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The Effect of Some Spice Extracts on Storage Stability of "Yayik Butter"

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Abstract: The effects of ethyl acetate extracts of sage (*Salvia fructicosa*), cinnamon (*Cinnamomum verum*), clove (*Dianthus caryophylium* L.), thyme (*Thymus vulgaris*), sumac (*Rhus coriaceae*), rosemary (*Rosmarinus officinalis*), cumin (*Cumium cyminum*), ginger (*Zingiber officinale*) and oregano (*Origanum vulgare* L.) on butter stability were investigated. All extracts were individually added to butter at 0.2% and 0.5% levels. For comparison, 0.01% BHA was added in butter as positive control and non additive-negative control also was prepared and tested. The butter samples were stored at 5 and 25°C for 120 days. The effectiveness of extracts on stability of butter samples were changed with different storage temperatures. The extracts of clove, thyme, rosemary, ginger, sumac, cumin, sage and cinnamon showed similar antioxidant effect with butylated hydroxyanisole (BHA) in butter. Free fatty acid (FFA) value in butter treated with cumin, sumac, rosemary, clove, sage and thyme ethyl acetate extracts was significantly lower than that of the negative control sample and was similar with positive control. The storage temperatures were significantly effective on storage stability of butter. Spices extracts did not show significant effect on sensorial quality of butter. According to the results of stability analysis (PV, IC_{50}, FFA and TBA), the extracts of clove, sumac, thyme, cumin and ginger showed significant positive effect on storage stability of butter.

Key words: Butter · Storage stability · Spice extracts · PV · TBA · DPPH

INTRODUCTION

Butter is produced from milk, cream and yoghurt in different areas of Turkey. The butter produced from fresh yoghurt or 'tulum yoghurt' (strained yoghurt produced from cow, goat or sheep milk) is called 'yayik butter' and has been traditionally produced in Turkey for centuries. Sheep, goat or cow milk can be used in the production of 'yayik butter'. This butter is widely produced and consumed and is still a popular Turkish product. It has a characteristic flavour that plays an important role in its popularity. Today, there is a special demand for this product among consumers and its portion of the market should be increased to meet the demands of Turkish consumers and others. Although microbiological quality of the yayik butter is high, it's shelf life not very long. The microflora may be affected by differences in traditional processing methods, raw milk quality, packaging materials [goat's skin, clay (soil) cup or cleaned rumen] and storage conditions [1-4].

Deterioration of milk fat can occur by two main mechanisms: fatty acid release and oxidation of C=C bonds. Release of fatty acids occurs by cleavage (hydrolysis) of a fatty acid from a triacylglyceride molecule. Oxidation of C=C bonds results in formation of hydroperoxide radicals that form high molecular weight compounds over time with increased viscosity and propensity for foaming. Oxidation is promoted by the presence of oxygen at high temperatures and high aw. It was found that pure winter butter was more stable than pure butter from summer season [5]. Lipid oxidation in butter is one of the reasons for quality degradation during storage. This process is associated with the presence of free radicals that lead to the production of aldehydes responsible for the development of rancid flavors and changes in the flavour of butter [6,7]

In determining storage stability and quality of butter, the peroxide value reflecting the oxidation of fatty acids, the amount of free fatty acid and the degree of lipolysis are taken into consideration. When the amount reaches 1.8 mg KOH/g fat, there is a perceptible off-flavour in butter. In a study carried out that the relation between the amount of FFA and peroxide value against butter flavour was analyzed. Samples with FFAs exceeding 3.3 mg

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KOH/g fat were recognized as rancid or spoiled by 59 % of the panelists. An off-flavour is also perceived in butter. An off-flavour is also perceived in butter when peroxide values reach 2 meq O_2/kg fat. Interestingly, the acceptable value is set at 10 meq O_2/kg fat by the Food Regulations in Turkey [8,9].

