Lipid Oxidation in Potato Slices Under Conditions Simulating the Production of Potato Granules

Marianne Lilja Hallberg* and **Hans Lingnert**
SIK, The Swedish Institute for Food Research, P.O. Box 5401, S-402 29 Göteborg, Sweden

The formation of volatile compounds in potato slices was analyzed by means of gas chromatographic headspace analysis. The experimental variables selected for the treatment of the potato slices were chosen to simulate the conditions during the first stages of an "add-back type" of process for production of potato granules. The potato slices (2 cm thick) were exposed to air of low temperature (4°C) and water at blanching temperature (76°C). Both the surface and the middle of each slice were analyzed for volatile compounds. Hexanal was the most abundant aldehyde formed. At the elevated temperature, in particular, there was an obvious formation of hexanal. After 15 min of blanching, the amount of hexanal was higher in the middle of the slices than at the surface. This difference in hexanal concentration was probably due both to the leakage of hexanal into the blanching water from the surfaces of the potato slices, and to the inactivation of lipoxygenase at the surfaces which prevented further oxidation during the subsequent chilling period. The hexanal formation indicates that lipid oxidation occurs during the process. The formation of other volatile compounds also is discussed.

KEY WORDS: Gas chromatography, hexanal, lipid oxidation, potato slices, volatile compounds.

A raw potato tuber is a complex mixture of various components. Starch is the most abundant compound but the tuber also contains one-half of a percent of lipids on a dry weight basis (1). In the intact tuber the lipids are mostly bound in the membranes of the cells. However, the tuber also contains large amounts of lipolytic enzymes (2). These enzymes are released immediately when the tuber is damaged, thereby initiating rapid degradation of endogenous lipids. The subsequent oxidation of the liberated free fatty acids causes off-flavor in the potato product due to formation of volatile compounds (3).

In previous studies of potato granule production, we found that free fatty acids (FFA) were hydrolyzed in the first part of the process (4). The process was of the "add-back type," a common industrial potato granule process. The hydrolysis was probably due to lipolytic enzymes. This enzymatic hydrolysis of the lipids was further studied at low temperature in a model system of potato slices, and compared with samples from the industrial process (5). The present study was focused on the oxidation of the lipids in a similar model system. The experimental conditions (temperatures, times, size of potato slices) were chosen to simulate the industrial process. In this process, potato tubers are sliced (2 cm thick) and transported through initial stages both by a conveyor belt and by cold water before reaching a blanching bath. While in the blanching bath, the potato slices are heated by water (76°C) for 15 min and then cooled in water (10°C) for 10 min before steam-cooking.

*To whom correspondence should be addressed.

In these model experiments two different temperatures were chosen: 4°C, corresponding to the low temperature in the first part of the process and 76°C representing the blanching temperature. The experiment at 4°C was performed in air in a cold storage room of constant temperature, while the heating at 76°C was performed in water. The lipid oxidation was followed by measuring the formation of volatiles using a gas chromatographic headspace analysis technique. Both the surface and the middle of the 2-cm thick potato slices were studied to investigate the influence of oxygen exposure and cell damage on the lipid oxidation.

MATERIALS AND METHODS

Studies on raw tubers. The raw potato tubers were of the Swedish variety, Bintje. To analyze the initial volatile content, prior to storing potato slices at 4°C and 76°C, respectively, the raw tubers were first washed and chilled in ice water to a temperature of below 4°C. After chilling, the tubers were peeled, cut in half, and a thin slice (1–2 mm) was instantly taken from each section surface. The thin slices (about 5–7 g) were immediately put into boiling water (50 mL) and refluxed for three minutes to inactivate the enzymes. The water had been purified through an Elgastat spectrum reverse osmosis and deionization system (Elga Ltd., High Wycombe Bucks, England).

After the slices were boiled, the condenser was rinsed with 10 mL of water. The potato/water sample was chilled on ice and homogenized directly in the distillation flask, with an Ultra Turrax for 30 s at a fast speed. The slurry was then immediately analyzed for volatile compounds by the headspace technique described later. The results given are based on the analysis of five individual tubers.

