Efficiency of Antioxidants from Natural Sources in Bakery Products

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ABSTRACT

A soda cracker biscuit was processed using a fine powder of marjoram, spearmint, peppermint and basil, and their purified ether extracts as natural antioxidants.

Addition of purified ether extract of each of the four plant materials gave an excellent antioxidant effect on the biscuit compared with the effect of BHA at concentrations of 0.01, 0.02, and 0.03%.

Addition of a fine powder of all plant materials at 0.5% gave an antioxidant effect on the biscuit, compared to the control sample.

Addition of a 1% mixture of equal amounts of the four plant powders caused a pro-oxidant effect in the biscuit.

INTRODUCTION

The onset of rancidity in baked goods follows quite a different pattern from that of fat alone. The keeping quality of crackers and cookies is of great economic importance since these products are often stored for extended periods before they are consumed, and they are not protected from oxidation.

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Numerous compounds have been developed synthetically and may be added to fats to inhibit oxidation. Many of these compounds have been patented as antioxidants. Some that have been tried include the o- and p-dihydroxy benzenes, such as hydroquinone, and pyrogallol, the aromatic amines, glutamine, legumes and cereal flours. Sometimes antioxidants show a synergistic effect; an example is a solution for protection of nuts, and composed of 14% butylated hydroxy anisole, 6% propyl gallate and 3% citric acid in ethyl alcohol. A small amount is used in nut candy (Stuckey, 1954; Meyer, 1978).

The use of petroleum extracts of sage, nutmeg, rosemary, clove, cardamon, white pepper, black pepper, mace and marjoram as natural antioxidants was reported by Lotter (1971). It is considered that rosemary flavonoids had synergistic effects but no primary antioxidative properties. Also, alkaline and acidic extracts of thyme, marjoram and oregano have been used as natural antioxidants in lard (Anon, 1985).

This work was carried out to study the effects of some plant materials and their extracts on the stability of fat in soda cracker biscuits.

MATERIALS AND METHODS

Materials

Plant materials (herbs)

The plants marjoram (*Majorana hortensis*), spearmint (*Mentha viridis*), peppermint (*Mentha piperita*) and basil (*Ocimum basilicum*) were air-dried and knocked to isolate the leaves and the flowering top from the herbs (plant materials). Then the leaves and flowering tops were ground to a fine powder.

Butylated hydroxyanisole

Butylated hydroxyanisole (BHA), a synthetic antioxidant (purity 99.9% using GLC), was obtained from the Naarden International Company in Holland.

Active dry yeast

Active dry yeast was obtained from S.I. Lesaffre Co. Paris, France, under the commercial name 'Saf-Lavure'.

Flour

French flour (72% extraction) used for soda cracker biscuit and Commercial Soft Australian wheat flour (72% extraction) used for pan bread and toasted bread were obtained from Bisco Misr Company (Cairo Factory).

Shortening

Hydrogenated vegetable oil was obtained from the Misr Co. For Oil and Soap, Zagazig Factory.

Commercial glucose syrup

Commercial glucose syrup (hard candy type) was obtained from the Egyptian Co. for Starch and Glucose, Musturod, Cairo. Its specification was according to the Egyptian standard of glucose No. 359/1970.

Skimmed milk powder

Skimmed milk powder obtained from Bisco Misr Co., Cairo Factory was used in the production of biscuit.

Malt flour

This was obtained from El-Ahram Beverage Co., El-Dokki, Giza.

Methods

Preparation of purified ether extracts

One hundred grams of the plant materials (fine powder) were extracted with 240 ml of diethyl ether under reflux for 2 h. The mixture was filtered and the residue was extracted again with fresh solvent. The combined filtrates were freed of solvent. The crude ether extract was washed with 100 ml of cold water several times and then with 100 ml water at 80°C several times. It was then dissolved in methanol and bleached with active carbon by stirring at 60° C for 15 min. Up to 20% by weight (of the crude ether extract) of carbon was used. The bleached solution was freed of solvent and the product was a fine white powder (Chang *et al.*, 1977).