Health protection and economic reasons have necessitated investigations aimed at enhancing the oxidation stability of lipids and lipid-containing products such as butter. There is an increasing trend towards adding suitable harmless natural antioxidants to these products and, in particular, an increasing interest in herbs and spices as sources of natural antioxidants [10,13]. A quality consistency issue may also arise since antioxidant level and composition found in plants can be affected by the time of harvesting, storage and plant species and the variety [14,15]. In spite of scientific documentation about the antioxidative effect of many spices and herbs, today it is mainly extracts from leaves of rosemary and sage that are used as antioxidative spice additives. A range of commercial products containing extracts of rosemary are available; some of the products are water dispersible, others are oil soluble and in order to exploit the synergistic effect, some of them are combined with tocopherols. The stabilization effect of the additives depends strongly on the composition of the complex lipid system and of the lipid-containing foods, as well as on the conditions of processing and storage (temperature, irradiation, partial oxygen pressure). That is why, prior to practical use in the food industry, any spice or spice extract should accordingly be tested in the actual food under realistic conditions. In experiments with foods, spices should be evaluated at concentrations that are accepted by the senses and with all interfering compounds present. It is important to mention that it is difficult to compare the antioxidant activities of herbs and spices because of lack of reference methods for comparing this activity [16,17].

In this study, effects on the stability of Turkish spices extracts such as sage, cinnamon, clove, thyme, sumac, rosemary, cumin, ginger and oregano in butter samples stored at different temperatures were evaluated.

MATERIALS AND METHODS

Sage, cinnamon, clove, thyme, sumac, rosemary, cumin, ginger and oregano spices were purchased from local markets city of Konya, Turkey. Crystalline BHA was obtained from Sigma Chemical Company (St. Louis, MO). Unsalted butter was produced in a local dairy plant in Konya, Turkey as shown in Fig. 1.

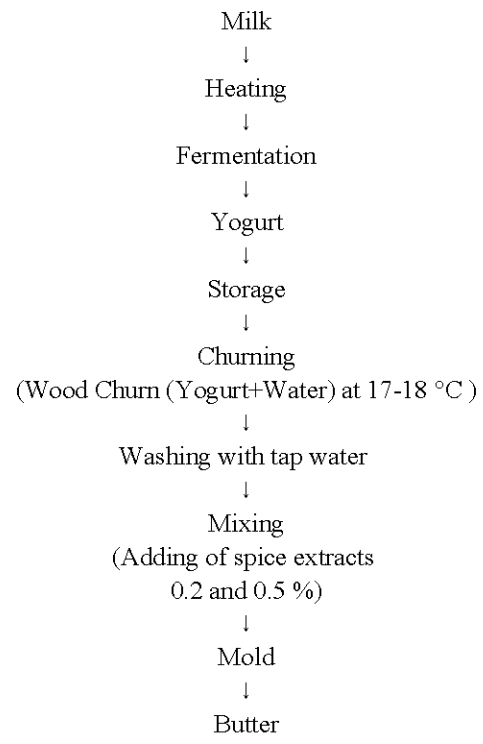

Fig. 1: The yayik butter production stages

The ethyl acetate (E. Merck, Darmstadt, Germany) extracts of spices were prepared according to the procedure of Shon *et al.* [18]. Spices were ground to a fine powder. 100 g of each ground spices samples were soaked in ethyl acetate for 24 h to obtain an extract which is easily soluble in butter. The mixture was then filtered and the filtrate was evaporated to dryness by a vacuum evaporator at 30°C.

Negative control sample were prepared each time, under the same conditions, without adding any extract and antioxidant. Spice extracts added butter samples (at 0.2% or 0.5%) (w/w) or positive control (0.01% BHA added) were placed in series of glass flasks. The flasks were stored in an incubator at 5 and 25°C, in the dark (Fig. 1). A total of 616 samples were prepared (2 replicates x 2 storage temperature x 22 treatments x 7 storage intervals). Butter samples were periodically evaluated for progression of oxidation, rancidity and acidity.

Physicochemical Analyses: The pH value of butter was determined by pH meter (pH 340i/SET 206 WTW, Weilheim, Germany). The content of milk fat (%) and non-fat solid of butter were measured according to the standard method [19]. The a_w of the butter samples was measured using a commercially available measuring

system (Model AQUALAB 3TE; Decagon Devices, Pullman, Washington). All determinations were done in triplicate.

