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Suitability of antioxygenic salts for stabilization of fried snacks

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Fried potato chips, banana chips and fried Bengalgram (*Cicer arietinum*) dhal were treated with antioxygenic salts containing butylated hydroxyanisole (BHA), butylated hydroxytoluene and tertiary butylated hydroquinone (TBHQ), and stored at 37°C in polypropylene packs. Treatment with antioxygenic salts considerably retarded the rate of autoxidation of fats in the fried products, as indicated by changes in peroxide value, overall acceptability and concentration of total steam-volatile carbonyls. Maximum protection was provided by the antioxygenic salt containing TBHQ and minimum protection by the BHA-salt. During storage, the concentrations of all the carbonyls increased, but increases in the concentrations of pentanal, hexanal, heptanal, hexenal, heptenal, octenal and 2,4-decadienal were largest. Concentrations of antioxidants in antioxygenic salts also tended to decrease during storage. © 1997 Published by Elsevier Science Ltd

INTRODUCTION

Fried products are popular as snack foods. These are prepared from a variety of raw materials and vary in size, shape and composition, but all are prepared by deep fat frying in vegetable oils and have relatively large proportions of fat/oil. They have a very low moisture content and can therefore be stored under ambient conditions. Off-flavour and rancidity resulting from fat peroxidation is the major cause of spoilage in these products. Because of their high volatility, incorporation of antioxidants in oils has not proved very effective, but sprinkling of antioxygenic salts after frying and use of antioxidant-treated packaging materials have given encouraging results (Henderson *et al.*, 1960; Smith, 1967; Sharma *et al.*, 1992). Efficacy of antioxygenic salts is expected to be governed by a number of factors, such as nature and concentration of antioxidant, nature of the fried products and adhesion characteristics of the salt. The present paper reports the effect of three antioxygenic salt preparations, previously developed in the laboratory, on the storage stability of potato chips, banana chips and fried Bengalgram dhal, vis-à-vis stability of antioxidants in the salt composition during storage. Carbonyls and pyrazines have been reported to be the major volatile compounds in potato chips and are known to influence the flavour of the chips (Deck *et al.*, 1973; Buttery & Ling, 1972; Mukherjee *et al.*, 1965). In the present study, an attempt has been made to quantitatively measure the changes in carbonyl composition of potato chips both with and without antioxygenic salt treatments.

MATERIALS AND METHODS

Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tertiary butylated hydroquinone (TBHQ) were procured from reputed suppliers. All other chemicals were of analytical reagent grade. Chloroform and n-hexane were refluxed with 2,4-dinitrophenylhydrazine (DNPH) and hydrochloric acid for 4 h and distilled to make them carbonyl-free before use. Good-quality table salt was procured from the market. Antioxygenic salts were prepared by dissolving known quantities of antioxidants and citric acid in distilled ethanol and coating the alcoholic solution over salt in a rotary vacuum evaporator as described previously (Sharma *et al.*, 1991). Antioxygenic salts were packed in polypropylene (PP) (75 μm) packs of 25 g lots and stored at room temperature (15–34°C) and 37°C.

Preparation of fried chips

Commercially available good-quality potatoes were washed, peeled and sliced. The potato chips were dipped in water containing 500 ppm sodium metabisulphite for 20 min and then fried in refined sunflower oil (Sundrop;

I.T.C., Calcutta) in an aluminium frying pan. During the frying operation, the potato chips (0.5 kg) were added to the sunflower oil (2 kg) at 200°C. Immediately after the chips had been added, the temperature dropped to about 150°C and slowly increased to 180°C, when the chips were removed. Fried chips had fat and moisture contents of 40% and 3%, respectively.

Fried chips were divided into four equal lots. One lot was sprinkled with the table salt while the other three lots were sprinkled with antioxygenic salts containing BHA, BHT and TBHQ, respectively, at a level of 2% salt on the basis of weight of chips. During sprinkling the chips were mixed thoroughly in a stainless steel vessel and packed in PP (75 μm) packs in 100 g lots for storage studies and analysis. Similarly, chips were prepared from banana (*Muse paradasiaca*, the Indian variety 'Nendran').

