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Extending shelf life of sunflower oil by aromatization with garlic and onion

Nashwa, F. S. Morsy

Food Science Dep., Faculty of Agriculture, Cairo University, 12613, Egypt

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Abstract

This study was performed to investigate the effectiveness of garlic and onion compared to butylated hydroxy toluene (BHT) on retarding oxidation of cold infused sunflower oil stored for 6 months. Garlic and onion powders or their essential oils were added to sunflower oil in a wide range of concentrations. Sensory evaluation of the flavored oil samples was carried out. Panelists preferred significantly the sunflower oil flavored by cold infusion with garlic and onion powders at 5% and 10 % levels or their essential oils at 0.01% and 0.02% levels. The progress of oxidation was assessed in terms of acid value, peroxide value, and oxidative stability determined by Rancimat. The yield and Gas Chromatography-Mass Spectrometry analysis of the garlic and onion essential oils were determined. These results suggested that garlic or onion could be used as a natural flavoring material for improving oxidative stability of sunflower oil.

Keywords: Natural flavoring, garlic, onion, sunflower oil, oxidative stability

1. Introduction

Vegetable oils with higher contents of polyunsaturated fatty acids, are more susceptible to oxidation. Lipid oxidation of oils can not only produce rancid odors, unpleasant flavors and discoloration, but can also decrease the nutritional quality and safety due to degradation products, resulting in harmful effects on human health [1]. Refined sunflower oil is widely used for cooking [2]. Sunflower oil needs to be stabilized by supplementation with antioxidant agents [3].

Herbs and spices are used all over the world to improve the taste and flavor of food products [4]. Some of the biologically active compounds in herbs are oil-soluble and therefore, herbs can be used to flavor edible oils. The infusion of oils with herbs responds to the consumer demand for oils with added value, such as oils with improved sensorial properties [5] and display a high antioxidant activity [6]. In addition, consumers prefer food products, which do not contain synthetic additives [7]. For this reason, opportunities are being sought to utilize the antioxidant properties of plants. While the presence of volatile aroma compounds and phenolic compounds in a wide variety of herbs has been well studied, little information is available on their partitioning into oils after infusion [7].

The flavor is considered as one of the most important sensory properties determining the food acceptance by the consumer [8]. Seasonality of the aromatic plants does not allow their use in the flavored oils manufacture throughout the year. Nevertheless, market studies have demonstrated that consumers are interested in this kind of product [9]. Therefore, in order to overcome the previous problems a possible approach is the use of the essential oils as a flavoring agent instead of the whole plant [10].

Corresponding author: *e-mail:* nanafsm@yahoo.com

Onion (*Allium cepa* L.) and garlic (*Allium sativum* L.), are the most popular spices and flavoring agents used in the food industry, as well as in household preparation of foods for their nutritional and aromatic properties [11,12,13]. Global fresh onion and garlic production reached 82 and 24 million tonnes, respectively in the year 2012 [14]. Onions and onion flavors (essential oil) are important seasonings widely used in food processing [15]. Onion and garlic could be dried and preserved for several months [16]. Alliums were revered to possess antibacterial and antifungal activities, due to the organo sulfur compounds and other numerous phenolic compounds, which arouse great interest [17,18].

Due to the increasing attention in natural additives, essential oils from several plants have been used more widely, especially in conjunction with other preservations under the concept of "hurdle technology." Thus, essential oils can serve as the alternative additives or processing aid as green technology [19].

Although the majority of the essential oils are classified as generally recognized as safe (GRAS), their use in foods as preservatives is often limited due to flavor considerations, since effective antimicrobial doses may exceed sensory acceptable levels [20].

The main objectives of this study were to select the appropriate level of garlic and onion powders and their essential oils to flavor sunflower oil and to identify whether those levels would improve the oxidative stability of the flavored oil during cold storage.

2. Materials and Methods

2.1. Materials

Refined, bleached and deodorized sunflower oil with no added antioxidants was purchased from Cairo Oil and Soap Company, Egypt. Garlic and onion powders were purchased from Haraz stores, Cairo, Egypt. All chemicals and reagents used were of analytical grade and were purchased from Fluka Chemicals (Fluka, Buchs, Switzerland). Butylated hydroxy toluene (BHT) was purchased from Sigma Chemical Co (St. Louis, MO, USA).