Free Radical Scavenging Activity: The stable 1,1-diphenyl-2-picryl hydrazyl radical (DPPH) was used for determination of free radical-scavenging activity of the extracts [20]. Different concentrations of each spice extract were added, at an equal volume, to methanolic solution of DPPH (100 mikroM). After 15 min at room temperature, the absorbance was recorded at 517 nm. BHA was used as standard controls. 50% inhibition (IC_{50}) values denote the concentration of sample, which is required to scavenge 50% of DPPH free radicals. Lower absorbance of the reaction mixture indicated higher free radical scavenging activity. The IC_{50} providing of extract concentration was calculated from the plot of inhibition percentage against extract concentration. Tests were carried out in triplicate.

Peroxide Value (PV): Approximately 5 g butter was weighed into an erlenmeyer flask and dissolved in 10mL chloroform. Then, 15mL acetic acid and 1mL saturated potassium iodine (KI) were added and mixed for 1 min. The mixture was left in the dark at room temperature for 5 min. Then, distilled water (75 mL) was added and the mixture shaken vigorously. Prepared starch solution (1%, 1 mL) was added and the resulting solution titrated with 0.002 N sodium thiosulphate ($Na_2S_2O_3$) until the color became clear. The peroxide value was calculated using the formula [21]:

$$PV = [(V1-V0)\ N]/M$$

V1 is the amount of $Na_2S_2O_3$ used for titration (mL),
V0 is the amount of $Na_2S_2O_3$ used for the blank (mL),
N is the normality of $Na_2S_2O_3$ and M is the amount of sample (g).
PV is expressed as milliequivalents (meq) of active oxygen per kg of butter.

Free Fatty Acids: The FFA content was evaluated according to the method described by Atamer [4] and results were expressed as mg KOH/100g fat. About 5-10 g butter sample was weighted into an erlenmeyer flask, 30mL neutralized ethanol and few drops of phenolphthalein indicator were added and the mixture was warmed to promote dissolution. The solution was titrated with a solution of 0.1 N KOH until the pink color was stable for at least 20 s.

Thiobarbituric Acid (TBA): TBA value was determined according to a modified version of the method described by Kuruppu *et al* [22]. Butter sample (0.2-1.0 g) was weighted in a screw-capped test tube and 10 mL of a 7.5% trichloroacetic acid solution and 0.01 g BHA were added. The mixture was shaken vigorously for exactly 1 min by means of a vortex mixer (Labnet, VX-100). After that, 3 mL of 1% solution of TBA were added and the tube was placed in a boiling water bath for 40 min. After cooling, the fat was removed from the reaction mixture by shaking it with 3 mL chloroform followed by centrifugation. The optical density of the pink aqueous phase containing the reaction product was measured at 530 nm.

Sensory Testing: The sensory testing was carried out following the Weibull Hazard method, where the initial number of panelists was n_0=3 and the constant with which the number of panelists was increased for each subsequent test was n_c=1. After that the number of tasters for each period was increased by n_{c+} n_f with n_f=number of unacceptable responses for the previous test time. The interval between sensory testing was reduced by approximately ½ for the next time when failure is =50%. The panelists were recruited among students (50% male, 50% female, 18-28 years of age) and staff (50% male, 50% female, 26-45 years of age) of the Selcuk University and were required to consume butter at least once in two days. Approximately 15 g of butter sample was placed into cups that were labeled with random three digit numbers. A tray of butter samples in random order was prepared for each of the panelists approximately 30 min-1h before sensory testing. The samples were served at room temperature. Panelists were asked to taste the samples by spreading on a bread slice and to rinse their mouths with water between samples and to determine whether butter samples were acceptable or not [23].

Statistical Analysis: All analyses were run in triplicate and results reported here are the means of the three runs. The data were subjected to ANOVA using randomized complete block design with statistical analysis system-ANOVA procedure [24].