Preparation of fried Bengalgram dhal

Dehusked Bengalgram dhal (5 kg) was soaked in 10 litres of distilled water and left for 2 h. Excess water was decanted and Bengalgram dhal was fried at 180°C to a moisture level of < 3% and sprinkled with salt, both with and without antioxidants as indicated above.

Analysis

Peroxide value, moisture, petroleum ether-extractable fat in potato chips, banana chips and fried Bengalgram dhal were determined by AOCS methods (AOCS, 1973). For determining the concentration of antioxidant in the salt, 0.5 g samples were extracted with 10 ml of acetonitrile and the extract was filtered through a 0.5 μm PTFE filter. The filtrate (20 μl) was directly injected into the high-performance liquid chromatography (HPLC) system comprising a Shimadzu LC-6A chromatograph fitted with an RP-18 column (5 mm i.d. × 300 mm).

The antioxidants were eluted with methanol–water (90:10) and the concentrations of BHA, BHT and TBHQ were monitored by measuring absorbance at 280, 292 and 293 nm, respectively; the concentrations of antioxidants were calculated from the areas under the respective curves.

Sensory evaluation

Initially and after every month of storage, the fried snacks were given to a panel of ten trained judges for quality evaluation. Taste, colour, flavour, texture and overall acceptability were graded on a 9-point hedonic scale, with 9 for excellent and 1 for highly disliked.

Isolation of carbonyls

Potato chips (50 g) were steam-distilled in an all-glass distillation apparatus and the distillate was passed through 2,4-DNPH solution (0.1%) in 2 N hydrochloric acid. The reaction mixture was kept overnight at room temperature (15–34°C). The precipitate was filtered and the filtrate extracted with carbonyl-free chloroform (200 ml). The chloroform extract was washed repeatedly with 0.1 N hydrochloric acid and water, evaporated to dryness and mixed with the precipitated 2,4-DNPHs.

Separation of DNPHs by thin-layer chromatography (TLC)

DHPHs were dissolved in $CHCl_3$ and 100 μl of the solution was applied in the form of a band on a MgO–Celite (3:1) plate dried at room temperature and subsequently activated at 80°C for 1 h. The plate was developed in benzene–petroleum ether (60–80°C) (60:40). In this system, the DNPHs were separated into three bands corresponding to saturated aldehyde and ketones, 2-enals and 2,4-dienals. The bands were scraped off, extracted with chloroform and the concentration of carbonyls was calculated by measuring absorbance at 340 nm using $E^{1\%}_{340} = 22500$.

Separation of DNPHs by HPLC

Extracts of TLC-separated bands were further separated by HPLC on an RP-18 column with acetonitrile–water as mobile phase, using gradient elution and setting the UV detector at 336, 370 and 390 nm for saturated aldehydes and ketones, 2-enals and 2,4-dienals, respectively. For the first 12 min, the mobile phase consisted of an acetonitrile–water 60:40 mixture. From 12 to 26 min the proportion of water in the mobile phase was reduced to 20% by following the B curve (concave 2) profile. For the next 4 min the mobile phase consisted of acetonitrile–water 80:20; subsequently, the concentration of water was allowed to increase to 40% in 5 min by linear gradient. In HPLC separation, DNPHs were separated based on the chain length of the aldehyde or ketone in each class. Among saturated aldehydes and ketones, ketones migrated faster than saturated aldehydes having the same number of carbon atoms. The concentrations of the various constituents were determined by injecting known amounts of the corresponding DNPHs and calculating the concentrations from the peak areas. The HPLC separation of a mix of pure DNPHs of 2-alkanones and n-alkanals is shown in Fig. 1.

For determining the extent of recovery in the analytical procedure, standard solutions of hexanal, 2-hexenal and 2,4-decadienal were prepared in carbonyl-free chloroform and known quantities of carbonyls were added to freshly prepared potato chips at the time of steam distillation and subjected to the analytical procedure. The increase in peak areas for the potato chips was compared with the area of peaks obtained by direct injection of the DNPHs of the respective aldehyde. The overall recovery of hexanal, 2-hexenal and 2,4-decadienal

ranged from 85% to 89% and maximum variation among replicates did not exceed 3% from the mean value.