Studies on potato slices kept at chilling temperature. To prepare potato slices for the experiment, the raw tubers were first chilled in ice water to a temperature of below 4°C, as described previously. Then the tubers were peeled and cut into 2-cm thick slices. These slices were kept in darkness at 4°C in air and after 30- and 60-min intervals some slices were withdrawn for analysis. Each time three 2-cm slices were analyzed. Thin slices (1–2 mm) were cut from both the surface and from the middle of each 2-cm slice. These thin slices were separately boiled and homogenized as described previously, prior to the analysis of volatiles.

Studies on potato slices kept at elevated temperature. The potato tubers were chilled in ice water to a temperature below 4°C. Then the tubers were peeled, cut into 2-cm thick slices and put in small metal baskets which were instantly put into a water bath at a temperature of 76°C. After intervals of 5 and 15 min, the baskets containing the potato slices were removed from the water and chilled in ice for 10 min. Samples from the surface and the middle of each potato slice were prepared for analysis of volatile compounds as described above. Three 2-cm slices were analyzed at each heating time.

Analysis of water content. Thin potato slices (1–2 mm) were dried at 110°C until constant weight was reached (about two hours). The original water content of the tubers was calculated from the loss of weight.

Analysis of volatile compounds. The analysis of volatile compounds was performed as described by Hall *et al.* (6). The procedure was briefly as follows: The aqueous slurry of potato tissue was poured into a specially constructed long-necked glass vessel (250 mL). The funnel was rinsed with another 10 mL of water, resulting in a total slurry volume of approximately 70 mL. The slurry was kept at constant temperature (25°C) and gently stirred during 30 min of equilibration and during the following sampling. The sampling was performed by purging two liters of helium over the sample (40 mL/min) and leading it through a polymer adsorbent, Chromosorb 102 (Johns-Manville—Alltech Associates, Arlington Heights, IL) in which the volatile components in the headspace were trapped. As previously described, three replicates were analyzed for each set of time/temperature conditions, except for the raw tubers which were analyzed five times. The volatiles were desorbed thermally and separated on a Varian 4600 Gas Chromatograph (GC). A fused silica capillary column, DB1, 60 m × i.d. 0.32 mm (J&W Scientific, Inc., Folsom, CA) was used. The GC was temperature programmed, 30–200°C at a rate of 4°C/min. The volatiles were detected by a flame ionization detector (200°C), and identified by a gas chromatograph/mass spectrometry system (Finnigan 9610-4023), using the same column. The mass spectra identification was made by using the National Bureau of Standards library of references as well as our own reference spectra. A Hewlett-Packard lab data system (HP 3357) was used for data collection and evaluation.

Temperature measurement in potato slices. In separate experiments the surface and center temperatures of the potato slices were followed continuously during heating in the blanching bath. Thermocouples of copper/constantan type T were placed into the potato slices. The thermocouples had a diameter of 0.25 mm. The temperature was measured 1 mm from the surface of the slices and in the center of the 2-cm thick potato slices. The data were collected and recorded every second by a Schlumberger Solartron 3530 Orion logging system connected to a Luxor ABC 800 microcomputer.

RESULTS AND DISCUSSION

Change of temperature during blanching. The change of temperature in potato slices during blanching was studied first. Figure 1 shows the temperature graphs of the surface and of the center of the potato slices when heated for 15 min at 76°C, and then chilled at 10°C. The surface of the potato slices reached the temperature of the water bath after about 11 min, while it took 15 min before the center of the slices reached 75.5°C.

In the oxidation studies, 5- and 15-min intervals of blanching were chosen. After 5 min the temperature at the surface had reached 69°C and the center of the slices only 50°C, while after 15 min the whole potato slice had reached approximately 76°C. Ten minutes of chilling was chosen for the experiments. During this period all samples were chilled to below 15°C.