RESULTS AND DISCUSSION

Physicochemical Properties: The a_w values of butter samples were given in Table 1. Butter samples showed significant differences between the a_w values with little fluctuations but slight decreased through the end of storage period. 0.5 % extract containing samples had

Table 1: The water activity contents of extract added butter samples

	Storage Temperature			
	5°C		25°C	
	Rate of Extracts (%)			
	0.2	0.5	0.2	0.5
Sage	0.961 a	0.942 p-s	0.921 y	0.955 c-e
Cinnamon	0.954 c-f	0.948 j-l	0.942 o-r	0.937 uv
Clove	0.953 c-g	0.940 r-t	0.952 d-h	0.935 vw
Rosemary	0.952 e-h	0.942 q-s	0.958 b	0.939 s-u
Thyme	0.961 a	0.941 q-s	0.950 g-j	0.950 h-j
Sumac	0.954 c-f	0.944 n-q	0.953 c-g	0.951 f-i
Ginger	0.945 m-p	0.943 o-r	0.945 l-o	0.954 c-f
Oregano	0.949 i-k	0.948 jk	0.947 j-m	0.948 j-l
Cumin	0.955 cd	0.946 k-n	0.953 c-g	0.956 bc
Negative Control	0.944 n-q	0.944 n-q	0.953 h-j	0.953 h-j
Positive Control	0.934 w	0.934 w	0.924 x	0.924 x

* Means in every column and index without common superscript differ significantly at $p<0.01$.

Table 2: The pH contents of spice extracts added butter samples

	Storage Temperature			
	5°C		25°C	
	Rate of Extracts (%)			
	0.2	0.5	0.2	0.5
Sage	5.706 a-g	5.576 c-g	5.732 a-g	5.926 ab
Cinnamon	5.873 a-c	5.656 b-g	5.827 a-f	5.710 a-g
Clove	5.805 a-f	5.583 c-g	5.633 b-g	5.533 e-g
Rosemary	5.800 a-f	5.667 b-g	5.922 ab	5.768 a-g
Thyme	5. 877 a-c	5.795 a-f	5.705 a-g	5.991 a
Sumac	5.237 hi	5.038 i	5.540 e-g	5.989 a
Ginger	5.520 fg	5.987 a	5.755 a-g	5.807 a-f
Oregano	5.454 gh	5.558 c-g	5.792 a-f	5.632 b-g
Cumin	5.847 a-e	5.849 a-e	5.811 a-f	5.549 d-g
Negative Control	5.865 a-d	5.865 a-d	5.866 a-d	5.866 a-d
Positive Control	5.663 b-g	5.663 b-g	5.927 ab	5.927 ab

* Means in every column and index without common superscript differ significantly at $p<0.01$.

lower a_w values than the samples containing 0.2 % extract. The samples stored at 25°C showed much higher decrease in a_w than the samples stored at 5°C during storage (Table 1). The a_w values of spice extracts added butter samples stored at 5°C ranged between 0.940 (0.5% clove extract added) and 0.961 (0.5% thyme and sage extract added) and the average value was 0.951. The a_w values of samples stored at 25°C varied between 0.935 (0.5% clove extract added) and 0.958 (0.2% rosemary extract added) with the average value 0.946. BHA added butter samples showed the lowest a_w (0.925-0.935), while the negative control samples showed 0.950 (stored at 5°C) and 0.945 (stored at 25°C) a_w values. a_w values of the samples with spice extracts exhibited fluctuations which was not observed in the a_w values of negative and positive control samples. The oxidation rate of lipids strongly depends on a_w. The lower activity caused higher level of free radical concentration throughout the storage period. It was indicated that the rate of the oxidation was high at a very low water activity and decreased with the increase of this activity [25]. However, at higher water activity (usually above 0.5 a_w) the rate of oxidation increases with the increase of the water activity.

The differences between the pH values of spice extracts added butter samples were statistically significant. pH values were not stabile during storage but pH values significantly decreased through the end of storage period ($P<0.01$) (Table 2). The pH values of extract added samples stored at 5°C showed ranging between 5.038 (0.5 % sumac extract added) and 5.987 (0.5 % ginger extract added) with the average value 5.657. pH values of samples stored at 25°C ranged between 5.533 (0.5 % clove

Table 3: The non-fat solid contents of spice extracts added butter samples at the end of storage (%)

