Lipid Oxidation in Potato Chips

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ABSTRACT

Qualitative and quantitative analyses of volatile compounds in fresh and aged potato chips and unused fresh and aged frying oils showed that oxidation of oils was mainly responsible for volatile compound changes in potato chips during storage. The lipid oxidation of potato chips was determined by measuring the peroxide value of potato chips and the amount of volatile compounds and oxygen content in the headspace of potato chip bottles by gas chromatography. The correlation coefficients between volatile compounds and oxygen content, volatile compounds and peroxide value, and peroxide values and oxygen content were -0.93, 0.95 and -0.93, respectively. These high correlation coefficients indicated that volatile compound changes in potato chips during storage were mainly due to the oxidation of oil. The lipid oxidation of potato chips during storage can be studied by measuring oxygen content and the amount of volatile flavor compounds in the headspace. The potato chips produced in oil containing an antioxidant tertiarybutyl hydroquinone (TBHQ) had better oxidation stability than the chips fried in oil without TBHQ.

INTRODUCTION

The consumption of fats and oils in the United States has reached 10 billion pounds per year and continues to increase annually. Fifteen percent of these fats and oils is used for the production of deep fat fried foods (1). The production of potato chips reaches 3.5 billion pounds annually and uses 11% of the US potato crop (2). A significant problem of potato chips is the development of a stale or rancid flavor during storage.

Several studies have been done in identifying off-flavor compounds in aged potato chips (3-6). Nineteen monocarbonyl compounds have been identified in stale potato chips, and the total quantity of aldehydes and ketones increased gradually with storage time (5). These compounds could arise from oil oxidation in the chips (5, 6). Other compounds such as pyridines, sulfides, thiazoles, alcohols, phenols and esters have been identified as contributing to both good and bad flavors of potato chips (6-9). However, whether the quantitative changes of these compounds are taking place in potato chips during storage has not yet been reported.

Several methods have been used to monitor the oxidative stability of oils and lipid foods. One common method is to measure peroxide values. Although a linear relationship has been observed between peroxide values and flavor scores during the initial stages of lipid oxidation of oil and lipid foods (10, 11), this method alone is not a very good flavor quality indicator because the peroxide value increases to a maximum and then decreases as storage increases.

The depletion of oxygen in the air surrounding the product has been used to monitor the oxidation process. Quast and Karel (10) used an oxygen probe inserted in the headspace to measure oxygen depletion. Gas chromatography (GC) is another method for directly measuring the oxygen in the headspace of bottles containing foods (11).

Analysis of the volatile compounds produced from oxidation of foods has also been used to evaluate flavor quality of oil and lipid foods (12-14). A simple headspace analysis technique utilizing pentane as an indicator has a good correlation with undesirable flavor development in potato chips (12).

The purpose of this work was to ascertain the origin of major volatile compound changes in potato chips during storage and to study analytical methods which could assess the oxidation stability of potato chips.

MATERIALS AND METHODS

Origin of Volatile Compounds Changes in Potato Chips During Storage

Potato chips and a sample of the soybean frying oil were provided by Buckeye Potato Chip Co. (Columbus, OH). To study the origin of major volatile compound changes in potato chips during storage, unopened bags of potato chips and 100 mL serum bottles containing 70 mL unused fresh frying oil were stored at 55 C in a forced draft air oven. To analyze the volatile compounds in fresh and aged potato chips, oils from fresh and 14-day-old potato chips were first recovered by a hydraulic press. Fifteen grams of potato chips were transferred to a cell and pressed at 15,000 pounds per square inch using a Carver Laboratory hydraulic press (Summit, NJ). The oil flowed from the cell through a tiny hole at the bottom and was collected in a small aluminum pan. The volatile compounds in the oils expressed from fresh and aged potato chips in the unused fresh and aged frying oils were analyzed by the U-tube GC method described in detail by Min (13), and Jackson and Giacherio (14). The initial GC temperature was held at 90 C for 2 min, then programmed at 8 C/min to 230 C, and then held for 5 min. The flow rate of nitrogen gas was 40 mL/min.