2.2. Essential oil extraction

Onion and garlic essential oils were extracted from 100 g of each of garlic and onion powders by steam distillation for 3 hours using a Clevenger type apparatus. The essential oils were dried over anhydrous sodium sulfate, stored in dark glass bottles, and kept at 4°C until analysis. The yield of essential oil obtained from each plant material was calculated.

2.3. Gas chromatography-mass spectrometry

Gas chromatography analysis was performed on a Shimadzu GCMS-QP 2010 Ultra gas chromatograph (Kyoto, Japan) fitted with flame ionization detector and RTX–5 column (30 m × 0.25 mm, film thickness 0.25 μm) with helium as carrier gas at 1.33 mL/min. The injection port was maintained at 210°C, the detector temperature was 230°C. The split ratio was 1:10 and ionization voltage maintained at 70 eV. One μL sample was injected. The oven was programmed as follows: at 40 °C for 2 min and then increased to 210°C at 5°C/min at which the column was maintained for 5 min. The compounds were identified by the authentic standards purchased from Fluka Chemicals (Fluka, Buchs, Switzerland) and by matching the mass spectrum of individual compounds with that of NIST and Wiley library. The concentration of each compound was determined by area normalization.

2.4. Preparation of flavored sunflower oil

Sunflower oil samples (each 50 ml) were flavored by i: infusion of garlic or onion powder into the investigated oil at 2.5, 5, 10 and 20% (w/v), or ii: direct addition of garlic or onion essential oil at 10, 20, 50, 100 and 200 ppm (0.001, 0.002, 0.005, 0.01 and 0.02 %). Sunflower oil without any flavoring material was served as a control. All flavored oil samples were prepared in six replicates. The obtained oil samples were sealed and stored in dark glass bottles in the refrigerator at 5 ºC as recommended by [21] with daily shaking to develop flavor. Sensorial evaluation of oil samples was carried out after filtration according to [22] every 5 days until the perception of garlic and onion flavors at the lowest concentration. Perception of flavor in the experimental oil was noticed after 15 days of infusion.

Sensorial evaluation of all flavored oil samples was conducted. Highly acceptable samples were selected for further investigation. Oil samples containing the accepted levels of garlic and onion powders or their essential oils, were stored under the same storage conditions for another 5.5 months, besides control oil samples.

2.5. Evaluation of flavored sunflower oil oxidative stability using a rancimat apparatus

The oil resistance to oxidation at 100 ºC with an airflow of 20 L min^{-1} was evaluated using a Rancimat 679 apparatus (Metrohm AG, Switzerland). The test was carried out using 3 ml of each of the sensory accepted oil samples before (after infusion at 5 ºC for 15 days) and after storage for 6 months in the refrigerator. The volatile oxidation products released during oxidation were stripped from the oil and carried into a conductivity cell containing distilled water, whose conductivity increased progressively. The oxidative stability was expressed as the induction time (the time (h) that corresponds to the rapid change in the slope of the curve representing the changes in water conductivity vs. time.). The relative stability was calculated according to the formula below:

Relative stability = Induction time of the flavored oil/ Induction time of the control sample.

2.6. Quality characteristics of oil

Free acidity and peroxide value of the investigated oil samples were determined before and after storage for 6 months in the refrigerator according to [23].

2.7. Sensory evaluation

Ten panelists carried out sensory evaluation of flavored sunflower oil. The panelists were asked to evaluate the products for odor, taste and overall acceptability (Fresh bread was used as a carrier and flavored sunflower oil was added at a constant ratio according to Ayadi *et al*. (2009) [4].

2.8. Statistical analysis

All analytical determinations were performed at least in triplicate. Values of different parameters were expressed as the mean ± standard deviation. For the sensorial analysis, analysis of variance and low significant difference (LSD) test were carried out in order to determine the consumer acceptability and the significance of differences among the sample average, respectively. Duncan's multiple range test and significant differences were determined at the 5% significance level according to [24].

3. Results and discussion

3.1. Chemical composition of onion and garlic essential oils

The yield of the essential oils obtained from garlic and onion powders was found to be 0.48±0.01 % and 0.17±0.01 %, respectively. These results are in agreement with those reported by [16, 25].