	Storage Temperature			
	5°C		25°C	
	Rate of Extracts (%)			
	0.2	0.5	0.2	0.5
Sage	1.57 bc	0.60 n-q	1.47 b-d	1.99 a
Cinnamon	1.64 b	1.56 bc	1.20 d-g	1.52 bc
Clove	1.20 d-g	1.11 f-i	0.99 g-k	0.97 g-l
Rosemary	1.13 f-i	1.42 b-e	1.06 f-j	1.15 e-h
Thyme	0.79 j-p	0.79 j-p	0.36 q	0.79 j-p
Sumac	0.71 k-p	0.84 i-o	0.99 g-k	0.78 j-p
Ginger	0.69 l-p	0.65 m-p	0.53 pq	0.96 g-l
Oregano	0.59 n-q	0.84 i-o	0.69 l-p	0.94 g-m
Cumin	0.94 g-m	1.06 f-j	1.33 c-f	0.98 g-l
Negative Control	0.58 o-q	0.58 o-q	0.54 pq	0.54 pq
Positive Control	0.99 g-l	0.99 g-l	0.96 g-l	0.96 g-l

* Means in every column and index without common superscript differ significantly at $p<0.01$.

Table 4: The average peroxide values determined in butter samples during storage (meq o_2/kg fat) and IC_{50} values of spices extracts (μg/ml)

		Storage Temperature			
		5°C		25°C	
		Rate of Extracts (%)			
	IC_{50}	0.2	0.5	0.2	0.5
Sage	51.60	4.08 i-n	1.78 o	26.31 d	34.08 a
Cinnamon	53.84	4.83 i-k	3.58 j-o	3.97 i-n	3.95 i-n
Clove	11.94	11.39 g	14.37 f	3.66 j-o	2.34 no
Rosemary	14.56	21.81 e	20.34 e	3.41 j-o	3.11 k-o
Thyme	13.27	5.11 ij	2.76 l-o	8.80 h	1.78 o
Sumac	19.17	4.21 i-n	2.92 k-o	11.25 g	3.61 j-o
Ginger	16.89	3.55 j-o	2.29 no	4.48 i-m	4.59 i-l
Oregano	26.28	5.64 i	32.33 b	29.24 c	10.68 g
Cumin	15.55	3.46 j-o	2.50 m-o	5.74 i	3.39 j-o
Negative Control	--	4.38 i-m	4.38 i-m	11.53 g	11.53 g
Positive Control	--	2.37 no	2.37 no	3.39 j-o	3.39 j-o

* Means in every column and index without common superscript differ significantly at $p<0.01$.

extract added) and 5.991 (0.2 % oregano extract added) with an average value 5.725. pH values of negative and positive control samples were 5.750 and 5.980, respectively, when the samples stored at 5°C and these values were 5.560 and 5.660, respectively, when the samples stored at 25°C. There were not a significant correlation between oxidation degree and a_w as well as between pH values. The washing process or water used for washing may cause these differences in pH.

The non-fat dry matter content is 1.2-1.5 % on average in standard butter production. If butter produced by churning is washed, the content is even significantly below 1 %. From a nutritional point of view the non-fat dry mass is of little importance, although it can have a major impact in bacteriological and sensory terms. Therefore in order to avoid detrimental changes in butter products, care must be taken to ensure good distribution of the aqueous phase, with the droplet size not exceeding 10 Micrometer. It is well known that homogeny dissolution of non-fat solids and water molecules in butter is not possible. Similar changes to milk fat content were also obtained for non-fat solids of butter samples. 0.2 % thyme extract added butter sample showed the lowest (0.36 %), 0.5 % sage extract added sample showed the highest (1.99 %) non-fat solid content. Negative control sample had non-fat solid as 0.58 % at 5°C and 0.54 % at 25°C. Positive control sample had 0.96 % at 5°C and 0.99 % at 25°C of non-fat dry matter (Table 3). It was reported that the whey amounts of butter from cow's which were fed up with different feeds ranged between 1.42 % and 2.28 % [26]. Non-fat solids are one of the important constituents of butter, which affect its quality and storage stability. Butter, which contains high levels of non-fat solids, has lower storage stability and shelf life, since high content of non-fat solid stimulates both microbiological and chemical deterioration [1,4].

