Material and Methods

Reagents and Glassware. The chemicals used such as BHT, iodine monochloride, n−hexane and acetic acid were purchased from BDH Chemical Laboratories; however, ethanol, phenolphthalein and HCl were obtained from Merck. BHA, sodium thiosulphate, potassium iodide, chloroform and carbon tetrachloride were obtained from Fluka Chemicals. Quick fit glassware made of Pyrex was used for in the experiments and was dried at 150°C before use [11]. The herbs (Fenugreek, Mint, Liquorice) were collected from the local market.

Extracts from Herbs. Extracts from these herbs (Fenugreek, Mint, Liquorice) were obtained in 80% of methanol by a previously reported method [8]. The extracts were subjected to evaporation until dry under reduced pressure at 40–45°C and stored at −18°C for further analysis.

Stabilization of sunflower oil and Antioxidant activity testing. Six samples of the sunflower oil (5 g each) were taken for control in 250 ml of glass stoppered flasks. Among these, in two flasks the synthetic antioxidant [BHA (250 ppm), BHT (200 ppm)], in three flasks extracts of Liquorice, Mint and Fenugreek of 200, 500 and 1000 ppm respectively were added. In the last sixth flask no herb extract or synthetic antioxidant was added and was labeled as a control speciment.

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Measurement of peroxide, free fatty, iodine, conjugated diene and conjugated triene values.
The IUPAC standard method [12] as adopted by us in our previous contribution [11] was used for the determination of free fatty acids (FFA), peroxide (PV) and iodine (IV) values during ambient storage of sunflower oil, while the values of the conjugated dienes and trienes were calculated by the method of Xu and Godbaer [13].

RESULTS AND DISCUSSION

Influence of synthetic antioxidants and Herbs extracts on FFA

The changes in free fatty acid value have been noted during ambient storage of sunflower oil after addition of synthetic antioxidants and natural herbs as sources of natural antioxidants. These changes are graphically shown in Fig.(1). The gradual increase in the FFA value was observed after the addition of synthetic antioxidants (BHA and BHT) except a slight decrease in the FFA value by the 15th day. After the 15th day the values gradually increased again. These results argue that the addition of BHA and BHT played a part in the retardation of the rancidity in sunflower oil. The free fatty acids were reduced from 18.8% to 14.2% with BHA and from 18.4% to 14.1% with BHT during 45 days of ambient oil storage. These findings are comparable to the results presented by Kiyomi and Kathy regarding the antioxidant potential of BHA alone or with other antioxidants during ambient storage at both high and ambient temperature [14].

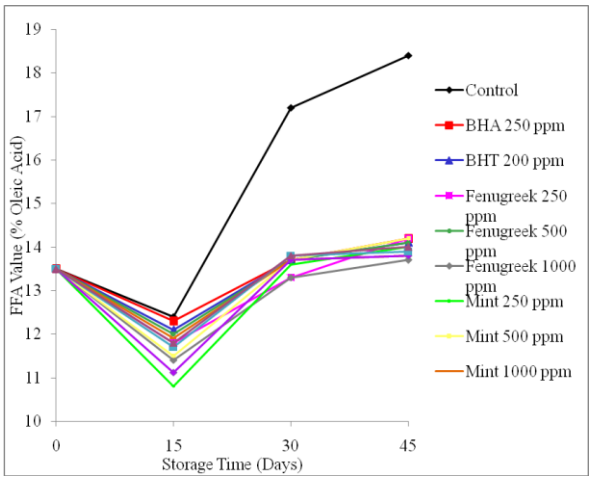

Fig. 1. Influence of storage conditions on the free fatty acid values.

The addition of herb extracts caused a significant reduction in the FFA value at ambient storage of sunflower oil. The FFA value decreased from 18.4% to 13.8% with 1000 ppm mint extracts and from 18.4% to 13.7% with Fenugreek (1000 ppm) and from 18.4% to 14% with Liquorice (1000 ppm) extracts. A significant difference was observed between the control sample and the samples that were stabilized with herbs. 1000 ppm extracts of Fenugreek and Mint caused more reduction in the FFA than BHA and BHT while the samples stabilized with the same concentration of Liquorice showed parallel potential to that of BHA and BHT. The FFA value of samples stabilized with herb extracts was found to decrease roughly as a function of the increase in concentration of the extracts. The storage period and FFA also possess a direct proportional relationship except for a small deviation of a slight decrease in the FFA value observed at the 15th day which then follows a regular pattern of increase like the synthetic antioxidants.