Preparation of soda cracker biscuit

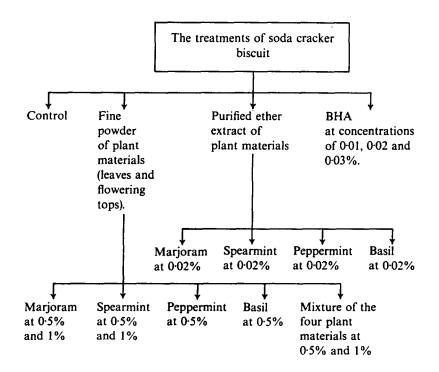
The method described by Smith (1972) for preparing soda cracker biscuit was used with a simple modification in the recipe to adapt dough for the present hard biscuit lines of Bisco Misr Co. (Cairo Factory). As indicated in Table 1, fine powders of the marjoram, spearmint, peppermint, basil and the mixture of all four plants were added at concentrations of 0.5% and 1% by weight of the dough. Also added were 0.02% of the purified ether extracts of marjoram, spearmint, peppermint and basil by weight of shortening (0.001 434% of dough 'total mix'). Butylated hydroxyanisole (BHA) concentrations of 0.01%, 0.02% and 0.03% by weight of shortening (0.000 717%, 0.001 434% and 0.002 151% of dough 'total mix') were also used as antioxidants.

Ingredients	Mass (kg)	Instructions		
Active dry yeast	0.67	Yeast suspension		
Water (26.7°C)	9-07			
Flour	136-08	ſ		
Shortening	15.88	Mix. for 10–20 min. to		
Commercial glucose		a stiff dough,		
Syrup (hard candy type)	6.334	ferment to 12–14 h		
Skimmed milk powder ^a	6.834	at 27.8°C. Dough		
Sodium chloride ^a	3.25	temperature should b		
Malt flour ^a	1.367	26·7°C		
Cream of tartar	0.15	l		
Water (32·2°C)	36.67			
After fermentation				
Ammonium bicarbonate ^a	4.767			
Sodium metabisulfite ^a	0.133			
Sodium bicarbonate	0.285			

 TABLE 1

 Recipe for Preparing Soda Cracker Biscuit

^a Modified.



All samples were shaped, cut and baked at the hard biscuit lines of Bisco Misr Co. After baking all treatments were packaged in cellophane nitrocellulose film.

Peroxide value

The crude fat was extracted from soda cracker biscuits every 2 weeks as follows.

A hundred grams of crushed soda cracker biscuit was placed in a closed flask, 200 ml of diethyl ether was added to the biscuit, the flask was shaken for 1 h, then filtered. The solvent was evaporated at 50°C. The peroxide value of the fat was determined according to the procedure described in the AOCS (1964).

RESULTS AND DISCUSSION

The soda cracker biscuit was processed and stored at room temperature for 135 days. At intervals of 15 days the hydrogenated vegetable oil was extracted from the biscuit and analyzed for peroxide value to evaluate efficiencies of the additives as antioxidants. The obtained results are shown in Tables 2, 3 and 4.

 TABLE 2

 Effect of BHA and Purified Ether Extracts of the Plant Materials on the Peroxide Value of Shortening of Soda Cracker Biscuit during Storage at Room Temperature

Storage Co period (days)	Control	BHA			Purified ether extracts of the plants			
	-	0.01%	0.02%	0.03%	Marjoram 0·02%	Spear- mint 0 [.] 02%	Pepper- mint 0 [.] 02%	Basil 0∙02%
0	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15
15	2.98	2.69	2.55	2.45	2.32	2·19	2.22	2.40
30	3.97	2.83	2.69	2.65	2.50	2.30	2.34	2.58
45	6.73	5.59	3.59	2.92	2.70	2.42	2.48	2.78
60	7.68	7.33	4.44	2.99	2.74	2.60	2.68	3.04
75	5.04	5.35	3.95	3.29	3.15	3.04	3.09	3.23
90	4.06	7.20	3.33	2.60	4.15	3.82	3.90	5.23
105	4.34	1.64	1.56	1.46	6.83	6.05	6.16	7.91
120	4·73	1.45	1.49	1.32	4.30	4.28	2.28	5.62
135	5.71	1.32	1.21	1.12	1.55	1.32	1.49	1.56

BHA: butylated hydroxyanisole.

Plant materials: ground leaves and flowering tops.

