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Analysis of Heat Processed Oils Containing Four Different Spices: Fenugreek, Cumin, Black Cumin, Coriander

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Abstract

In the present work sunflower oil was heated in the presence of four different spices namely fenugreek, cumin, black cumin and coriander. Four different sets were prepared with the oil and each of the respective spices. Each set was heated from 70°C to 250°C. From time to time samples were withdrawn and their acid values, peroxide values, p-anisidine values and iodine values were evaluated. It was observed that at all temperatures black cumin displayed the minimum acid value. Hence black cumin was able to considerably prevent the hydrolysis of the oil to fatty acid. However, in case of peroxide value determination, it was observed that under initial heating conditions, coriander generated lower peroxide value. But at higher temperatures once again black cumin treated oil displayed lower peroxide values. Again, both black cumin and coriander treated oils demonstrated low p-anisidine values. Iodine values of both coriander treated and black cumin treated oils were initially quite high, followed by gradual lowering along with temperature.

***Keywords:** Fenugreek; Cumin; Black cumin; Coriander; Sunflower oil*

Introduction

Spices are generally used for providing a distinct flavor to the food. Apart from that spices also serve many other functions when added to food products. These include providing aroma, texture and color to the food. Spices also provide antimicrobial, antioxidant and protective functions beneficial in human health. Different spices are well-known sources of various phytochemicals which contribute towards their effective antioxidant activity [1]. Essential oils and extracts obtained from many plants have recently gained popularity and scientific interest. Commonly studied spices included clove, peppermint, allspice, cinnamon, oregano, rosemary, saffron, basil, parsley, birch leaves, marjoram, black pepper, cardamom etc. The mean antioxidant content of these spices ranged from 44 to 277 mmol/100 g [2-6]. The studies showed that the consumption of these spices would be quite beneficial to one and all, in terms of preventing free radical related abnormalities.

Spices belong to such a category of plant products which are rich in antioxidants. They contain different active compounds like carotenoids, polyphenolic compounds, etc. which effectively prevent the formation of several reactive oxygen species, thus providing adequate antioxidant efficacy.

The potential for antioxidant spices to reduce or prevent the formation of oxidation products during the cooking process at high temperatures is important because studies have shown that fried foods contain significant amounts of reactive oxygen species. Consumption of these products is associated with a high risk of developing diseases related to them such as cancer, atherosclerosis, arthritis etc. Hence the present work was designed to study the effect of heating edible oils in presence of different spices of indigenous variety. A comparative study was performed among four different spices based on their ability to protect sunflower oil on heating. The different parameters that were studied after heating the oils at high temperatures include acid value, peroxide value, p-anisidine value and iodine value.

Experimental Procedure

Materials

Sunflower oil, spices (fenugreek, cumin, black cumin, coriander) were purchased from the local market. All other chemicals were of analytical grade and procured from Merck India Ltd, Mumbai, India. The clean spice samples were stored in a glass container and kept at -20°C deep-freezer before analysis.

Methods

1) Sample preparation: About 25 g of each of the selected spices were weighed in a Petri dish. The weighed spice was ground and finally about 20 g of the ground spice was taken.

2) Addition of the spice to the oil: About 500 ml refined sunflower oil was taken in a conical flask. The ground spice was added to the oil and the mixture was heated on a hot plate. The temperature was increased gradually from 70°C to 250°C and at 20° interval 10 ml of oil was withdrawn and analyzed for four parameters as specified below.

3) Parameter study: The following tests were performed with the collected oil:

The AOCS Official Methods were employed for determinations of acid value, peroxide value, p-anisidine and iodine values in the oil samples [7].

a) Acid value: About 2-3 g of oil was taken in a conical flask. To this 20-25 ml of neutralized alcohol was added and the mixture was heated for 2-3 min. Then the solution was titrated with standardized sodium hydroxide solution under hot condition using phenolphthalein indicator.

