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Evaluation of Tertiary Butylhydroquinone as an Antioxidant In Powdered Roasted Peanuts Products[1]

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ABSTRACT

A fifteen month shelf life study was conducted to determine the effectiveness of tertiary butylhydroquinone (TBHQ) as an antioxidant in products made from roasted peanuts (*Arachis hypogaea L.*). Five levels of TBHQ were studied, 0.0%, 0.01%, 0.02%, 0.03%, and 0.04% based on the fat content of the peanuts. Total carbonyl assays performed monthly served as indices of rancidity. Results indicate that the shelf life of the product may be extended up to thirteen months using the 0.02% level of TBHQ now allowed by the Food and Drug Administration. In addition, the quantitative determination of total carbonyls proved to be an acceptable indicator of rancidity of roasted peanuts.

Key words: Roasted peanut products, Shelf life, Total carbonyl content, Antioxidants.

The loss of "fresh roasted" aroma and flavor in nut products is a major problem in the peanut industry. The development of off flavors after ten weeks storage in a new powdered roasted peanut product, consisting of 80% peanut butter and 20% whey, instigated the work presented herein. In an attempt to extend the shelf life of the product, an antioxidant preservative system consisting of Tenox 20A was selected and a fifteen months storage study conducted. Tenox 20A contains 20% active tertiary butylhydroquinone (TBHQ) antioxidant which has been reported (11) (12) to be more effective than butylated hydroxanisole (BHA), butylated hydroxytoluene (BHT), or propylgallate (PG), in plant products. Tenox 20A also contains 3% anhydrous citric acid as a sequestrant for trace metals. Since sweet whey was used to powder the peanut butter, the high ash content normally found in whey is believed to have contributed to the early rancidity problem found in this product when no antioxidant was used. Previous reports (9) (10) have suggested that a large portion of the flavor and aroma of raw and roasted peanuts may be ascribed to their carbonyl content. Young and Holley (13) noted a rise in carbonyls with increased storage time and higher carbonyl levels in the volatile fraction from off flavored peanuts. Kawahara and Dutton (7) found that the removal of the carbonyl fraction of rancid soybean oil eliminated rancid odors detected previously. Quantitative estimates of total carbonyl content, were selected as indicators of rancidity. The purpose of this study was to evaluate the effectiveness of the TBHQ system in preventing lipid oxidation in the powdered roasted peanut product.

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Materials and Methods

The formulation of powdered roasted peanuts was reported earlier (6). The peanuts used were high quality spin blanched Florunners from the 1976 crop, stored at -23°C until sample preparation. Peanuts were air roasted at 177°C until a medium roast was obtained and ground into a very smooth peanut butter in an Urschel Comitrol Colloid Mill. A stock solution consisting of 5% Tenox 20A, and 95% Durkex 500 oil was prepared. Tenox 20A contains 20% active TBHQ antioxidant. The fluid properties of the oil were used to insure proper dispersion of the antioxidant. Since Tenox 20A contains 20% TBHQ by weight, this stock solution contained 1% TBHQ. The present level of TBHQ allowed by the Food and Drug Administration is 0.02% based on the oil content of the product (4). A control and four levels of TBHQ, 0.01%, 0.02%, 0.03%, and 0.04% were used in this study.

The preservative solutions were mixed with the peanut butter and then 20% low density whey, by weight, was incorporated into the mixture with a ribbon blender. The resulting powdered peanut product was comminuted by a Fitz Mill, at low speed, through a 1.9 cm (0.75") screen to break up large particles. Samples were packed in cans immediately, without vacuum or gas and stored in the dark at room temperature 22-27°C) for the duration of this study.

The procedure developed by Henick et al. (5) for carbonyl determination was adopted with certain modifications. Unlike previous experiments (2) in which the oil was pressed from the nut for analysis, 40 ml. of benzene was added to 2 grams of the powdered peanut butter. Samples were stirred thoroughly by hand, stoppered, and stored for one hour, prior to centrifuging. Samples were centrifuged for twenty minutes at 1400 xg and the benzene layer removed. Five ml. aliquots of each sample's benzene phase were pipetted into tared 50 ml. beakers. The beakers were placed over a water bath and the benzene evaporated under a hood. Samples were then dried in a 56°C oven for one hour, cooled to room temperature, the weight of each beaker recorded, and the amount of fat present in 5 ml. of the benzene phase calculated.

