Comparison of Flavor Compounds of Potato Chips Fried in Palmolein and Silicone Fluid

Fiona L. Martin and Jennifer M. Ames*

School of Food Biosciences, The University of Reading, Reading RG6 6AP, United Kingdom

ABSTRACT: The importance of the frying oil as a heat-transfer medium and as a source of flavor precursors for the formation of potato chip flavor was investigated. Potato slices were fried in palmolein or silicone fluid, and the volatile flavor compounds of the resulting chips were isolated onto Tenax and analyzed by gas chromatography–mass spectrometry. Although the heat-transfer coefficients of the oils did not differ significantly, their temperature profiles during frying were different, probably due to greater turbulence on placing potato slices in palmolein, leading to more efficient heat transfer. Levels of Strecker aldehydes and sulfides in chips fried in the two media were not significantly different, but levels of pyrazines were significantly higher in palmolein-fried chips. Amounts of 2,4-decadienal were also significantly higher in palmolein-fried chips, but there was no significant difference in hexanal levels between the samples.

Paper no. 9915 in *JAOCS 78*, 863–866 (August 2001).

KEY WORDS: Aroma, flavor, model system, oil, palmolein, potato chips, potato crisps, pyrazines, silicone fluid, Strecker aldehydes.

Potato chips (also known as potato crisps) are prepared by deep-fat frying potato slices. Chip flavor is affected by factors including potato tuber composition, frying oil composition, and temperature and time of frying (1).

Reports of the flavor components of potato chips have been reviewed by Whitfield and Last (2) and Maga (3). About 60 of the approximately 150 volatile compounds identified come mainly from lipid degradation, with the polyunsaturated fatty acids of the frying oil likely to be their main precursors. Some authors have studied the effect of oil type (4) and composition (5) on potato chip flavor, but the relative importance of the frying oil in flavor development, i.e., as a heat-transfer medium or as a source of flavor precursors, has not been reported. The aim of the current study was to investigate the role of the frying oil in flavor development in potato chips by comparing the flavor compounds formed by frying in palmolein and silicone fluid.

EXPERIMENTAL PROCEDURES

Materials and reagents. Potatoes, cultivar Saturna, specific gravity range 1.086–1.096, palmolein, and metalized laminate chip bags were provided by United Biscuits (Billingham, United Kingdom). Silicone fluid, 200/20cS (Dow Corning®, Midland, MI) and petroleum ether (boiling point 40–60°C, general purpose reagent) were from BDH (Poole, United Kingdom). 1,2-Dichlorobenzene (min. 98%) was from Aldrich (Gillingham, United Kingdom). High-purity water was produced in-house using a Purite (High Wycombe, United Kingdom) Labwater RO50 unit and was used throughout.

Measurement of convective heat transfer. Measurements were based on the lumped capacity analysis described by Miller *et al.* (6). A Séléction (Magimix, Paris, France) professional system deep-fat fryer was connected to an external thermostat, allowing the temperature to be controlled to ±1°C. Measurements were obtained using each frying medium at 160, 170, and 180°C in triplicate. The oil was held at the set temperature for 20 min and stirred mechanically to ensure even heating. Then the mechanical stirrer was switched off, and an aluminum (alloy 2024) transducer (1.43 cm diameter) was lowered into the oil. The temperature of the transducer was recorded until it had reached the oil temperature. It was then removed from the oil, cooled to room temperature, and rinsed with petroleum ether to prevent the surface from becoming coated with oil, prior to the taking the next set of measurements.

The heat-transfer coefficient (h) was related to the measured time temperature data by Equation 1:

$$\ln\left(\frac{T_o - T_m}{T - T_m}\right) = h \times \frac{3t}{\rho C_p r} \qquad [1]$$

where T is the transducer temperature (°C) at time t (s), T_m is the oil temperature (°C), T_o is the initial transducer temperature (°C), ρ is the density of aluminum (kg/m^3), C_p is the specific heat of aluminum (J/kg °C), r is the radius of the aluminum transducer (m), and h is the heat-transfer coefficient (W/m^2 °C). Plots of $\ln[(T_o - T_m)/(T - T_m)]$ against $3t/\rho C_p r$ had a gradient, h. The linear region of the plots (transducer temperature = 20–80% of the oil temperature) was used to calculate h.

Preparation of potato slices. Potatoes were washed, peeled, sliced (1.4 ± 0.1 mm), rinsed in cold water for 2 min, and stored in water at room temperature (max. 1 h) before use. They were blotted on paper towels to remove excess surface water prior to weighing and frying.

Frying procedure. Palmolein or silicone fluid (3 L) was heated to 180°C for 20 min in the deep-fat fryer before use. The fryer was switched off as the slices (25 g) were placed in the frying medium and remained off throughout frying (2.5 min). Fried slices (chips) were drained and cooled on paper towels before sealing in chip bags. About 20 batches of potato slices were fried in each medium on the same day, and there was little difference in flavor compound profile between the first and last batch. Chips from the different batches fried in each medium were thoroughly mixed prior to analysis.