Fig. 1a shows the GC-MS analysis of the garlic essential oil obtained by steam distillation. Diallyl sulfide (21.55%), methyl-2-propenyl disulfide (3.34%), diallyl disulfide (27.45%), 1-allyl-3-methyl-trisulfide (8.01%), diallyl trisulfide (26.28%), allyl methyl tetrasulfide (3.44%) and diallyl tetrasulfide (9.93%) were identified as the major components of garlic essential oil. Levels of the major constituents are in agreement with those reported by [26]. Fig. 1b shows the GC-MS analysis of the onion essential oil obtained by steam distillation. Disulfide methyl propyl (4.12%), disulfide dipropyl (33.34%), diallyl tetrasulfide (5.12%), trisulfide methyl propyl (10.82%), trisulfide dipropyl (25.77%), trans propenyl propyl trisulfide (5.56%) and 2-tridecanone (10.25%) were identified as the major components of onion essential oil. Levels of the major constituents are in agreement with those reported by [27].

3.2. Sensory evaluation

Cold infusion of garlic and onion powders and addition of their essential oils were used to impart their flavor to sunflower oil. The mean sensory scores for odor and taste of the flavored sunflower oil samples after 15 days of cold storage are shown in Table 1.

Results show that intensity of odor and taste of the investigated spices was proportional to their concentration in sunflower oil. Results in Table 1 show that sensory attributes of garlic or onion infused sunflower oil samples at 5 and 10% levels or flavored by 100 or 200 ppm of their essential oils were significantly higher than the other investigated levels. Oils of garlic and onion have 500 times the strength of their dried materials [25,28].

Moreover, significant decrements in the sensory descriptor (pungency) proper for the flavored sunflower oil were recorded at higher concentration of garlic and onion powders. The pungent sensation of onion or garlic is sulfury [28].

3.3. Oxidative stability of flavored sunflower oil

Results in Table 2 indicate the freshness and high quality of the refined sunflower oil used (with no added antioxidant), since its acid value and peroxide value and induction time were 0.05±0.01 mg KOH g^{-1} oil, 0.10±0.01 meq O_2 Kg^{-1} oil, and 8.38±0.04 h (at 100 ºC) using accelerated oxidation test (Rancimat). Result of oxidative stability is in agreement with that reported by [29].

Infusion of garlic or onion powders into the sunflower oil at the investigated levels (5% and 10%) for 15 days at room temperature exhibited similar relative stability values as the control oil. The addition of the essential oil of garlic or onion to sunflower oil at 200 ppm increased its oxidative stability by ≥ 30%, representing 75% of the efficacy of the BHT at the same level.