S. S. Bassiouny et al.

Storage period (days)	Plant powder						
	Control	Marjoram 0∙5%	Spear- mint 0·5%	Pepper- mint 0·5%	Basil 0·5%	Mixture of the four plants 0.5%	
0	2.15	2.15	2.15	2.15	2.15	2.15	
15	2.98	3.73	3.91	3.16	3.17	3.14	
30	3.97	3.98	3.53	4.21	3.61	3.62	
45	6.73	4.66	3.64	4.64	4.59	5.64	
60	7.68	4.96	4.90	5.38	5.11	6.04	
75	5.04	6.17	6.70	7.11	6.20	6.87	
90	4.06	7.57	7.25	7.74	7·79	7.39	
105	4.34	6.40	6.30	7.50	6.98	6.79	
120	4.73	5.57	5.69	6.34	5.90	6-53	
135	5.71	4.27	4·39	5.66	4.92	6.12	

TABLE 3
Effect of 0.5% Plant Materials Powder on Peroxide Value of Shortening of Soda Cracker
Biscuit during Storage at Room Temperature

Plant materials: ground leaves and flowering tops.

TABLE 4 Effect of 1% Plant Material on Peroxide Value of Shortening of Soda Cracker Biscuit during Storage at Room Temperature

Storage period (days)	Control	Plant material powder				
		Marjoram 1%	Spearmint 1%	Mixture of the four plant materials 1%		
0	2.15	2.15	2.15	2.15		
15	2.98	3.16	3.08	5.81		
30	3.97	4.51	5-93	6.09		
45	6-73	4.65	6.41	6.72		
60	7.68	6.47	7.46	8·30		
75	5.04	7.73	7.60	9.61		
90	4.06	9.87	8.34	10.58		
105	4.34	7.49	7.22	10.09		
120	4·73	6.60	6.99	11.92		
135	5.71	5.32	5.02	12.33		

Plant materials: ground leaves and flowering tops.

From the results in Table 2, it is observed that peroxide value for the soda cracker biscuit control sample increased from 2.15 to 7.68 (meq/kg fat) after storage for 60 days, then it decreased to 4.06 after storage for 90 days and increased again until the end of storage where it reached 5.71 meq/kg fat (hydrogenated vegetable oil).

Peroxide values for samples which contained BHA at percentages of 0.01 and 0.02% increased from 2.15 to 7.33 and 4.44 after storage for 60 days while samples which contained 0.03% BHA increased from 2.15 to 3.29 after storage for 75 days. Then they decreased to 1.32, 1.21 and 1.12, respectively, at the end of the storage.

Peroxide values for samples which contained purified ether extracts of the plants of marjoram, spearmint, peppermint and basil at 0.02%, were determined. The values increased from 2.15 to 6.83, 6.16 and 7.91 for marjoram, peppermint and basil, respectively, after storage for 105 days; then they decreased to 1.55, 1.49 and 1.56, respectively, at the end of the storage. On the other hand, the peroxide value of spearmint increased from 2.15 to 6.28 after storage for 120 days then it decreased to 1.32 at the end of storage.

From the results in Table 3, it can be seen that peroxide values for samples which contained 0.5% marjoram, spearmint, peppermint, basil and the mixture of the four plant materials after storage for 90 days increased from 2.15 to 7.57, 7.25, 7.74, 7.79 and 7.39, respectively; then they decreased at the end of the storage period to 4.27, 4.29, 5.66, 4.92 and 6.12, respectively.

Table 4 shows that addition of 1% marjoram and spearmint powder increased the peroxide value from 2.15 to 9.87 and 8.34 after 90 days; then it continuously decreased until it reached 5.32 and 5.02 at the end of the storage period. Results also showed that addition of 1% mixture of the four plant materials increased the peroxide value of the soda cracker biscuit from 2.15 until it reached a value of 12.33 at the end of the storage period.