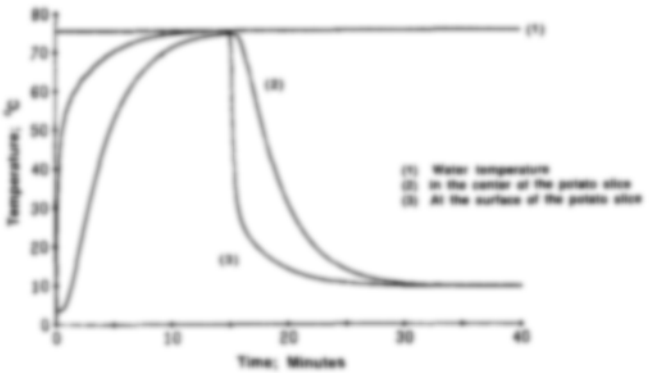

FIG. 1. The change in temperature at the surface and in the center of a potato slice put in a blanching bath at 76°C for 15 min and then transferred to a chilling bath at 10°C.

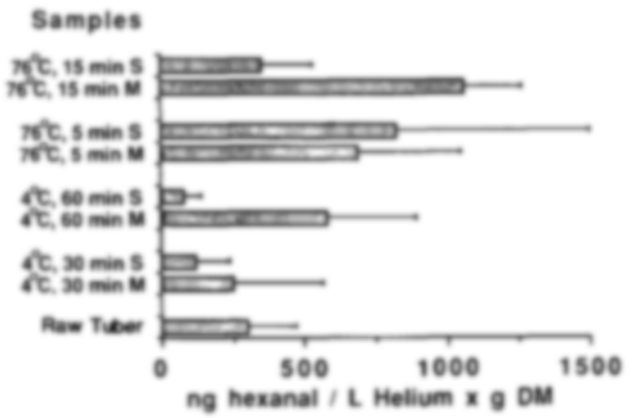

FIG. 2. The formation of hexanal at the surface and in the middle of potato slices. (M = middle; S = surface). The potato slices were kept either at 4°C in air for 30 or 60 min or in water of 76°C for 5 or 15 min, followed by chilling in ice for 10 min. "Raw tuber" refers to the initial hexanal content.

Formation of hexanal. Hexanal is a volatile compound which is very often used as an indicator of lipid oxidation in food and in model systems. It was also found to be the most abundant aldehyde formed in this study. Hexanal is mainly formed from hydroperoxides of n-6 fatty acids, such as the 13-hydroperoxide of linoleic acid (7). The formation of hexanal in this study is shown in Figure 2.

The main cause of lipid oxidation is probably the potato enzyme, lipoxygenase, which catalyzes the oxidation of linoleic acid to 9-hydroperoxyoctadecadienoic acid (8). The 9-hydroperoxide isomer makes up 95% of the hydroperoxy product, the other 5% formed is the 13-hydroperoxide isomer. Chan *et al.* (9) reported that the 9-hydroperoxyoctadecadienoic acid can be isomerized to the 13-hydroperoxide isomer at 40°C.

The lipolytic enzymes of potato cause an immediate and rapid hydrolysis of fatty acids from the lipids when the potato tissue is disrupted (10). The enzymes, lipolytic acyl hydrolase and lipoxygenase, have shown some activity even at 0°C (8,11). Therefore, it is practically impossible to obtain no volatile compounds when analyzing raw tubers. Consequently, the hexanal concentration of the

raw tuber shown in Figure 2 may, at least partly, be an artifact. Some enzymatic oxidation may have occurred when the potato was cut and before the enzymes were heat-inactivated during the boiling. It is also possible that further nonenzymatic oxidation occurred due to air exposure during the chilling and homogenization steps prior to the headspace sampling, where the slurry came under helium atmosphere. To minimize this oxidation, all sample preparation steps were performed as quickly as possible throughout this study. All procedures were standardized, so significant differences from the hexanal content in raw tuber in Figure 2 correspond to an actual formation or loss of hexanal during the time/temperature treatment indicated.

As shown in Figure 2, the hexanal concentration did not increase at the low temperature (4°C) during the first 30 min. On the contrary, the amount of hexanal near the surface of the potato slices decreased. After 60 min a further decrease of the hexanal concentration near the surface can be noticed. From these results, it is impossible to tell whether any oxidation took place at this low temperature. It cannot be excluded that the oxidation and hexanal formation were slower than the hexanal losses by, for instance, evaporation or further reactions.