RESULTS AND DISCUSSION

Initially, the antioxygenic salts contained 0.26, 0.25 and 0.30% of BHA, BHT and TBHQ, respectively. But, on storage at room temperature and 37°C, the concentration of antioxidants decreased considerably (Table 1). Both storage temperature and nature of antioxidants influenced storage losses. After 6 months of storage, only 38.7, 78.4 and 84.2% of the initial levels of BHT, BHA and TBHQ, respectively, were retained at room temperature compared with 10.2, 65.2 and 70.3% retention at 37°C. Losses were much higher in BHT than BHA and TBHQ. In PP packs all three antioxygenic salt preparations tended to become yellowish or brownish on storage, suggesting oxidative degradation.

Suitability of antioxygenic salts for fried products

In order to study the relative efficacy of various antioxygenic salts in retarding lipid peroxidation during storage, potato and banana chips and fried Bengalgram dhal were treated with antioxygenic salts and the rates of autoxidation were determined by following changes in peroxide value. The results are given in Table 2. It can be seen that all three antioxygenic salt preparations were effective in retarding oil autoxidation during storage. Among the three antioxygenic salt preparations, the one based on TBHQ provided maximum protection, followed by BHT-treated salt, while the salt containing BHA exhibited the lowest antioxidant activity. The same pattern of protection was observed in all five products. The overall acceptability of fried products during storage was also highest when treated with salt containing TBHQ, followed by BHT and BHA samples. Also, commercially fried products, when treated with antioxygenic salts, autoxidized much more slowly than