Acid value=(56.1 × N × V)/W

N=Strength of sodium hydroxide,

V=Volume of sodium hydroxide,

W=Weight of oil taken.

b) Peroxide value: In about 3-5 gm of oil taken in a stoppered flask, a mixture of chloroform and acetic acid (in a ratio of 3:2) was added. Then 10 ml of saturated potassium iodide solution was added to it and kept in dark for 5 min. To it 30 ml of distilled water was added and the mixture was titrated against (N/100) standardized thio solution using starch as indicator. Subsequently a blank was also done without the presence of the oil.

Peroxide value=[(S – B) × N × 1000]/W

S=volume of sample solution,

B=volume of blank solution,

N=Strength of thio solution,

W=Weight of oil taken.

c) p-Anisidine value: 0.4-0.5 g oil was taken in a 25 ml volumetric flask. It was dissolved and diluted to volume with iso-octane. The absorbance of the solution was measured at 350 nm in a cell using the reference cell filled with iso-octane. Exactly 5 ml of the test solution was pipetted out into one test tube and 5 ml iso-octane in another test tube. Exactly 1 ml p-anisidine reagent was added to each test tube and was shaken. After exactly 10 minutes the absorbance (As) of the solution in first test tube was measured at 350 nm using the solution from the second test tube as a blank in the reference cell.

p-anisidine value= 25 × (1.25As – Ab)/W

Where, As= Absorbance of the sample,

Ab= Absorbance of the blank,

W= Weight of the oil taken.

d) Iodine value: 0.1-0.2 g oil was mixed with 25 ml carbon tetrachloride taken in an iodine flask. Then 20 ml Wijs' solution was added to it and shaken vigorously. It was kept in dark for 30 minutes. Then 1 ml of 10% KI solution was added followed by the addition of 100 ml distilled water and immediately titrated against standardized (N/10) thio solution using starch as indicator. A blank test was performed without the sample.

Iodine value=[(B – S) × 12.69 × N]/W

B=Titre value of blank test.

S=Titre value of sample.

N=Strength of thio solution.

W=Weight of the oil taken.

4) Statistical analysis: Statistical analysis was performed using one-way analysis of variance (ANOVA). When ANOVA detected significant differences between mean values, means were compared using Tukey's test. For statistical studies Origin Lab software (Origin Lab Corporation, Northampton, UK) was used. Statistical significance was designated as $P<0.05$. Values are expressed as Mean ± SEM.

Results and Discussion

Several parameters of the sunflower oil were analyzed. On heating the oil from 70°C to 250°C it was observed that acid value of the oil increased from 0.2 to 0.5, iodine value decreased from 142.8 to 119.5, p-anisidine value increased from 3.4 to 18.2 and finally peroxide value increased from 3.2 to 17.3. The temperature selected for heating the oil was in correlation to that involved in the domestic cooking processes. Along with the heating experiments of oils in presence of the four different spices another set was heat-treated in absence of any spice. This set was the control.

a) Analysis of acid values: Acid value of the sample oils withdrawn at different temperatures of heating were determined to record the amount of free fatty acid generated in the system. Acid value increased from 0.204 to 0.501 for oils heated without the addition of any spice (TABLE 1). The acid value of the oil heated in presence of black cumin was significantly low at all temperatures in which it was treated. Again, it was observed that fenugreek did not serve very effectively in preventing the degradation of the oil to its component fatty acids. The acid values of coriander treated oil were at par with that of the cumin treated oil. Higher acid values in fenugreek treated oil indicated that higher oxidative damage of the oil was encountered when it was heated in presence of this spice unlike when the other three types of spices were used. This study was in correlation with the previously reported results by Ghosh, et al [8].