But, after 60 min at 4°C, hexanal was formed in the middle of the 2-cm thick potato slices. This is surprising since potatoes can be stored for long times at this temperature. However, in the intact potato the oxygen content is probably very low due to respiration and limited oxygen diffusion. In this experiment, obvious drying and darkening of the surface of the slices were noticed after one hour. It is very probable that oxygen, for example, or components from the damaged surface had diffused into the center, activating the lipolytic enzymes or otherwise making the oxidation possible. In any case, this indicates that lipid oxidation may be relevant in sliced tuber tissue even at this low temperature.

After 5 min in water at 76°C, a substantial hexanal formation was noted, with slightly more at the surface than in the middle of the slices. After 15 min, a further increase of the hexanal concentration was observed in the middle of the slices, while the concentration at the surface had markedly decreased. This indicates that the hexanal formed at the surface was either leaking into the blanching water or possibly reacting further.

Lipoxygenase has a temperature optimum between 50°C and 60°C, and in potato strips (10 × 8 mm) there is reported to be less than 2% activity left after 6 min at 70°C (12). This means that after 15 min at the blanching temperature (76°C) the enzyme should be inactivated, at least at the surface. During subsequent chilling there should be no more enzymatic degradation of the lipids, so that any hexanal which was formed may leak into the blanching water. After blanching for only 5 min there is probably still enzyme activity left, even near the surface of the slices. Therefore, the formation of hexanal could continue during chilling, while at the same time there could be hexanal loss to the surrounding water. But, even after 15 min there could still be some enzyme activity remaining in the middle of the slices, which could continue to oxidize the lipids further during the chilling period. In any case, the formation of hexanal demonstrates that the lipids are obviously oxidized during the blanching process.

Formation of other aldehydes. Other volatiles also were found in the potato slices. Figures 3A and 3B show the aldehydes found in the largest amounts in the raw tuber besides hexanal. These were pentanal, heptanal and 2-heptenal. Pentane, another well-known lipid oxidation product, also was present. Octanal, 2-nonenal, nonanal and decanal were found in smaller amounts. They are shown in Figures 4A and 4B. Two products of the Maillard reaction, 2- and 3-methyl-butanal (13) also were found. During blanching, the content of 2-methyl-butanal increased slightly, but the data are not shown.

The development of these other aldehydes showed no fully uniform pattern, but several similarities with that of hexanal can be noticed. The concentration of all of the aldehydes (except nonanal at 4°C) increased in the middle of the slices during 60 min at 4°C and 15 min at 76°C. In a few cases, however, there was first a drop in the aldehyde concentration (decanal at 4°C and nonanal at 76°C). At 76°C the behavior of pentanal, octanal and decanal at the surface of the potato slices resembled that of hexanal. The concentration increased during the first 5 min, but had decreased again after 15 min. At 4°C the concentration of most of the volatile aldehydes at the surface went through a maximum in a similar way. The reason for this was probably the same as that discussed for hexanal: a balance between the formation and the losses of aldehydes. Most of these aldehydes were likely produced as a result of lipid oxidation. For instance,