Oxidative Stability of Potato Chips

To study the oxidative changes of potato chips during storage, 20 g of potato chips, crumbled in a household blender to particle size of ca. 4-5 mm, were placed in a 100 mL serum bottle and air-tightly sealed with a Teflon-coated rubber septum and an aluminum cap. These crumbled chips were also stored at 55 C in a forced draft air oven. The oxidative stability of potato chips during storage was determined by analyzing volatile compounds and oxygen content in the headspace and peroxide value of chips.

Volatile compounds and oxygen content in the headspace of the air-tightly sealed serum bottles were determined using a Hewlett Packard Gas Chromatograph HP-5880. Two mL of headspace gas were removed through the rubber septum with a 10-mL gas syringe and injected directly into the gas chromatograph. The GC column was a 10 ft × 1/8 in. stainless steel column packed with 80/100 mesh Tenax GC coated with 10% polymetaphenoxylene. The flow rate of nitrogen carrier gas was 20 mL/min. The oxygen content was analyzed at an isothermal temperature of 35 C using a thermal conductivity detector. The volatile compounds were analyzed at 140 C isothermal temperature using a flame ionization detector.

The gas chromatographic peak areas of oxygen and volatile compounds were determined by an HP 5880 electronic integrator and expressed in electronic counts.

The peroxide value in the expressed oil from potato chips was determined by the AOCS procedure (15).

Identification of Volatile Compounds

The compounds in the oil isolated from potato chips by the hydraulic press and frying oils as well as volatile compounds in the headspace were identified by a combination of mass spectra obtained by gas chromatography-mass spectrometry (GC-MS), HP Model 5985 and GC retention time. The GC conditions for the GC-MS analyses were the same as those conditions described earlier for U-tube and headspace gas chromatographic analyses.

Preparation of Potato Chips Containing Tertiarybutyl Hydroquinone (TBHQ)

Potato slices were obtained from Buckeye Potato Chips Co. (Columbus, OH). Frying oils containing 0, 50, 100, 150 and 200 ppm of TBHQ (w/w) were placed in a 2½-cup capacity deep fryer (Fry Baby Brand) and heated for 15 min to a temperature of 195 C. The potato slices were then placed in the hot oil and fried for 2¼ min at 195 C. Oils containing antioxidant were held at the frying temperatures (195 C) for ca. 2 hr while 13 batches of potato slices were fried for each level of TBHQ.

RESULTS AND DISCUSSION

Origin of Major Volatile Compounds Changes in Potato Chips During Storage

During the preliminary studies, the volatile compounds of potato chips were analyzed using the U-tube analysis method (13, 14). One gram of potato chips was crushed and then transferred into the U-tube, and volatile compounds were gas chromatographically evaluated. But the reproducibility of quantitative GC analyses was not good due to the difficulties of transferring the crushed potato chips to the U-tube. Therefore, to improve the reproducibility of GC analyses, the oils in potato chips were expressed by a hydraulic press, and the volatile compounds in the expressed oil were analyzed by the U-tube method. The GC profiles of volatile compounds of the expressed oil were very similar qualitatively to those of the original potato chips and quantitative reproducibilities of GC analyses of expressed oil were also very good. Therefore, the quantitative changes of volatile compounds of potato chips during storage were studied by analyzing the compounds in the oil expressed from potato chips.

The gas chromatograms of volatile compounds in oils expressed from fresh and aged potato chips as well as in unused fresh and aged soybean frying oils are shown in Figure 1. As indicated by GC profiles and identification of compounds, the same type of major volatile compounds such as pentane, 2-heptenal, isomers of 2,4-heptadienal, and isomers of 2,4-decadienal were present in both fresh and aged potato chips and unused fresh and aged frying oils. However, more of these compounds were found in the aged oil and aged potato chips than in their fresh counterparts. This indicates that the origin of major volatile compounds changes in potato chips during storage is due to the oxidation of oil. The compounds shown in Figure 1 were also previously identified in soybean oil, hydrogenated soybean oil and corn oil by Min (13), and Jackson and Giacherio (14) and in potato chips by Dornseifer and Powers (3), Mookherjee et al. (5), and Deck et al. (6). This finding further supports the postulations of Mookherjee et al. (5) that, as the storage time of potato chips increases, the volatile compounds which are oxidative decomposition products of oil increases. Mookherjee et al. (6) also reported that, as the volatile compounds formed from the oxidation of oil in potato chips increased, the flavor quality of chips decreased. Therefore, it should be possible to reduce the formation of volatile compounds in potato chips by slowing down the oxidative reaction of the oil.