Finally from the above results it was concluded that:

- (1) Addition of a purified ether extract of the four plant materials gave an excellent antioxidant effect on the soda cracker biscuit compared with the effect of BHA at 0.01, 0.02 and 0.03%.
- (2) Addition of either BHA or purified ether extracts of all plant materials prevents the accumulation of peroxides after decomposition. This behaviour indicates that the presence of synthetic or natural antioxidants slowed down the rate of peroxide formation since, in all cases, peroxide values after 135 days of all samples which contained synthetic or natural antioxidants at any given concentration were much lower than that of the control sample.
- (3) The low efficiency of BHA at concentrations of 0.01, 0.02 and 0.03%

could be due to the volatilization or decomposition of antioxidants during processing of soda cracker biscuits as was reported by Mohan and Chapman (1954), Dugan and Kraybill (1956), Micha *et al.* (1975), Lin *et al.* (1981), Augustin and Berry (1983), Abd-el-Azim (1985) and Warner *et al.* (1986). The high efficiency of the purified ether extracts of the four plant materials could be due to the stability of these natural antioxidants during heating.

- (4) Addition of all samples of plant materials powder at 0.5% gave an antioxidant effect on the soda cracker biscuit, compared with the control sample.
- (5) Addition of 1% marjoram and spearmint powder gave an antioxidant effect. The efficiency of the powders at concentrations of 1% were lower than at 0.5%.
- (6) Addition of 1% mixtures of equal amounts of the four plant powders gave a pro-oxidant effect on the soda cracker biscuit and the rate of peroxide formation increased.
- (7) Considering the results of organoleptic evaluation in a previous study (Sohair El-Kayati, 1987) it could be concluded that purified ether extracts at concentrations of 0.02% may replace the synthetic antioxidant, since these extracts had no effect on the organoleptic properties of the present biscuit.
- (8) A new type of biscuit could be produced by adding 0.5% marjoram powder. This additive improved the taste and odour (Sohair El-Kayati, 1987), and extended the shelf life of the new product.

An economic study should be conducted to determine the gain from this practice.

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REFERENCES

- Abde-el-Azim, N. A. A. (1985). Effect of added antioxidants on the quality characteristic of biscuit. MSc Thesis, Faculty of Agriculture, Cairo University, Egypt.
- Anon. (1985). Extraction of antioxidants from spices. House Food Industrial Co., Ltd. Kokia, Tokyo, Japan; CF Chem. Abs. (1985) 102, 23215.

- AOCS. (1964). Official and Tentative Methods of the American Oil Chemists Society (2nd edn). The American Oil Chemist's Society, Chicago, IL.
- Augustin, M. A. & Berry, S. K. (1983). Efficiency of the antioxidants BHA and BHT in palm olein during heating and frying. J. Am. Oil Chem. Society, 60, 1520.
- Chang, T.; Matijasevic, B. O.; Hsieh, O. & Huang, C. (1977). Natural antioxidants from rosemary and sage. J. Food Sci., 42, 1102.
- Dugan, L. R. & Kraybill, H. R. (1956). Tocopherols as carry-through antioxidants, J. Am. Oil Chem. Society, 33, 527.
- Lin, F. S., Warner, C. R. & Fazio, T. (1981). Alteration of phenolic antioxidants in heated vegetable Oil. J. Am. Oil Chem. Society, 58, 789.
- Lotter, G. (1971). Antioxidant effect of spice extracts and their constituents in lard. Ludwig Maximillian Univ., Munich, FRG, 148 pp. CF Food Sci. & Tech. Abst., 8(377) (1972).
- Meyer, L. H. (1978). Flavor changes in fat and oils. In Food Chemistry. AVI, Westport, CT.
- Micha, P., Tamar, B. & Arich, L. (1975). Effect of water and BHT on stability of cottonseed oil during frying. J. Sci. Food Agric., 26, 1655.
- Mohan, J. H. & Chapman, R. A. (1954). Behavior of antioxidants during the baking and storage of pie crust. J. Am. Oil Chem. Society, 31, 108.
- Smith, W. A. (1972). *Biscuits, Crackers and Cookies. Vol. 1.* Applied Science Publishers, London, p. 75.
- Sohair El-Kayati. (1987). Studies on essential oils. PhD Thesis, Faculty of Agriculture, Zagazig University, Zagazig, Egypt.
- Stuckey, B. N. (1954). Antioxidants in candy and candy packaging materials. Mfg Confectioner, 34, 47. CF Chem. Abs., 50 (1956) 8936.
- Warner, C. R., Daniels, D. H., Lin, F. S. D., Joe, F. L. & Fazio, T. (1986). Fate of antioxidants and antioxidant-derived products in deep-fat frying and cookie baking. J. Agric. Food Chem., 34, 1.