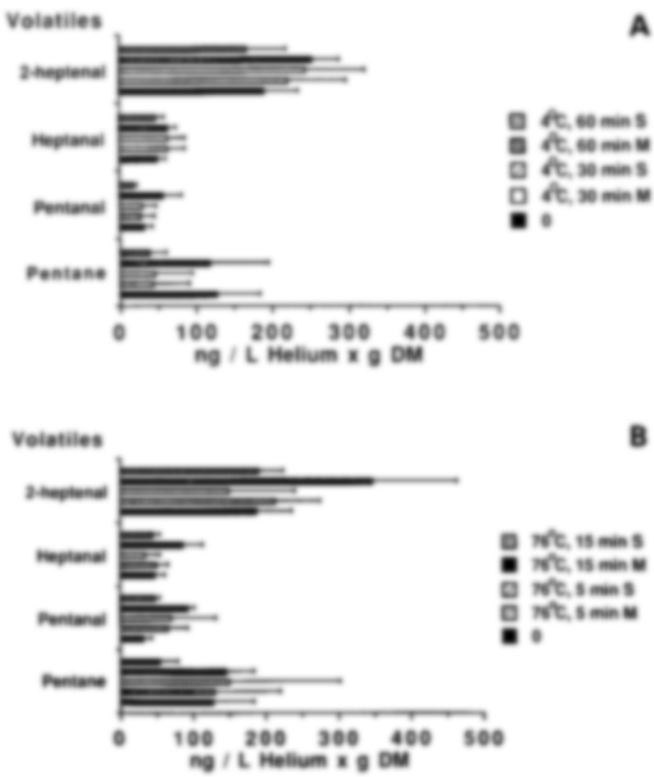

FIG. 3. The formation of 2-heptenal, heptanal, pentanal and pentane at the surface and in the middle of potato slices. (M = middle; S = surface). The filled bars indicate the initial concentrations. (A) The potato slices were kept at 4°C in air for 30 or 60 min. (B) The potato slices were kept in water of 76°C for 5 or 15 min followed by chilling in ice for 10 min.

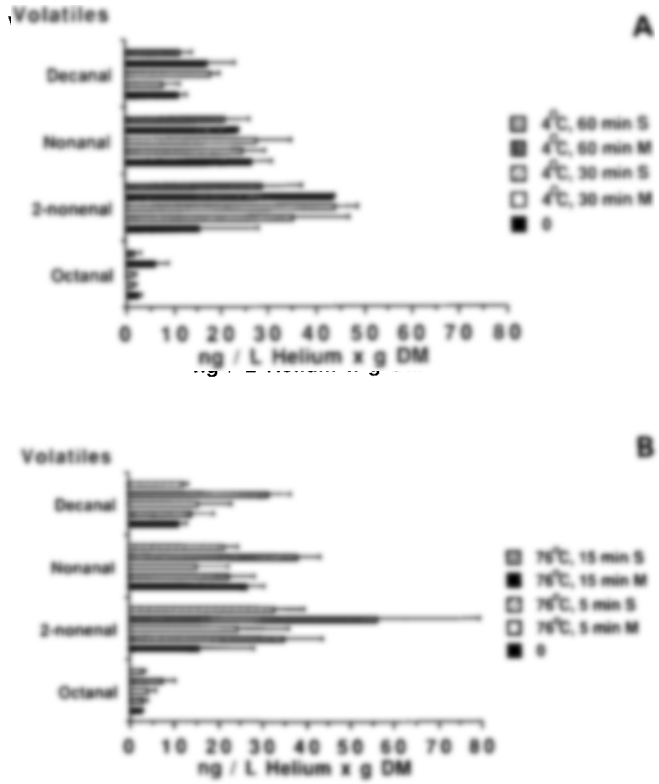

FIG. 4. The formation of decanal, nonanal, 2-nonenal and octanal at the surface and in the middle of potato slices. (M = middle; S = surface). The filled bars indicate the initial concentrations. (A) The potato slices were kept at 4°C in air for 30 or 60 min. (B) The potato slices were kept in water of 76°C for 5 or 15 min followed by chilling in ice for 10 min.

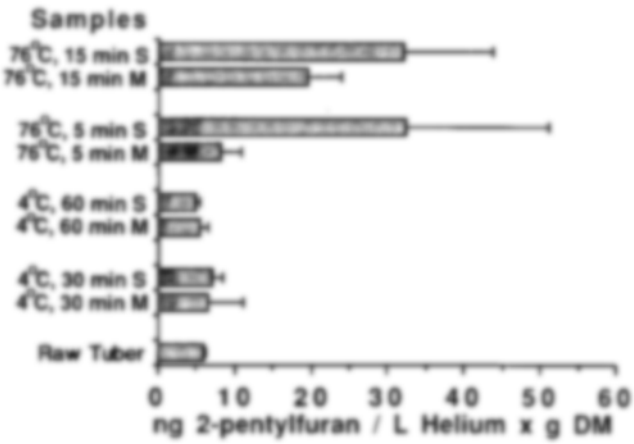

FIG. 5. The formation of 2-pentylfuran at the surface and in the middle of potato slices. (M = middle; S = surface). The potato slices were either kept at 4°C in air for 30 or 60 min or kept in water of 76°C for 5 or 15 min followed by chilling in ice for 10 min. "Raw tuber" refers to the initial 2-pentylfuran content.