Influence of synthetic antioxidants and Herb extracts on PV

Peroxide values regarding the control sample and samples stabilized with synthetic as well as extracts were determined and are presented in Fig.(2). This figure shows that PV of the control samples was 146 meq/kg on the day when the analysis was started and after 45 days of storage it was 151 meq/kg. The synthetic antioxidants added to the oil samples caused a gradual increase in PV. A slight decrease in the PV value was observed on the 15th day of storage when the PV was decreased from 151 meq/kg to 148.1 with BHA and from 151 meq/kg to 147.8 meq/kg with BHT.

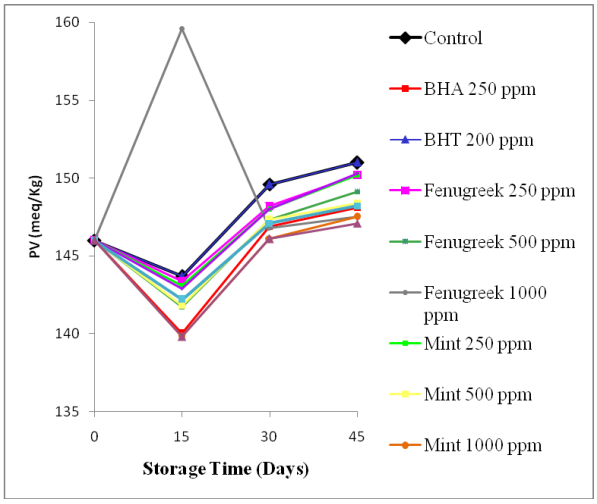

Fig. 2. Influence of the storage conditions on PV.

Fenugreek was reduced from 151 meq/ kg of the control sample to 150.2, 149.1 and 147.5 meq/kg on the 45th day of ambient storage by the addition of its 250, 500 & 1000 ppm methanolic extracts respectively. The PV of the sunflower oil samples

stabilized with 250, 500 & 1000 ppm methanolic extracts of Mint also reduced from 151 meq/kg for the control sample to 150.2, 148.4 and 147.5 meq/kg on the 45th day of storage. The addition of 250, 500 & 1000 ppm methanolic extracts of Liquorice also reduced the PV from 151 meq/kg (control) to 150.3, 148.2 and 147.1 meq/kg respectively on the 45th day of storage. As the high value of peroxides attributes to the formation of unstable hydroperoxides that ultimately convert to short chain acids, aldehydes, alcohols and ketones and thus cause flavor and odor changes [15] so the highest PV was observed in control samples which gradually decreased upon addition of varied concentrations (250, 500 and 1000 ppm) of methanolic extracts of herbs (Fenugreek, Mint and Liquorice).

Table 1. Influence of storage conditions on IV.

Herbs	Concentration (ppm)	Days			
		0	15	30	45
Control		100.3	90.4	49.6	47.8
BHT	200	90	95.2	76	62.7
BHA	200	90	97	74	60.1
	250	90.0	90.4	61.6	55.0
Fenugreek	500	90.0	95.7	74.6	61.6
	1000	90.0	100.0	80.0	78.3
	250	90.0	90.4	63.8	53.3
Mint	500	90.0	90.5	74.6	60.0
	1000	90.0	100.0	82.0	80.0
	250	90.0	90.3	61.9	56.9
Liquorice	500	90.0	94.3	74.6	73.0
	1000	90.0	94.0	75.0	63.3

Table 2. Influence of storage conditions on CD content of sunflower oil.

Herbs	Concentration (ppm)	Days			
		0	15	30	45
Control		0.575	0.695	0.459	0.469
	250	0.575	0.728	0.515	0.426
Fenugreek	500	0.575	0.718	0.434	0.408
	1000	0.575	0.687	0.445	0.424
	250	0.575	0.669	0.465	0.406
Mint	500	0.575	0.659	0.4	0.437
	1000	0.575	0.671	0.463	0.422
	250	0.575	0.683	0.425	0.418
Liquorice	500	0.575	0.677	0.434	0.405
	1000	0.575	0.675	0.463	0.428

Table 3. Influence of storage conditions on CT content of sunflower oil.