TABLE 1. **Study of acid values of sunflower oils after heating with different spices.**

Temperature (◦C)	**Control oil**	**Fenugreek treated oil**	**Cumin treated oil**	**Black cumin treated oil**	**Coriander treated oil**
70	0.204 ± 0.01^{a}	0.257 ± 0.06^{b}	0.202 ± 0.008^{c}	0.153 ± 0.009^{d}	0.216 ± 0.02^{e}
90	0.254 ± 0.05^{a}	0.259 ± 0.11^{b}	0.205 ± 0.006^{c}	0.165 ± 0.007^{d}	0.220 ± 0.01^{e}
110	0.335 ± 0.02^{a}	0.267 ± 0.08^{b}	0.209 ± 0.005^{c}	0.169 ± 0.002^{d}	0.223 ± 0.01^{e}
130	0.428 ± 0.08^{a}	0.349 ± 0.12^{b}	0.0218 ± 0.001^{c}	0.178 ± 0.003^{d}	0.226 ± 0.08^{e}
150	0.448 ± 0.10^{a}	0.349 ± 0.14^{b}	0.217 ± 0.006^{c}	0.179 ± 0.002^{d}	0.226 ± 0.11^{e}
170	0.452 ± 0.04^{a}	0.427 ± 0.22^{b}	0.240 ± 0.007^{c}	0.189 ± 0.001^{d}	0.228 ± 0.08^{e}
190	0.467 ± 0.09^{a}	0.428 ± 0.23^{b}	0.249 ± 0.009^{c}	0.196 ± 0.005^{d}	0.247 ± 0.07^{e}
210	0.483 ± 0.07^{a}	0.430 ± 0.31^{b}	0.248 ± 0.006^{c}	0.208 ± 0.004^{d}	0.263 ± 0.09^{e}
230	0.492 ± 0.06^{a}	0.439 ± 0.41^{b}	0.269 ± 0.007^{c}	0.217 ± 0.007^{d}	0.273 ± 0.06^{e}
250	0.501 ± 0.12^{a}	0.474 ± 0.09^{b}	0.291 ± 0.003^{c}	0.234 ± 0.005^{d}	0.286 ± 0.05^{e}
Values are expressed as mean ± S.E.M, n=3. Means were compared using Tukey’s test. Columns not sharing a common superscript are statistically significant ($p<0.05$)					

b) Analysis of peroxide values: Peroxide values of the heated oils were determined from time to time by withdrawing oil samples and then analyzing them by established methods. It was observed that the oil treated with black cumin showed the highest resistance towards the production of undesired oxidized by-products ranging from 2.75 meq/kg to 4.48 meq/kg (TABLE 2). Unlike black cumin, fenugreek and cumin were not very effective in preventing oxidation of sunflower oil as indicated by their rapidly increasing peroxide values. Coriander treated oil was also effective in preventing the oxidation of sunflower oil but not as effectively as prevented by black cumin. In fact, the peroxide value of black cumin treated oil displayed low generation of oxidation products even after treatment at 250°C (<5 meq/kg). In all the other cases with increasing temperature an average to high amount of oxidation products were synthesized (>5 meq/kg).

TABLE 2. **Study of peroxide values (in meq/kg) of sunflower oils after heating with different spices.**

Temperature (◦C)	**Control oil**	**Fenugreek treated oil**	**Cumin treated oil**	**Black cumin treated oil**	**Coriander treated oil**
70	3.19 ± 0.22^{a}	3.09 ± 0.25^{b}	2.34 ± 0.09^{c}	2.75 ± 0.26^{d}	2.18 ± 0.23^{e}
90	3.21 ± 0.32^{a}	3.08 ± 0.18^{b}	4.79 ± 0.20^{c}	2.81 ± 0.13^{d}	2.23 ± 0.24^{e}
110	4.25 ± 0.21^{a}	3.54 ± 0.23^{b}	4.85 ± 0.19^{c}	2.85 ± 0.32^{d}	3.13 ± 0.29^{e}
130	6.66 ± 0.34^{a}	4.10 ± 0.34^{b}	5.11 ± 0.38^{c}	2.90 ± 0.18^{d}	3.53 ± 0.12^{e}
150	8.74 ± 0.54^{a}	5.08 ± 0.62^{b}	6.05 ± 0.27^{c}	2.96 ± 0.33^{d}	4.10 ± 0.08^{e}
170	11.18 ± 0.41^{a}	5.04 ± 0.19^{b}	6.97 ± 0.12^{c}	3.12 ± 0.29^{d}	5.57 ± 0.21^{e}
190	13.65 ± 0.91^{a}	5.13 ± 0.55^{b}	7.14 ± 0.42^{c}	3.26 ± 0.71^{d}	6.01 ± 0.09^{e}
210	15.15 ± 0.78^{a}	6.067 ± 0.43^{b}	7.30 ± 0.33^{c}	3.33 ± 0.81^{d}	6.07 ± 0.44^{b}
230	16.79 ± 0.77^{a}	6.069 ± 0.17^{b}	7.52 ± 0.71^{c}	4.22 ± 0.52^{d}	6.07 ± 0.16^{b}
250	17.28 ± 0.54^{a}	7.64 ± 0.44^{b}	8.38 ± 0.18^{c}	4.48 ± 0.28^{d}	7.21 ± 0.08^{e}