Oxidative Stability of Potato Chips

Gas chromatograms of the headspace gas in bottles obtained with a thermal conductivity detector are shown in Figure 2. The sample bottles were removed from the oven and cooled to room temperature before analysis. Mass spectra and gas chromatographic retention times indicated that the first and second peaks were oxygen and carbon dioxide, respectively. The oxygen concentration decreased

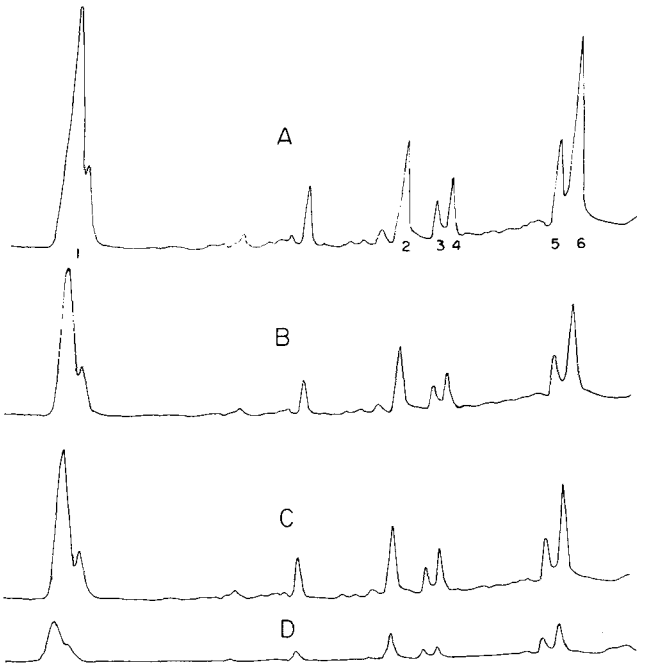

FIG. 1. Comparisons of gas chromatograms of volatile compounds in oils expressed from potato chips and oils used for the production of potato chips (A – aged potato chips for 14 days at 55 C, B – fresh potato chips, C – aged oil for 5 days at 55 C, and D – fresh oil). Identification: (1) pentane, (2) 2-heptenal, (3) and (4). Isomers of 2,4-heptadienal, (5) and (6). Isomers of 2,4-decadienal.

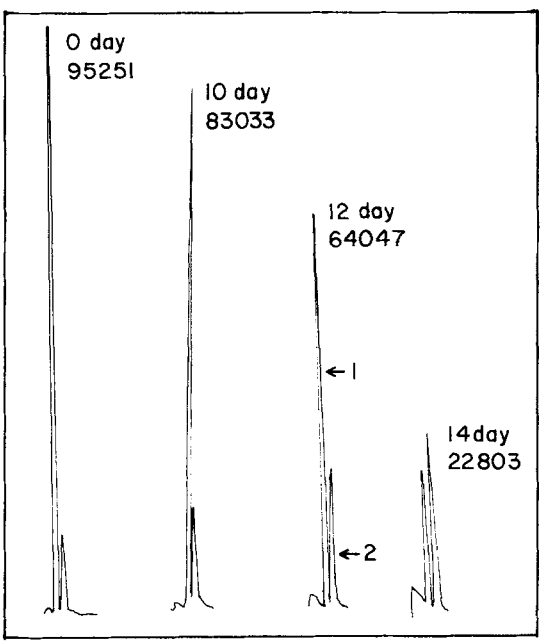

FIG. 2. Changes in gas chromatogram profiles of headspace in a serum bottle containing potato chips during storage at 55 C were obtained by a thermal conductivity detector. (1) Oxygen, (2) carbon dioxide.