The benzene phase of each sample was also used to determine the carbonyl content. In both the fat and carbonyl determinations, duplicates of each sample were run and two aliquots from both the sample and the duplicate were analyzed, yielding a total of four readings for each sample. Five ml. of each sample's benzene phase were pipetted into 50 ml. volumetrics containing 3 ml. of 4.3% trichloroacetic acid and 5 ml. of 0.05% 2,4 dinitrophenyl hydrazine. A reagent blank was included. The volumetrics were stoppered and placed in a steam bath at 60°C for 30 minutes, thus converting the carbonyls present to their 2,4 dinitrophenyl hydrazones with the trichloroacetic acid acting as a catalyst. The volumetrics were cooled to room temperature and 10 ml. of a freshly prepared 4% ethanolic KOH solution was added to each flask. Samples were diluted to volume with ethanol, shaking to mix, and allowed to stand fifteen minutes before colormetric readings were made. The 2,4 dinitrophenyl hydrazones which give a bright yellow color, ranged from light amber to deep wine colors under the alkaline conditions, the hue increasing as the total carbonyls increased.

Absorbence readings were made at 430nm and 460nm using a 1 cm. cuvette in a Bausch and Lomb Spectronic 70. Calculations were made according to the method suggested by Chipault et al. (3).

$$\text{Unsaturated carbonyl} = \frac{4.204\ A_{460} - 3.266\ A_{430}}{W}$$

$$\text{Saturated carbonyl} = \frac{5.971\ A_{430} - 4.533\ A_{460}}{W}$$

A_{430} and A_{460} are the absorbencies observed at 430nm and 460nm. W is the weight of the fat contained in a 5 ml. aliquot. Unsaturated and saturated carbonyls were combined to give a total carbonyl value.

By adding ingredients such as caseinate, sucrose, calcium carrageenan and glycerides to the powdered peanut butter, frozen desserts, icings, puddings, beverages and many other new food products are obtained. The powder alone however, is not a palatable product. The whey masks the roasted peanut flavor slightly making flavor assays very difficult. A formal taste panel was not considered to be feasible for this reason. It had been noted that the aroma of the powder did change dramatically during storage, therefore samples were rated monthly by a small in house panel on the basis of aroma alone. Samples were judged to have either a fresh roasted, bland, stale or rancid odor.

Results and Discussion

The application of TBHQ proved to be effective in reducing the total carbonyls produced. Figure 1 illustrates the rapid oxidation of the untreated control in contrast to the slow rise in carbonyls for treated samples. Total carbonyls in the control increased with increased storage time as illustrated in Fig. 1, yielding a curvilinear regression correlation coefficient of 0.99.