c) Analysis of p-anisidine values: Both p-anisidine value and peroxide values are indicative of the shelf-life stability of oils. While peroxide values quantify the primary oxidation products of oil (hydroperoxides), p-anisidine value measures the amount of secondary oxidation products obtained from the conversion of the primary oxidation products (aldehydes, ketones etc.). This is responsible for about 50% of volatile compounds during lipid oxidation [9]. Incidentally, the oil treated with cumin seeds seemed to accelerate the conversion of primary to secondary oxidation products, as the p-anisidine values showed significantly higher values on heating than the spice-free oil (TABLE 3). However, the presence of black cumin once again seemed to significantly retard the conversion of primary oxidation products to the secondary oxidation products. In fact, the p-anisidine values remained constant on heating to higher temperatures. Coriander treated oil also showed slow conversion rate of primary to secondary oxidation products as indicated by the gradual increase of p-anisidine values. Thus, lower p-anisidine values for black cumin and coriander treated oils indicated a longer shelf-life of the oil heated in presence of this spice.

TABLE 3. **Study of p-anisidine values of sunflower oils after heating with different spices.**

Temperature (◦C)	**Control oil**	**Fenugreek treated oil**	**Cumin treated oil**	**Black cumin treated oil**	**Coriander treated oil**
70	3.42 ± 0.12[a]	2.90 ± 0.11[b]	9.5 ± 0.13[c]	2.58 ± 0.54[d]	2.78 ± 0.44[e]
90	3.59 ± 0.56[a]	2.98 ± 0.32[b]	15.36 ± 0.62[c]	2.89 ± 0.43[d]	2.95 ± 0.34[b]
110	4.04 ± 0.34[a]	3.14 ± 0.43[b]	12.27 ± 1.12[c]	3.14 ± 0.32[d]	3.09 ± 0.32[e]
130	5.85 ± 0.29[a]	3.58 ± 0.09[b]	13.77 ± 0.92[c]	3.13 ± 0.22[d]	4.08 ± 0.31[e]
150	7.35 ± 0.55[a]	4.51 ± 0.18[b]	13.07 ± 0.24[c]	3.14 ± 0.24[d]	5.02 ± 0.54[e]
170	9.20 ± 0.63[a]	4.61 ± 0.15[b]	21.27 ± 0.72[c]	3.18 ± 0.61[d]	5.55 ± 0.32[e]
190	11.31 ± 0.81[a]	5.18 ± 0.14[b]	22.18 ± 0.55[c]	3.50 ± 0.21[d]	5.70 ± 0.61[e]
210	13.44 ± 0.72[a]	6.00 ± 0.18[b]	22.31 ± 0.17[c]	3.60 ± 0.42[d]	6.39 ± 0.23[e]
230	15.86 ± 0.53[a]	8.37 ± 0.19[b]	23.64 ± 0.18[c]	4.36 ± 0.14[d]	6.65 ± 0.40[e]
250	18.20 ± 0.44[a]	9.71 ± 0.22[b]	23.73 ± 0.44[c]	5.08 ± 0.16[d]	7.32 ± 0.35[e]
Values are expressed as mean ± S.E.M, n=3. Means were compared using Tukey’s test. Columns not sharing a common superscript are statistically significant (p<0.05)					