Table 5: The average TBA values determined in butter samples during storage (malonaldehyde equivalent/g fat)

	Storage Temperature			
	5°C		25°C	
	Rate of Extracts (%)			
	0.2	0.5	0.2	0.5
Sage	0.216	0.137	0.323	0.535
Cinnamon	0.260	0.119	0.324	0.559
Clove	0.552	0.415	0.221	0.297
Rosemary	0.488	0.347	0.188	0.154
Thyme	0.306	0.272	0.147	0.548
Sumac	0.241	0.141	0.297	0.387
Ginger	0.231	0.185	0.423	0.744
Oregano	0.507	0.662	0.238	0.206
Cumin	0.200	0.174	0.131	0.205
Negative Control	0.232	0.232	0.284	0.284
Positive Control	0.201	0.201	0.217	0.217

* Means in every column and index without common superscript differ significantly at $p<0.01$.

Oxidation Quality: The average PV of butter samples are given in Table 5 as meq O_2 /kg fat. PV of butter samples increased throughout the storage period. The increase in PV of butter samples stored at 5°C was less than those stored at 25°C. Storage temperature was significantly effective on PV of butter samples ($P<0.01$). It was reported that PV of ethanol extract of clove added butter cake samples increased from 0.56 to 15.45 meq O_2/kg fat after 4 weeks of storage at 27 °C [27]. In another study on butter, PV of control sample increased from 0.00 to 11.00 meq O_2/kg, PV of the butter samples containing, phenolics (gallic acid) extracted from spices, increased from 0.00 to 5.10 meq O_2/kg after 84 days storage at 50°C [28]. It was found that PV content in yayik butter was higher than that of milk butter and higher storage temperature increased PV content [2].

Generally, PV of butters samples with 0.5 % spice extracts were less than that of the negative control, except for those containing oregano, clove and rosemary extracts. Ginger extracts showed prooxidant effect at % 0.5 concentration and at 25°C storage. The clove and rosemary spice extracts at 0.2% concentration and clove and oregano at 0.5% concentration showed prooxidant effect at 5°C (Table 4). It was reported that very high doses of antioxidants can lead to pro-oxidant effects. There are many reports describing that polyphenols act as pro-oxidants in the presence of metal ions [29]. It was also reported that some soluble plant phenolics can have pro-oxidant activities under certain conditions. The pro-oxidant activity of green tea extracts has been demonstrated in the presence of metal ions [30]. Additionally, gallic acid is well known as an antioxidant, even though its activity as a pro-oxidant has been reported as well. Gallic acid compounds also showed prooxidant effect by stimulating the copper-dependent oxidation of low density lipoprotein. These prooxidant effects of gallate compounds correlated with the copper reducing activity [31].

The extracts obtained by extraction were screened for their possible antioxidant activity by DPPH free radical-scavenging test system. Free radical-scavenging capacities of the corresponding extracts measured by DPPH assay are show in Table 4. The highest radical scavenging activity was showed by BHA. The radical scavenging activity in the spice extracts was determined in the following order: Clove> Thyme> Rosemary> Cumin> Ginger> Sumac> Oregano> Sage> Cinnamon. The antioxidant effect of clove, thyme, rosemary, ginger and sumac was higher than that of other spice extracts according to IC_{50} data.

During the entire 120 days of storage, 0.5 % levels of sage followed by ginger, cumin, thyme and sumac extracts were the most effective on retarding oxidation at 5 °C. The butter samples containing 0.5 % levels of thyme, clove, rosemary and sumac extracts had lower PV than the other samples at 25 °C. Sage and ginger extracts for 0.5 % concentration at 5 °C, thyme, clove and rosemary extracts at 25 °C exhibited better antioxidant effect than BHA (Table 4). 0.5% ginger extract exhibited the same antioxidative effect as 0.01% BHA added sample at 5 °C; while 0.5% sumac and cumin extracts and 0.2 % rosemary and clove extracts exhibited the same affect at 25 °C. The IC50 value of these spices extracts also lower as shown in Table 4. Several research groups have determined antioxidant and protective effects of sage, sumac, cumin, clove and oregano and their extracts on fats and oils [32-34].