in the headspace as storage time increased. The disappeared oxygen most likely reacted with oil to form volatile compounds shown in Figure 1. Most of the carbon dioxide may be formed by the Strecker degradation of nonenzymatic browning reaction during storage (16). The carbon dioxide formed from pure oil under storage conditions similar to those of potato chips was very small. A gas chromatogram of volatile compounds in the headspace gas of potato chips is shown in Figure 3. The major compounds present were

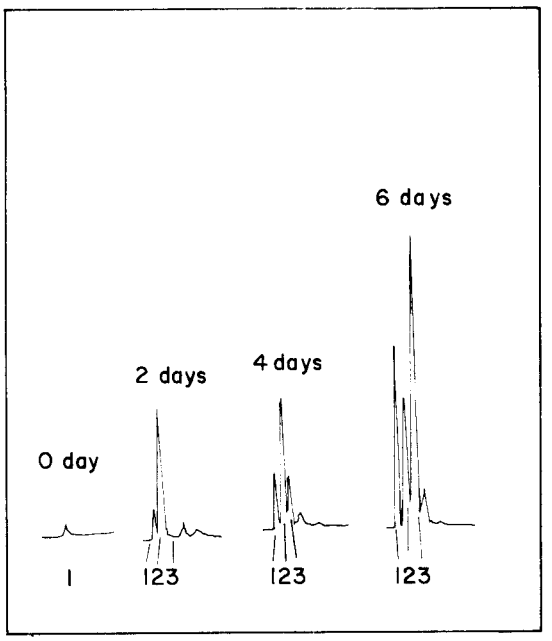

FIG. 3. Changes in gas chromatogram profiles of headspace of serum bottles during storage at 55 C. Chromatograms were obtained by a flame ionization detector. (1) Propane, (2) butane, and (3) pentane.

propane, butane and pentane. As storage time increased, the volatile compounds, especially pentane, increased. Pentane has been reported as a decomposition product of oxidative reactions in oil (12-14). Warner et al. (12) correlated pentane content in the headspace of potato chips with storage time and flavor scores. They reported that pentane content increased as storage time increased and flavor scores decreased. Since pentane concentration in the headspace increases as the storage period increases and flavor scores decrease, pentane could be used as a flavor quality indicator for potato chips as Warner et al. reported (12).

The peroxide values of potato chips are shown in Table I. The peroxide value increased as the storage period increased.

Correlation of Analytical Results

The peroxide values, oxygen content and the amount of volatile compounds in headspace of potato chips during storage are shown in Table I. The linear regression equation between peroxide values (y) and oxygen content (x) in the headspace was y = 40.8548 - 0.0005 x, and the correlation coefficient (r) was -0.93. Peroxide values increased as the oxygen content in the headspace decreased. This suggested that peroxides were formed by the reaction of oxygen and potato chips, as was expected. The equation between volatile compounds contents (y) and the peroxide values (x) was y = 227X + 3202, and the r was 0.95. That is, the amount of volatile compounds increased as the peroxide value increased. This indicated that the volatile compounds were formed by the decomposition of peroxides. The equation between volatile compounds content (y) and oxygen content (x) was y = 13780 - 0.1317x, and the r was -0.93. The volatile compounds increased as the oxygen content in the headspace decreased. This also suggested that these volatile compounds were formed by the interaction between oxygen and potato chips during storage. The high correlation coefficients among the 3 different analytical results (volatile compounds, oxygen content and peroxide values) further indicated that major volatile compound changes in potato chips during storage were mainly due to the oxidation of oil.

TABLE I

The Contents of Oxygen and Flavor Compounds in the Headspace and Peroxide Values in Potato Chips During Storage at 55 C

Storage (days)	Oxygen content[a]	Peroxide value	Amount of flavor compounds[a]
0	90687	0.0	1570
3	82607	1.2	3538
6	74901	1.3	3664
9	76067	2.2	4243
12	67886	2.2	4544
15	61933	5.1	5453
18	61074	7.2	5973
21	49478	11.4	6504
24	28628	25.0	7956
27	27135	34.9	12648

[a]The amounts of oxygen and flavor compounds were expressed in GC peak area integrator counts.