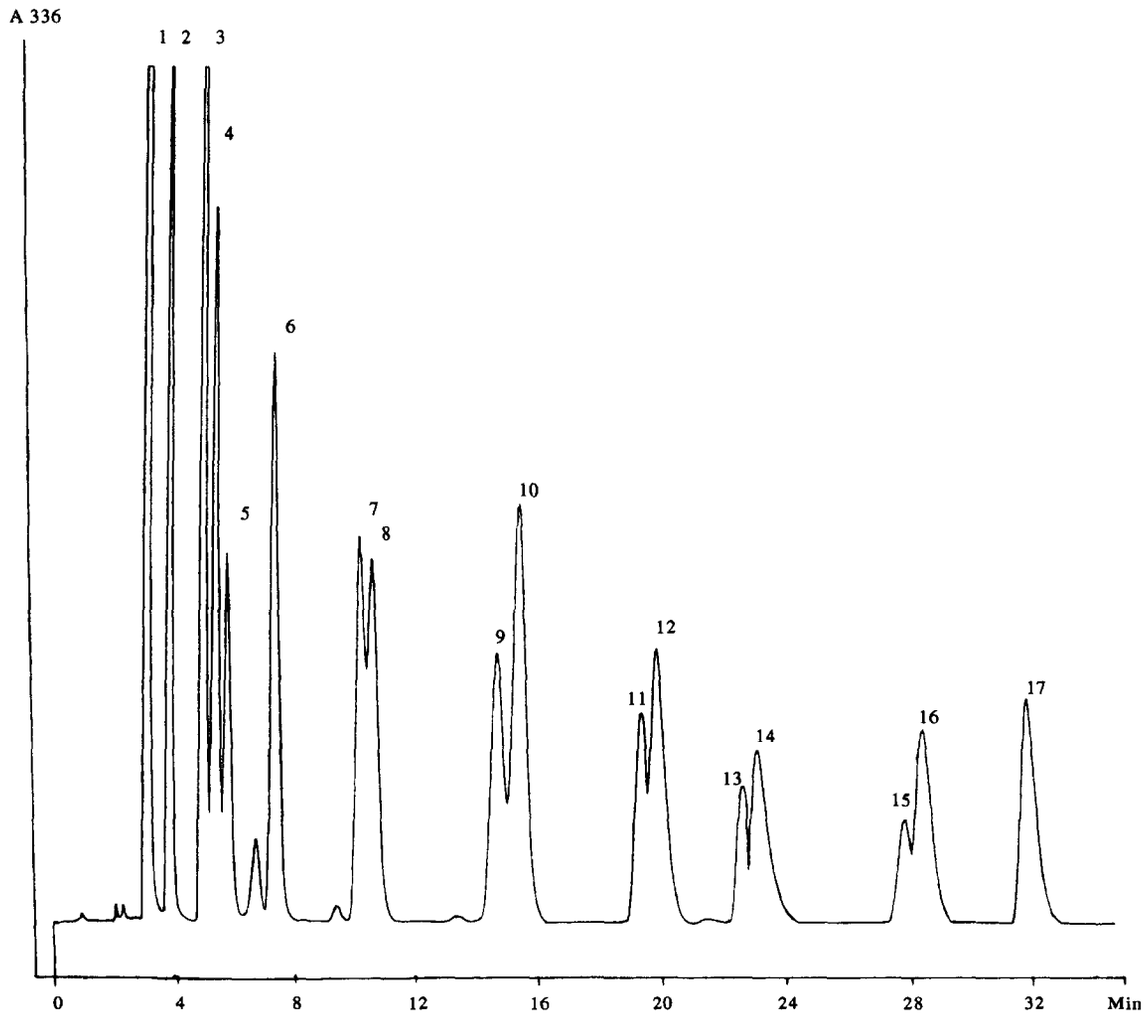

Fig. 1. RP–HPLC of a mixture of 2,4-dinitrophenylhydrazones of (1) formaldehyde, (2) acetaldehyde, (3) acetone, (4) propanal, (5) 2-butanone, (6) butanal, (7) 2-pentanone, (8) pentanal, (9) 2-hexanone, (10) hexanal, (11) 2-heptanone, (12) hetanal, (13) 2-octanone, (14) octanal, (15) 2-nonanone, (16) nonanal, (17 decanal).

the control samples, and TBHQ-treated salt imparted maximum stability. Among the three products fried in refined sunflower oil, Bengalgram dhal autoxidized at the slowest rate. Previously, also dhal starch and proteins were found to exert a retardatory effect on sunflower oil oxidation (Semwal *et al.*, 1994).

Table 1. Effect of storage temperature on the retention of antioxidants in the antioxygenic salts stored in polypropylene film (75 μm)

Storage period (months)	Temp. (°C)	Retention (%)		
		BHT	BHA	TBHQ
1	RT	87.0	99.8	99.2
	37	68.0	99.0	95.0
3	RT	70.8	93.0	90.0
	37	33.3	85.0	87.0
6	RT	38.7	78.4	84.2
	37	10.2	65.2	70.3
9	RT	ND	66.2	70.9
	37	ND	36.1	29.9

Results are means of duplicate samples; maximum variation did not exceed 3% of the mean.
Initial concentrations of BHA, BHT and TBHQ in salt were 0.26, 0.25 and 0.30%, respectively.
RT, room temperature; ND, not detected.

Carbonyls are known to form during storage of fatty foods, and their concentration has been correlated with the development of rancidity and off-flavours. The concentrations of total steam-volatile carbonyls, total saturated aldehydes and ketones, 2-enals and 2,4-dienals in potato chips treated with various antioxygenic salts and stored for 3 months are given in Table 3. It can be seen that total steam-volatile carbonyls in freshly fried potato chips was quite low (0.11 mg per 100 g) but increased many-fold on storage. The highest increase occurred in control potato chips (300 mg per 100 g), followed by chips containing BHA (201 mg per 100 g) and BHT (86.6 mg per 100 g), while the chips containing TBHQ-treated salt showed the lowest (5.82 mg per 100 g) increase in carbonyls, confirming the superiority of TBHQ-treated salt in extending the shelf-life of potato chips.