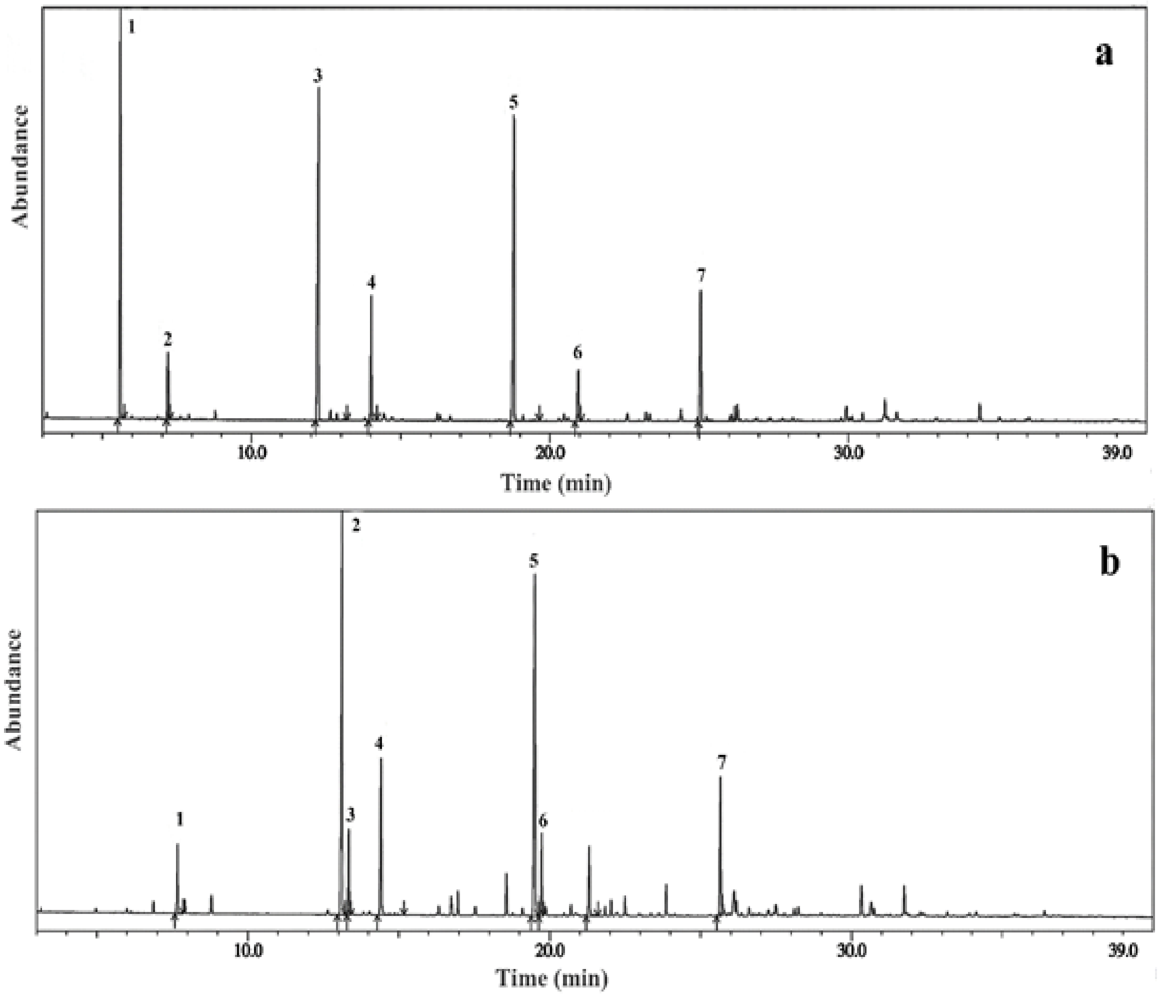

Figure 1. GC chromatograms of garlic (a) and onion (b) essential oils

Table 1. Sensorial evaluation of flavored sunflower oil after 15 days of flavoring process

Flavored sunflower oils	%	Odor	Taste	Overall acceptability
Garlic Powder	2.5	5 ± 1.0^{b}	4.33 ± 0.58^{b}	4.66 ± 0.76^{b}
	5	8.66 ± 0.57^{a}	8.33 ± 0.57^{a}	8.5 ± 0.5^{a}
	10	7.66 ± 0.57^{a}	8 ± 1.73^{a}	7.83 ± 1.15^{a}
	20	3.33 ± 0.58^{c}	4 ± 1.0^{b}	3.66 ± 0.58^{b}
$LSD_{0.05}$		1.33	2.03	1.49
Onion Powder	2.5	6.33 ± 1.53^{b}	6 ± 1.0^{b}	6.17 ± 1.04^{b}
	5	8.33 ± 0.60^{a}	8 ± 1.0^{a}	8.17 ± 0.29^{a}
	10	8.67 ± 0.58^{a}	9 ± 1.0^{a}	8.83 ± 0.28^{a}
	20	5.33 ± 0.58^{b}	5.6 ± 0.58^{b}	5.5 ± 0.5^{b}
$LSD_{0.05}$		1.72	1.71	1.15
Garlic oil	0.001	7 ± 1.0^{b}	5.66 ± 0.57^{b}	6.33 ± 0.57^{b}
	0.002	8 ± 1.0^{ab}	6.33 ± 0.56^{b}	7.17 ± 0.76^{b}
	0.005	7.67 ± 0.58^{ab}	7 ± 1.0^{b}	7.33 ± 0.76^{b}
	0.01	9 ± 1.0^{a}	8.67 ± 1.15^{a}	8.83 ± 1.04^{a}
	0.02	9 ± 0^{a}	8.66 ± 0.58^{a}	8.83 ± 0.29^{a}
$LSD_{0.05}$		1.56	1.48	1.33
Onion oil	0.001	5 ± 1^{c}	4.66 ± 0.58^{c}	4.83 ± 0.6^{d}
	0.002	5.33 ± 1.15^{bc}	6.0 ± 1.0^{bc}	5.66 ± 1.04^{cd}
	0.005	6.66 ± 0.6^{b}	7.33 ± 0.6^{ab}	7 ± 0.5^{bc}
	0.01	8.33 ± 0.6^{a}	8.33 ± 1.15^{a}	8.33 ± 0.76^{ab}
	0.02	8.66 ± 0.6^{a}	9.0 ± 1.0^{a}	8.80 ± 0.76^{a}
$LSD_{0.05}$		1.48	1.63	1.37

Data are reported as mean values ±standard deviation. Values not sharing a common superscript in each column for each material are significantly different, ($P < 0.05$)

Table 2. The antioxidant performance of garlic and onion on sunflower oil oxidative stability.