Reproducibilities of Volatile Compounds, Oxygen and Peroxide Value Analyses

The coefficients of variation for the reproducibilities of volatile compounds and oxygen analyses in the headspace of sample bottles and peroxide value analysis of potato chips for 5 replicates were 6%, 3% and 6%, respectively. Oxygen analysis method gave the best reproducibility and it was assumed that the reproducibilities of these 3 analytical methods were satisfactory.

Effect of TBHQ on the Oxidation Stability of Potato Chips

The peak area of pentane in the headspace of potato chips stored at 55 C for 9 days is plotted against the level of TBHQ added to frying oils (Fig. 4). As the level of TBHQ increased, the amount of pentane decreased.

The peroxide values of potato chips produced in the frying oils containing different levels of TBHQ are shown in Figure 5. The peroxide values of potato chips increased as storage time increased, and the higher the TBHQ content was in the frying oil, the lower was the peroxide value of

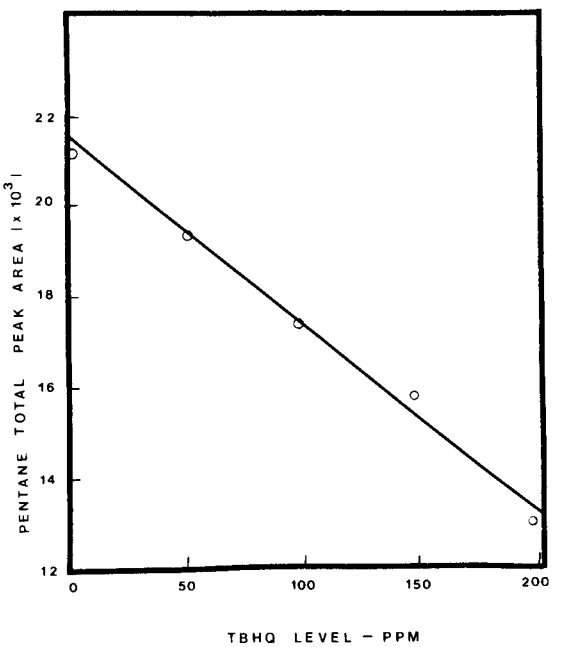

FIG. 4. Pentane content in the headspace of potato chips produced in oils containing different levels of TBHQ. The samples were stored for 9 days at 55 C.

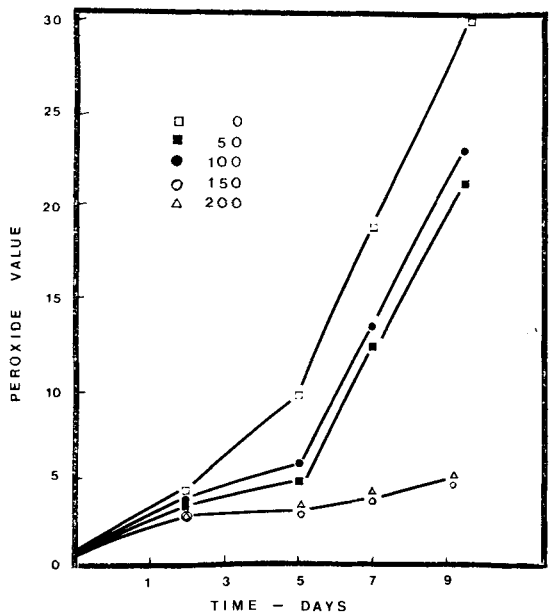

FIG. 5. Peroxide values of potato chips produced in oils containing different levels of TBHQ during storage at 55 C.

potato chips.

Although thermal destruction and loss through steam distillation of some phenolic antioxidants during frying of oils have been reported by Stuckey (17), the results in Figures 4 and 5 indicated that TBHQ added to the frying oil increased the oxidation stability of the potato chips. Since the higher the added TBHQ, the lower the pentane and peroxide values of potato chips, the total TBHQ content added in the potato chips could be up to 150 or 200 ppm which is the maximum legal limit of TBHQ based upon the oil content of potato chips (18).