Herbs	Concentration (ppm)	Days			
		0	15	30	45
Control		0.741	0.752	0.516	0.536
	250	0.741	0.811	0.527	0.488
Fenugreek	500	0.741	0.749	0.475	0.481
	1000	0.741	0.778	0.514	0.494
	250	0.741	0.736	0.485	0.494
Mint	500	0.741	0.767	0.525	0.483
	1000	0.741	0.707	0.522	0.504
	250	0.741	0.759	0.471	0.466
Liquorice	500	0.741	0.777	0.505	0.500
	1000	0.741	0.727	0.486	0.504

The PV of stabilized samples containing the highest concentration (1000 ppm) of extracts from herbs was roughly similar to BHA and BHT proving a good antioxidant potential of herb extracts. Increase in PV follows a regular pattern that is deviated slightly in 15th day of storage probably due to the possibility of initial ultimate capture of previously present oxidants in the oils by strong antioxidants present in the herbs.

Effect of synthetic antioxidant and Herb extracts on IV

The IV of control was 100.3 on the starting day of the analysis which reduced to 47.8 on the 45 day of storage. These results favor the development of rancidity during ambient storage of the refined sunflower oil.

Addition of synthetic (BHA and BHT) and natural (extracts from Fenugreek, Mint and Liquorice) antioxidants retarded this decreasing trend. IV was observed to be 60.1 and 62.7 upon addition of BHA and BHT on the 45th day of storage. Addition of variable concentrations (250, 500 and 1000 ppm) of methanolic extracts of herbs (Fenugreek, Mint and Liquorice) to sunflower oil samples furnished iodine values of 55, 61.6, 78.3, 53.3, 60, 80, 56.9, 73, 63.3 respectively on the 45th day of storage (Table 1). Thus, distinctly higher IV were obtained upon treatment of the antioxidants than the control samples while the IV of stabilized sunflower oil samples treated with 1000 ppm herb extracts were almost comparable to BHA and BHT. Similar to FFA and PV, a slight increase in IV on the 15th day of storage was observed.

Effect of synthetic antioxidant and Herb extracts on Conjugated Dienes and Trienes

CD and CT are usually assessed to estimate the free radical production in order to evaluate the effectiveness of antioxidants in oils by measuring the oxidative deterioration of the oils. Generally, the samples having a higher content of CD and CT have a high intensity of oxidation. CD and CT were observed in control samples after 45 days (0.469 and 0.536 respectively) and were decreased by the incorporation of 250, 500 and 1000 ppm of all three herb extracts (Table 2 and 3). These findings were similar to Sultana et al., [16]. Generally, a non-uniform increase in the values of CD and CT were observed, however all of the stabilized samples exhibited lower values of CD and CT as compared to the control sample.

CONCLUSIONS

The methanolic extracts of Fenugreek, Mint and Liquorice were used to stabilize the samples of sunflower oil during ambient storage that was approximately parallel to the antioxidant activity of BHA and BHT. Therefore, it is suggested that natural antioxidant extracts of Liquorice, Mint and Fenugreek can securely and safely be managed and used as a substitute of synthetic antioxidants to extend or protect the shelf life of fats and oils.

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СТАБИЛИЗИРАНЕ НА СЛЪНЧОГЛЕДОВО МАСЛО С ЕКСТРАКТИ ОТ СМИНДУХ, МЕНТА И СЛАДНИК

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(Резюме)

Извършени са изследвания по стабилизирането на слънчогледово масло при добавянето на синтетични антиоксиданти (бутилиран хидроксианизол, BHA и бутилиран хидроксилтолуен, BHT), както и метанолови екстракти от сминдух, мента и сладник при стайна температура и влажност. Антиоксидантният потенциал на тези растителни екстракти е оценена с помощта на пероксидното число, съдържанието на свободни мастни киселини, йодното число, спрегнатите двойни връзки (диени и тирени). Тези параметри показват, че значително високи концентрации на екстрактите (грубо до пет пъти над BHA и BHT) може безопасно да се използват за контрола на гранясването на слънчогледовото масло.