Various carbonyls in each class were further separated by reversed phase HPLC and the concentrations of individual carbonyls both in fresh and stored chips are given in Table 4. Although most of the carbonyls characterized in potato chips in the present study have been previously characterized by other workers, no detailed study has been reported on quantitative changes that occur during storage. Among saturated aldehydes, the

Table 2. Effect of antioxygenic salts on the storage stability of potato chips, banana chips and deep fat fried Bengalgram dhal stored in polypropylene film at 37°C

	Peroxide value[a] (mEq $O_2\,kg^{-1}$ fat)				Overall acceptability			
Storage period (days):	30	60	90	120	30	60	90	120
Potato chips (laboratory) containing:								
Salt	73.9	220	831	—	6.9±0.3*	6.2±0.6*	3.9±1.2*	—
BHA-salt	63.8	198	331	—	7.2±0.4*	6.8±0.1*	4.7±0.6*	—
BHT-salt	48.0	131	189	220.0	7.3±0.3	6.8±0.2*	6.7±0.3*	5.7±0.8*
TBHQ-salt	12.0	17.7	27.5	37.8	7.6±0.3	7.4±0.2	7.3±0.4	7.2±0.5
Potato chips (commercial) containing:								
Salt	13.5	19.4	46.9	65.0	7.2±0.4*	7.0±0.1*	6.2±0.4*	4.4±1.0*
BHA-salt	11.3	12.3	23.1	55.2	7.1±0.2*	7.0±0.3*	6.9±0.3*	4.8±0.3*
BHT-salt	8.6	9.6	13.1	24.0	7.4±0.3	7.4±0.2	6.9±0.2*	6.5±0.3*
TBHQ-salt	6.9	7.8	9.5	10.9	7.5±0.2	7.3±0.4	7.4±0.3	7.3±0.4
Bengalgram dhal deep fat fried containing:								
Salt	37.8	111	140	210	6.8±0.1*	6.2±0.5*	5.8±0.3*	3.2±0.5*
BHA-salt	39.6	118	130	181	6.7±0.2*	6.4±0.4*	6.0±0.3*	5.7±0.5*
BHT-salt	28.9	56.9	70.9	146	7.2±0.2*	6.7±0.2*	6.2±0.2*	6.2±0.3*
TBHQ-salt	20.6	25.9	30.1	40.1	7.5±0.3	7.5±0.3	7.5±0.3	7.1±0.8
Banana chips (lab) containing:								
Salt	52.6	147	455	1096	6.1±0.2*	5.1±0.2*	3.0±1.2*	—
BHA-salt	41.5	107	171	928	6.2±0.4*	5.6±0.3*	4.1±0.4*	—
BHT-salt	36.5	72.0	136	786	6.5±0.3*	5.8±0.4*	4.3±0.3*	—
TBHQ-salt	13.9	19.5	40.2	57.9	7.4±0.3	7.3±0.1	7.2±0.4	6.9±0.4*
Banana chips (commercial) containing:								
Salt	2.2	6.5	6.0	7.9	7.8±0.1	7.4±0.2	7.4±0.2	7.3±0.3
BHA-salt	2.3	5.0	5.5	6.6	7.7±0.2	7.3±0.3	7.4±0.2	7.2±0.8
BHT-salt	2.1	4.7	4.7	5.5	7.6±0.1	7.6±0.4	7.4±0.4	7.3±0.3
TBHQ-salt	2.2	3.8	3.7	3.9	7.8±0.2	7.6±0.5	7.3±0.4	7.3±0.1

Initial peroxide values of potato chips (lab), potato chips (commercial), Bengalgram dhal, banana chips (lab) and banana chips (commercial) were 8.3, 6.0, 7.8, 8.9 and 0, respectively.
Initial overall acceptability scores of potato chips (lab), potato chips (commercial), Bengalgram dhal, banana chips (lab) and banana chips (commercial) were 7.9±0.6, 7.8±0.5, 7.9±0.6, 8.0±0.8 and 7.8±0.5, respectively.
[a]Mean of three values; maximum variation among replicates did not exceed 3% of the mean.
*Significantly different from corresponding control sample ($P \leq 0.01$).