ACKNOWLEDGMENTS

Mass spectrometric service was rendered by the Technical Center, Borden Company, Columbus. A.G. Baroudi of Buckeye Potato Chips Co. provided assistance. Salaries and research support provided by State and Federal Funds appropriated to the Ohio Agricultural Research and Development Center, The Ohio State University. This is Journal Article No. 154-82. P. Baptie provided technical help.

REFERENCES

1. Chang, S.S., R.J. Peterson and T. Ho, JAOCS 55:718 (1978).
2. Potato Chip Information Booklet, Potato Chip Information Bureau, San Francisco, CA, 1978.
3. Dornseifer, T.P., and T.T. Powers, Food Technol. 118, 1963.
4. Dornseifer, T.P., and T.T. Powers, Ibid. 165, 1965.
5. Mookherjee, B.D., R.E. Dick and S.S. Chang, J. Agric. Food Chem. 13:131 (1965).
6. Deck, R.E., J. Pokorny and S.S. Chang, J. Food Sci. 38:345 (1973).
7. Deck, R.E., and S.S. Chang, Chem. Ind. (London) 1343 (1965).
8. Buttery, R.G., R.M. Siefert, D.G. Guadagni and L.C. Ling, J. Agric. Food Chem. 19:969 (1971).
9. Buttery, R.G., and L.C. Ling. Ibid. 22:912 (1974).
10. Quast, D., and M. Karel, J. Food Sci. 37:584 (1972).
11. Fioriti, J.A., JAOCS 54:450 (1977).
12. Warner, K., C.S. Evans, G.R. List, B.K. Boundry and W.F. Kivolek, J. Food Sci. 39:761 (1974).
13. Min, D.B., J. Food Sci. 46:1453 (1981).
14. Jackson, H.W. and D.J. Giacherio, JAOCS 54:458 (1977).
15. Official and Tentative Methods of the American Oil Chemists' Society, AOCS, Champaign, IL, 1973, Method Cd8-53.
16. Hodge, J.E., and E.M. Osman, in Food Chemistry, edited by O.R. Fennema, Marcel Dekker, Inc., New York, 1976.
17. Stuckey, B.N., Handbook of Food Additives: Antioxidants as Food Stabilizers, edited by T.E. Furia, CRC Press, Inc., Cleveland, OH, 1972, p. 185.
18. Code of Federal Regulation 21, Office of Federal Register, Washington, DC, 1982.

[Received October 18, 1982]

Fractional Crystallization and Gas Chromatographic Analysis of Fatty Acids as a Means of Detecting Butterfat Adulteration

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ABSTRACT

A method has been devised which gives the distribution of saturated and unsaturated fatty acids of pure and adulterated cow and buffalo ghee with lard or margarine. It involves fractionation of pure and adulterated butterfat into fractions by fractional crystallization. The composition of the fatty acids liberated by the hydrolysis of each of the fractions was determined by gas chromatography. Adulteration of cow and buffalo ghee with various levels of lard or margarine caused significant changes in certain fatty acids, i.e., 22:0, 18:1, 18:0 and 16:0. It is possible to determine the extent of admixture of lard or margarine to either cow or buffalo ghee by applying a simple regression equation for certain fatty acids. This technique provides a basis for the detection of lipid adulteration.

INTRODUCTION

Butterfat is much higher in price in comparison with other fat sources. Unethical suppliers used to adulterate butterfat with manufactured and other fats which are quite similar in chemical composition and less expensive. Adulteration of butterfat is a continuing problem for food law enforcement and commercial quality control laboratories. Substantial endeavors among scientists were made to find ways to detect butterfat adulteration. Consequently, several methods have been proposed in this respect such as differential thermal analysis (1) and various chromatographic techniques (2-4). The latter methods dealt with fatty acids, unsaponifiables and ratios of some compounds belonging to each lipid class and seem to be superior to the other methods in detecting lipid adulteration. Continuing efforts to achieve decisive techniques to check lipid adulteration are being made. The present investigation describes the fractional crystallization process at different temperatures in conjunction with gas chromatography as a satisfactory tool for characterization of lipid adulteration.