Parameters	Level of addition	Storage time			
		0.5 month		6 months	
		Induction time (h)	Relative stability*	Induction time (h)	Relative stability*
Control		8.38 ± 0.04	1	4.17 ± 0.02	1
Garlic powder	5%	8.47 ± 0.10	1.01	10.4 ± 0.10	2.49
	10%	8.59 ± 0.05	1.02	9.82 ± 0.02	2.35
Onion powder	5%	9.28 ± 0.04	1.1	9.62 ± 0.10	2.31
	10%	9.2 ± 0.10	1.09	9.5 ± 0.10	2.28
Garlic oil	100 ppm	9.39 ± 0.06	1.12	6.46 ± 0.02	1.55
	200 ppm	11.9 ± 0.07	1.42	9.28 ± 0.01	2.22
Onion oil	100 ppm	10.3 ± 0.10	1.20	6.82 ± 0.05	1.63
	200 ppm	10.93 ± 0.01	1.30	8.67 ± 0.02	2.07

Induction time of sunflower oil with 200 ppm BHT at zero time was 14.01 h (Relative stability = 1.67). * Relative stability = Induction time of the flavored oil/ Induction time of the control sample, where induction time is the time needed to reach the break point in the plotted curve from Rancimat analysis of sunflower oil . The data are reported as mean values ±standard deviation.

According to [30], diallyl disulfide and diallyl trisulfide appeared to be the most active antioxidants in the garlic volatiles. Okada and co-workers [31] have suggested that a combination of the al lyl group ($-CH_2CH=CH_2$) and the $-S(O)S-$ group is necessary for the antioxidant action of thiosulfinates in garlic extracts.

Ye and co-workers [15] suggested that the essential oil of onion exhibited moderate antioxidant activity.

A combination of a number of minor constituents in aromatic plant oils could have a synergistic role in increasing the oxidation stability [32].

Storage of the sunflower oil (control sample, without added antioxidant) for 6 months in the refrigerator decreased its oxidative stability by nearly 50%.

The relative stability of garlic or onion infused sunflower oil samples for 6 months was higher than that recorded for sunflower oil samples flavored with their essential oils. Some of the chemical compounds other than essential oil constituents of garlic and onion powders have antioxidant activity and synergistic effect [33].

The antioxidant activity of flavoring oils (garlic or onion) at 200 ppm level was remarkably higher than that recorded in 100 ppm level, regardless storage time of the flavored oil. Although oxidative stability of 6 months stored sunflower oil samples, flavored with garlic oil or onion oil at 200 ppm decreased partially to ~ 75% of its original value, it was still higher than that of the fresh oil (control sample) stored for only 15 days. Flavoring sunflower oil with garlic or onion powder at 5% level or their essential oils at 200 ppm kept its oxidative stability for 6 months from being altered. This indicated that flavoring process with garlic and onion slowed down the oxidation process during cold storage that extended for 6 months. None of the stored oil samples (control or flavored) exceeded the recommended limits of acid and peroxide values for refined sunflower oil (0.6 mg KOH g^{-1} oil, 10 meq O_2 kg^{-1} oil) according to [34] after 6 months of storage.

Oxidative deterioration of lipids can occur in the dark by a free radical mechanism, known as autoxidation. It proceeds through two different phases. During the first phase, called the induction period, the oxidation goes slowly and at a uniform rate. After the oxidation has proceeded to a certain point, the reaction enters a second phase, which has a rapidly accelerating rate of oxidation. The primary lipid oxidation products are hydroperoxides, which are colorless and odorless unstable compounds and further react to form secondary products such as hydrocarbons, alcohols, ketones and aldehydes, which can be oxidized to carboxylic acids [35,36].

4. Conclusions

This study clearly demonstrates that cold infusion of garlic or onion powders at the 5 % level or addition of their essential oil at 200 ppm improves the sunflower oil from being oxidized and maintain its quality at least up to six months under cooling conditions.

The statistical analysis of data shows that the sunflower oil samples, flavored with garlic or onion at these levels were ranked as the most acceptable.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.

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