d) Analysis of iodine values: Iodine value was found to decrease gradually with increasing heating temperature (TABLE 4.), indicating a loss of unsaturation with increasing heating temperatures. This agrees with the study conducted by Naz et al. [10] Where with increasing lipid oxidation, unsaturation of fats and oils was found to decrease. Sunflower oil has a high degree of unsaturation. With increasing temperature of heating, the unsaturated units tend to be oxidized, thus losing its unsaturation [11]. Once again it was observed that the decrease of iodine value was the least for black cumin treated oil in comparison to the other spice treated oils. This is in correlation with the fact that the heat induced oxidation was also minimal for the black cumin treated oil. Iodine values of the heat-treated fenugreek, cumin and coriander containing oils were at par with the spice-free oil as far as loss of unsaturation was concerned.

TABLE 4**. Study of iodine values of sunflower oils after heating with different spices.**

Temperature (◦C)	**Control oil**	**Fenugreek treated oil**	**Cumin treated oil**	**Black cumin treated oil**	**Coriander treated oil**
70	142.85 ± 1.65[a]	138.2 ± 1.34[b]	140.2 ± 1.44[c]	147.94 ± 1.82[d]	166.86 ± 1.33[e]
90	140.71 ± 1.82[a]	138.13 ± 1.89[b]	140.07 ± 1.71[a]	142.79 ± 1.67[c]	154.94 ± 1.57[d]

110	135.2 ± 1.55^{a}	130.12 ± 1.78^{b}	136.2 ± 1.11^{c}	138.29 ± 1.91^{d}	143.02 ± 1.64^{e}
130	122.0 ± 1.42^{a}	129.0 ± 1.91^{b}	128.6 ± 2.75^{b}	127.22 ± 1.92^{c}	120.51 ± 1.77^{d}
150	118.5 ± 1.37^{a}	107.9 ± 1.58^{b}	117.5 ± 1.65^{c}	125.92 ± 1.87^{d}	117.06 ± 1.29^{c}
170	105.4 ± 1.12^{a}	105.33 ± 1.77^{a}	107.7 ± 1.95^{b}	113.20 ± 1.88^{c}	110.18 ± 2.24^{d}
190	103.64 ± 1.52^{a}	102.99 ± 1.23^{a}	105.4 ± 1.85^{b}	108.63 ± 1.49^{c}	103.29 ± 2.05^{a}
210	91.3 ± 1.61^{a}	97.57 ± 2.05^{b}	96.14 ± 2.36^{c}	105.77 ± 1.83^{d}	99.85 ± 1.41^{e}
230	90.01 ± 1.35^{a}	90.38 ± 1.95^{a}	95.87 ± 1.78^{b}	102.91 ± 2.17^{c}	89.09 ± 1.43^{d}
250	89.5 ± 1.45^{a}	80.10 ± 1.52^{b}	80.86 ± 1.88^{b}	98.34 ± 1.52^{c}	79.19 ± 1.99^{d}

Conclusion

The behavior of heat treated oils in the presence and absence of four different spices, with gradually increasing temperatures were studied in the present work. The selected spices were fenugreek, coriander, cumin, black cumin and their effects were studied on refined sunflower oil. From the results it was observed that the acid values of the oil increased after gradual heating but in presence of spice the increase in acid value was quite slow. From peroxide value and p-anisidine value studies it was observed that in both the cases the primary and secondary oxidation products increased with temperature. The iodine value however decreased with increasing temperature for both spice treated and un-treated oils. However, the present study showed that black cumin was most effective as an antioxidant in preventing the rapid oxidation of oil under heat treatment based on several physicochemical tests. Coriander also showed considerable heat-resistant properties. However, fenugreek and cumin were effective against heat-induced degradation up to a certain extent, beyond which they failed to protect the oil. Thus, for cooking purposes, especially in the Indian cooking style, black cumin is highly recommended.

Conflict of Interest

The authors have declared no conflict of interest.

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