Table 6: The average FFA values determined in butter samples during storage (mg KOH/100g fat)

	Storage Temperature			
	5°C		25°C	
	Rate of Extracts (%)			
	0.2	0.5	0.2	0.5
Sage	2.491 i-m	1.718 o-r	2.353 k-n	3.421
Cinnamon	2.383 j-n	1.647 p-r	8.032 a	2.981 f-i
Clove	4.494 c-e	2.492 i-m	2.621 h-l	1.955 n-r
Rosemary	3.565 cd	3.061 e-h	2.367 k-n	1.637 p-r
Thyme	2.118 l-p	1.769 o-r	2.062 m-p	7.268 b
Sumac	1.516 qr	1.644 p-r	3.196 d-g	2.847 g-k
Ginger	2.948 f-i	7.019 b	2.883 g-j	2.791 g-k
Oregano	1.980 n-q	1.729 o-r	3.167 d-g	3.784 c
Cumin	2.182 l-o	1.448 r	1.724 o-r	1.931 n-r
Negative Control	1.931 n-r	1.931 n-r	3.716 c	3.716 c
Positive Control	1.821 o-r	1.821 o-r	2.514 i-m	2.514 i-m

* Means in every column and index without common superscript differ significantly at $p<0.01$.

It was investigated the antioxidant effects of essential oils and methanolic extracts of different spices in sunflower oil stored at 70°C. Sumac, rosemary and sage showed the most antioxidant effect. It appears that a relationship exists between the antioxidant effect and the chemical composition of tested spices [35]. In a study, the results showed that the extract of yellow sweet clover, which contains the highest amount of flavonoid and phenolic compounds, exhibited the greatest antioxidant activity [36]. Antioxidant properties of ethyl acetate extract against mutagens were related to their phenols and flavonoids which are heat stable and lose digestive juices are relatively low [18]. It was reported that the effectiveness of the various essential oils on linoleic acid oxidation was in the following descending order: caraway>sage>cumin> rosemary> thyme> clove [37]. Sage, rosemary, oregano, thyme and sumac exhibited a high antioxidant effect in sunflower oil stored at 50°C [10].

The permissible PV limit is 10 meq O_2/kg for butter. Shelf-life values were based on the permissible limit of 10 meq O_2/kg. Shelf-life for 0.5 % oregano extracts added butter samples at 5 °C and 0.5% sage extract added samples at 25°C were 14 days. Shelf-life of 0.2 % sage at 25°C, clove, rosemary added butter samples at 5°C and 0.5 % rosemary, oregano extracts added butter samples at 5°C were 60 day. Shelf-life of 0.2 % cinnamon, sage, oregano extracts added butter samples days at 5°C and thyme and sumac at 25°C were 120. Shelf-life of other butter samples was higher than 120 days and 90 days for negative control.

Malonaldehyde and TBA reactive substances are produced as a result of oxidation of polyunsaturated fatty acids. TBA values of treated butter samples are shown in Table 5. TBA values of 0.5 % spice extracts added butter samples at 5°C were generally lower than that of the negative control sample and similar to that positive control. The lowest TBA value was also determined for the samples containing 0.5 % sumac, cinnamon and sage extracts at 5°C and cumin, rosemary, clove at 25°C. The TBA value was significantly ($P<0.01$) increased from 30 days to 120 days. The TBA values of samples stored at 5°C were generally lower than those stored at 25°C. It was determined that the extracts of rosemary extract prepared in different solvents showed lower TBA values than that of control and similar to BHA and BHT[38]. The stabilization of meat lipids with ground spices was investigated. Significant inhibition of TBA reactive substances was observed for rosemary, clove, sage and oregano [39]. In a another study, TBA values of butter samples containing methanol extracts of clove increased from 0.18 to 0.81 mg malonaldehyde/g fat at 27°C after 4 weeks storage. BHA added samples had TBA values increased from 0.21 to 1.62 mg malonaldehyde/g fat. Phenolic compound (gallic acid) added samples had TBA values increasing from 0.31 to 1.41 mg malonaldehyde/g fat, whereas control sample had TBA values increasing from 0.31 to 2.35 mg malonaldehyde/g fat [28]. It was found that TBA content in yayik butter was higher than that of milk butter and higher storage temperature increased TBA content [2].