Table 3. Changes in the concentration of carbonyls (mg per 100 g sample) in potato chips stored in polypropylene at 37°C for 3 months

Carbonyls	Fresh chips	Stored chips containing:			
		Salt	BHA-salt	BHT-salt	TBHQ-salt
Saturated aldehydes and ketones	0.06	66.3	69.4	44.6	2.86
2-Enals	0.01	69.5	51.0	2.44	0.18
2,4-Dienals	0.004	33.0	18.5	9.24	0.46
Total carbonyls	0.11	300	201	86.6	5.82

Results are mean of two values; maximum variation between replicates did not exceed 3% of the mean.

Table 4. Concentration of carbonyls ($\mu g\, g^{-1}$) in potato chips stored in polypropylene film at 37°C for 3 months

Carbonyl	Fresh chips	Stored chips containing:			
		Salt	BHA-salt	BHT-salt	TBHQ-salt
Formaldehyde	—	1.85	5.57	4.02	0.61
Acetaldehyde	—	5.20	12.1	13.7	1.79
Propanal	—	6.63	6.52	—	—
Butanal	0.14	15.2	29.0	21.2	5.11
Pentanal	—	51.0	45.7	22.6	—
Hexanal	0.01	343	322	268	4.74
Heptanal	—	50.4	46.0	38.3	0.68
Octanal	—	6.30	3.51	1.51	—
Nonanal	0.01	10.6	8.99	3.88	0.54
Decanal	—	3.07	1.94	0.84	0.29
Acetone	0.05	4.21	2.93	1.37	0.54
Butanone	—	14.3	—	—	—
Pentanone	0.15	—	—	21.1	7.74
Octanone	—	13.6	—	—	—
Nonanone	—	0.09	0.07	0.03	0.01
Pentenal	—	4.28	2.16	0.11	—
Hexenal	—	90.7	7.30	0.08	0.01
Heptenal	0.01	78.3	60.4	1.78	0.09
Octenal	—	190	142	2.11	0.01
Nonenal	0.01	18.0	8.98	0.10	0.03
Decinal	0.01	17.5	10.3	0.21	0.02
Decadienal	0.02	304	157	76.8	4.50

Results are mean of three values; maximum variation among replicates did not exceed 3% of the mean.

largest increases occurred in pentanal, hexanal and heptanal concentrations in control, BHA- and BHT-treated potato chips. Among 2-enals, the largest increases occurred in hexenal, heptenal, octenal and nonenal in control and BHA-treated chips. Among 2,4-dienals, only 2,4-decadienal was identified and its concentration increased by many-fold in control, BHA- and BHT-treated samples. But in samples treated with TBHQ-salt, the increases in the concentrations of pentanal, hexanal, heptanal, hexenal, heptenal, octenal, nonenal and decadienal were marginal. Good correlations have been observed between the concentrations of pentanal, hexanal, heptanal and 2,4-decadienal with off-flavour development in a number of food products (Dupuy *et al.*, 1973, 1976; Warner *et al.*, 1978; Hoffman, 1961). The concentration of 2-hexenal has been observed to increase in stored potato chips by Dornseifer & Powers (1965). Substantial increases in the concentrations of n-hexanal, 2-pentenal, 2-hexenal and n-heptanal have been reported by Sapers *et al.* (1972) in stored potato flakes which developed hay-like odours. In the present study, the concentrations of most of the carbonyls that have been reported to be associated with the autoxidation of oleic acid, linoleic acid and linolenic acid increased in all the samples, but the extent of increase was much smaller in TBHQ-containing antioxygenic salt, which was also rated best in sensory analysis. The results of the present study show that incorporation of TBHQ-containing salt into freshly fried potato chips considerably retards the autoxidation in potato chips and thereby helps in minimizing flavour deterioration during storage. BHA- and BHT-containing salts, although useful in retarding the rate of autoxidation, are relatively less effective than TBHQ-salt. The concentration of antioxidants in antioxygenic salt decreases on storage at room temperature when packed in PP film pouches. Better methods of packaging and storage are needed to effectively utilize its full potential in the stabilization of fried products.

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