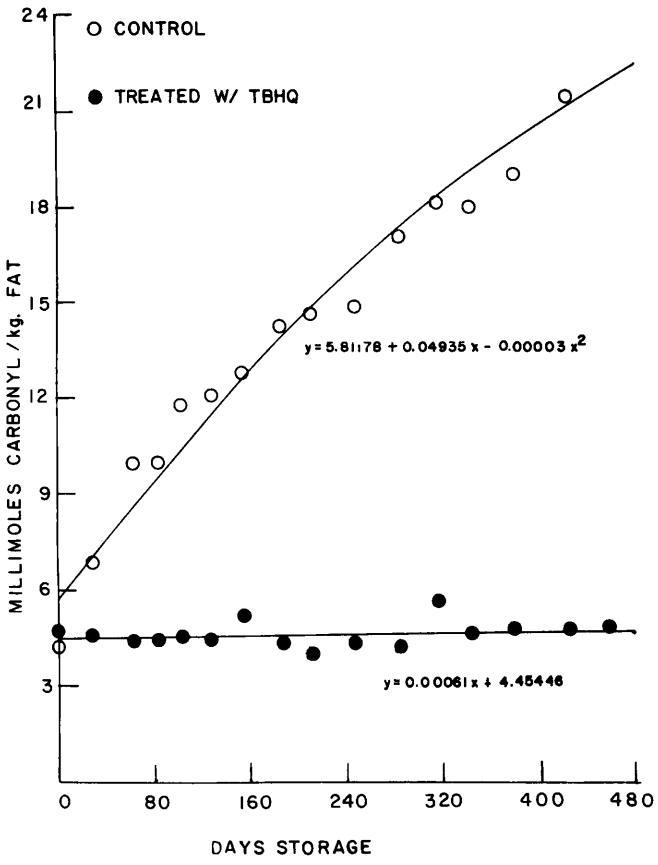

Fig. 1. Carbonyl levels determined during the fifteen month study. The regression line for treated samples represents a pooled value of all samples treated with TBHQ for that date.

Total carbonyls in samples treated with TBHQ remained relatively constant and exhibited only minor fluctuations during the fiteen month storage period. Total carbonyls for the untreated control increased by 280% while an average increase of only 6.5% was found for samples treated with TBHQ. A Waller Duncan K-Ratio t-test, t = 0.05%, (1) between means of both the control and treated samples, showed the control to be significantly different than treated samples. Due to the large difference in total carbonyls this comparison showed no statistical difference between samples treated with the antioxidant. As a result, the regression line in Figure 1 for treated samples represents the pooled values of all treated samples.

The same t-test between means of only samples treated with TBHQ showed that the mean of the 0.01% level was significantly different than those of the 0.02% and 0.03% levels. Means of the 0.02% and 0.03% levels in turn were significantly different than the 0.04% level at the t = 0.05% level. Correlation coefficients for the regression lines of treated samples averaged 0.17 compared with the control's correlation coefficient of 0.99. Correlation coefficients for treated samples are not significant, while the correlation coefficient for the control is significant at the t = 0.01% level (1).

Although these results might appear confusing at first, they are evidence that the antioxidant TBHQ was successful in preventing lipid oxidation. If an antioxidant is to be effective it must inhibit the formation of hydroperoxides which decompose to carbonyls and are catalyst to further oxidation (8). This fat oxidation mechanism is illustrated by the untreated control. In samples treated with TBHQ however, there is no significant increase in carbonyls indicating that this chain reaction was inhibited.

Organoleptic evaluations made during the fifteen months storage period indicated that the TBHQ was effective in preserving the product's "fresh roasted" aroma. As mentioned earlier, the panelist noted only the changes in the aroma of the samples. These changes were quite sharp and easily discerned. The purpose of this experiment was to observe the effects of TBHQ on carbony content as the latter was assumed to be largely responsible for off flavors and aromas. The organoleptic ratings served as checkpoints to insure this assumption. The 0.03% and 0.04% levels retained their fresh roasted odor during the entire 15 month study. A bland odor was detected after 13 months in the 0.01% and 0.02% levels. A bland odor was detected in the control without antioxidant after one month, a stale odor after 3 1/2 months and a rancid odor after 7 1/2 months.

Results of the carbonyl assays relate closely with organoleptic evaluations. The rapid increase of carbonyl in the untreated control is reflected in the rapid decrease of the organoleptic ratings. The very gradual rise in carbonyls for all treated samples is accompanied by a slight decrease in the organoleptic ratings of samples containing 0.01% and 0.02% TBHQ, after 12 1/2

months storage.

Analyses of the powders immediately after preparation yielded total carbonyl levels analagous to those reported by Brown et al. (2). No values have been reported for roasted peanuts stored for an extended period of time. Work is now underway to develop a quick and simplified procedure of carbonyl analysis that would be a reliable quality control tool. Effects of concentrations of TBHQ less than 0.01% have not been studied in this laboratory to date. A future study involving the application of a wider range of antioxidant levels to whole nuts has also been proposed.

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