Lipolysis Quality (FFA Value): FFA value of butter samples is given in Table 6. FFA content in butter samples increased throughout the storage period at both 5 and 25°C. FFA value of the negative control sample was the most increased during storage at both temperatures. FFA value of butter stored at 5°C increased less than that of stored at 25°C ($P<0.01$). It was evaluated the effect of

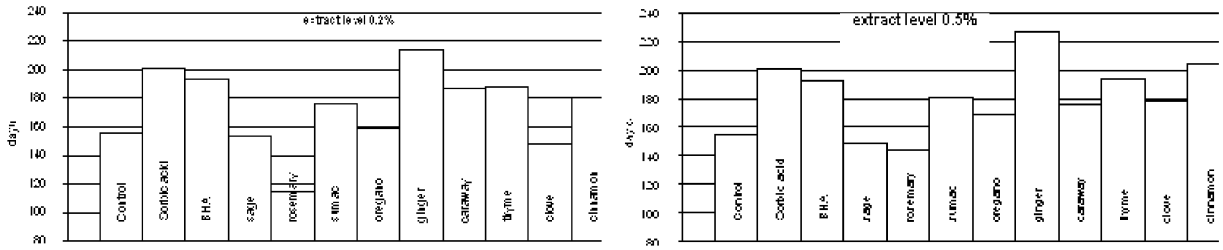

Fig. 2: Shelf-life of yayik butter with spice extracts stored in refrigerator temperature (5°C)

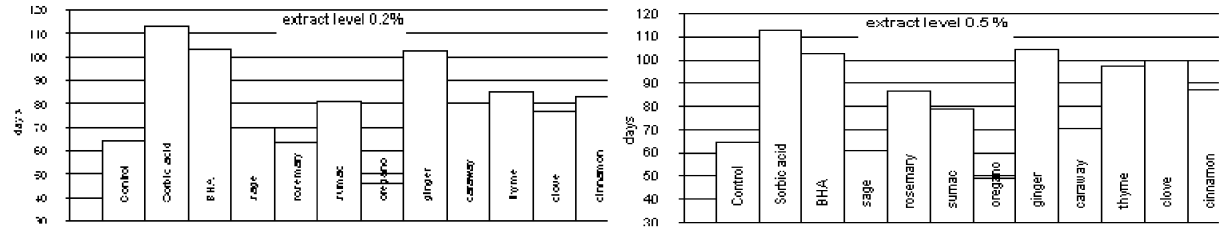

Fig. 3: Shelf-life of yayik butter with spice extracts stored in room temperature (25°C)

storage temperature on the increase of FFA. It was observed that the more high temperature given rise to the more FFA value in butters samples [11,40]. Increase of FFA in 0.5 % extract added butter samples was less than that with 0.2% extract, generally.

FFA of sumac extract added butter (1.516-1644 mg KOH/ l00g fat) at 5°C and 0.5% rosemary extract added butter (1.637 mg KOH/l00g fat) at 25°C were the lowest. FFA value in butter treated with sumac, oregano and thyme extracts at 5°C and cumin, ginger, rosemary, sage, thyme and clove extracts at 25°C was significantly lower than that of the negative control sample. Significant inhibitory properties were reported for cinnamon, cloves, sumac, thyme, oregano, rosemary and sage spices, theirs extracts and essential oils. Prevention of formation of FFA may be due to the antimicrobial effect of herb extracts [41,42].

Sensorial Quality: Weibull's distribution proved to be an adequate model to predict shelf-life of yayik butter using sensory techniques. Ginger, thyme and cinnamon extracts increased the shelf life of yayik butter which is comparable to BHA. The use of these spice extracts imparted an acceptable odour and taste to the product. 0.5% level of the extracts in increasing the shelf life of yayik butter was more effective than 0.2% level of the extracts. The shelf-life of the samples stored in the refrigerator was approximately two fold longer than the samples stored at room temperature according to the results of sensory analysis (Fig.2 and Fig. 3).

CONCLUSIONS

The results of this study show that extracts of clove, sumac, thyme, cumin and ginger in ethyl acetate exert a significant effect on the stability of butter, especially at 0.5 % level. Sage and ginger extracts was the most effective antioxidant. The increasing storage temperature decreased storage stability of butter samples. Rosemary, clove and oregano extracts at 5°C, or sage extract at 25°C showed a prooxidant effect in butter during storage stored. Thus, natural spice extracts and their combinations such as clove, sumac, thyme, cumin and ginger might be used to enhance the storage stability of butter.

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