2-nonenal is formed from the 9-hydroperoxyoctadecadienoic acid (7).

Formation of 2-pentylfuran. Buttery *et al.* (14) reported that the major volatile compound obtained at atmospheric pressure from potato oil was found to be 2-pentylfuran. One way to form this compound is by autoxidation of linoleic acid (15). It was also reported to increase greatly in boiled potatoes during warm-holding (16).

The formation of this compound in our experiment is shown in Figure 5. The raw tubers contained only a small amount of 2-pentylfuran, and at low temperature almost no further formation of this compound could be detected. However, at the elevated temperature there was an increase both in the middle and at the surface of the slices.

In contrast to the aldehydes, 2-pentylfuran was not found to decrease at the surface. This may be due to higher stability or lower water solubility as compared with the aldehydes. Actually, the concentration of 2-pentylfuran was higher at the surface than in the middle of the slices after both 5- and 15-min intervals of heating. This supports the assumption that the lipid oxidation is actually more pronounced at the surface of the slices, where the cell membranes have been disrupted and the oxygen availability is the highest.

In conclusion, it is obvious that lipid oxidation occurred in our model system and most likely will occur at least in the blanching step of the industrial potato granule process. Lipid oxidation has rarely before been demonstrated as early as during the actual food processing. Oxidation initiated during the process may continue during the storage of the final product and should influence the storage stability. It is, therefore, very important to take measures to protect against lipid oxidation early, even during food processing.

ACKNOWLEDGMENTS

The project was supported by grants from AB Felix, Sweden, and by the National Swedish Board for Technical Development. The authors also want to thank Claes-Göran Andersson for his help with the temperature measurements.

REFERENCES

1. Galliard, T., *J. Sci. Food Agric. 24*:617 (1973).
2. Galliard, T., and J.A. Matthew, *Ibid. 24*:623 (1973).
3. Buttery, R.G., C.E. Handel and M.M. Boggs, *J. Agric. Food Chem. 9*(3):245 (1961).
4. Lilja, M., and H. Lingnert, *Food Chem. 34*:1 (1989).
5. Lilja Hallberg, M., *J. Am. Oil Chem. Soc. 67*:784 (1990).
6. Hall, G., J. Andersson, H. Lingnert and B. Olofsson, *J. Food Quality 7*:153 (1985).
7. Frankel, E.N., in *Flavor Chemistry of Lipid Foods,* edited by D.B. Min, and T.H. Smouse, American Oil Chemists' Society, Champaign, IL, 1989, p. 1.
8. Galliard, T., and D.R. Phillips, *Biochem J. 124*:431 (1971).
9. Chan, H.W.-S., C.T. Constantine, F.A.A. Prescott and P.A.T. Swoboda, *Biochim. Biophys. Acta 398*:347-350 (1975).
10. Galliard, T., *Phytochem. 9*:1725 (1970).
11. Pun, W.H., A.A. Khan, I. Chung, M. Haydar and D. Hadziyev, *Pot. Res. 23*:57 (1980).
12. Fretzdorff, B., W. Bergthaller and B. Putz, *Ibid. 31*:25 (1988).
13. Buttery, R.G., and R. Teranishi, *J. Agric. Food Chem. 11*:504 (1963).
14. Buttery, R.G., R.M. Seifert and L.C. Ling, *Ibid. 18* :539 (1970).
15. Ho, C-T., M.S. Smagula and S.S. Chang, *J. Am. Oil Chem. Soc. 55*:233 (1978).
16. Karlström, B., Quality Changes During Warm-Holding of Foods in Catering Establishments, (in Swedish), Ph.D. Thesis, Chalmers University of Technology, Göteborg, Sweden, 1982.

[Received December 13, 1989; accepted November 2, 1990]