---

*To whom correspondence should be addressed at School of Food Biosciences, The University of Reading, Reading RG6 6AP, United Kingdom. E-mail: j.m.ames@afnovell.reading.ac.uk

Measurement of temperature profile of the oil during frying. The temperature of the oil during frying was monitored using a KM 330 digital thermometer with a general-purpose liquid immersion probe (Fisher, Loughborough, United Kingdom). The oil temperature was recorded every 30 s during frying.

Oil content of chips. Crushed chips (5 g) were extracted with petroleum ether for 4 h in a Soxhlet apparatus. Extracted oil was weighed after removal of solvent. Extractions were performed in triplicate.

Preparation and gas chromatography–mass spectrometry (GC–MS) of flavor isolates. Crushed chips (10 g) and water (40 mL) were placed in a 250-mL conical flask fitted with a Dreschel head and located in a 37°C water bath. 1,2-Dichlorobenzene in methanol (130.6 µg/mL, 1 µL) was injected onto a Tenax trap, (155 mm long, 3 mm i.d.), containing 85 mg Tenax TA (SGE, Milton Keynes, United Kingdom) and fitted at the exit of the conical flask. Volatile compounds were collected by passing nitrogen at 40 mL/min over the sample for 1 h. The Tenax trap was then connected directly to the nitrogen supply for 5 min to remove any residual water. Blank isolates were prepared using water (40 mL) in the sample flask.

Analyses were performed using a Hewlett-Packard HP 5890 series II gas chromatograph connected to an HP 5972 series mass selective detector (Palo Alto, CA). System control and data acquisition and analysis were achieved using an HP ChemStation. The fused-silica column (60 m long, 0.25 mm i.d.) was coated with a 0.25 µm film thickness of CP-Sil8 (Chrompak, London, United Kingdom). Helium at 1.5 mL/min was the carrier gas. With the GC oven switched off, the first 0.5 m of the column was cooled in solid CO_2 for 4 min. The Tenax trap was placed into the concentrated headspace injection system thermal desorption port (SGE) of the GC (heated to 280°C), and the desorbed volatiles were cryofocused onto the front of the column. After 5 min, the CO_2 was removed and the column temperature was raised to 40°C and held for 2 min, followed by a 4°C/min increase to 200°C, a 10°C/min increase to 250°C, and holding at 250°C for 15 min. The inlet purge came on when the temperature program began and backflushed the Tenax trap. Mass spectra were recorded in the electron impact (EI) mode, with an ionization current of 50 µA, a source temperature of 165–175°C, and a mass scan range of 32–450 *m/z* with 1.82 scans/s. Linear retention indices (LRI) for the volatile compounds were calculated with reference to a standard mixture of *n*-alkanes (C_6–C_{22}), run under the same conditions. Identifications of components were made by comparing mass spectra and LRI with those of authentic compounds held on laboratory databases and reported in the literature (7–9). Where both mass spectra and LRI data agreed with those in the literature, identities were considered to be positive. Where only mass spectral data were available, identities were considered to be tentative. Relative amounts of volatile compounds were calculated by reference to the internal standard (1,2-dichlorobenzene).

Statistical analysis. Data were analyzed using Student's *t*-test (Excel 2000; Microsoft, Redmond, WA).

RESULTS AND DISCUSSION

Silicone fluid was chosen as an alternative frying medium to palmolein since it is inert, odorless, stable at the temperatures used for this study, and contributes no spurious peaks to the GC–MS trace. The viscosity of a liquid affects its heat-transfer properties and, at 180°C, the particular silicone fluid chosen had a viscosity very similar to that of palmolein, i.e., ~3 mm^2/s.

Temperature profiles and heat-transfer coefficient of the frying media. The temperatures of the palmolein and silicone fluid taken every 30 s during frying are shown in Table 1. The difference in temperature of the two frying media was significant at 120 s ($P < 0.05$) and at 30 and 150 s ($P < 0.01$). The initial drop in temperature was greater for palmolein, but the temperature was lower for silicone fluid during the final stage of frying. Therefore, the potato slices were not exposed to exactly the same temperature profiles during frying in the two media.

Table 2 gives *h* for palmolein and silicone fluid at 160, 170, and 180°C. Values of *h* obtained for the two media and the different temperatures were not significantly different ($P > 0.05$) and were similar to those reported for various oils, including palm oil (6). Small increases in *h* have been reported for various food-grade oils heated to frying temperatures (6,10).

The values for *h* do not account for the different temperature profiles observed for the two frying media. When potato slices were fried, vigorous bubbling was observed in palmolein whereas the silicone fluid foamed, due to the interaction of water from the potato slices with the frying media. Thus, greater turbulence occurred in palmolein than in silicone fluid during frying. This would be expected to result in higher values for *h*, as well as well as higher internal chip temperature, during frying in palmolein. It is reported that, during frying of potato slices, *h* is related to the rate of water loss from the potato (11) and to the formation of bubbles of water vapor (12).

Oil content of chips. The oil content of chips was 38.2 ± 0.1 and 41.7 ± 1.4 g/100 g, respectively, when silicone fluid and palmolein were used for frying. This difference was statistically significant ($P < 0.05$).

Appearance of chips. Batches of chips fried in the different media had a crispy texture, a pale yellow color and were visually indistinguishable from each other.

Analysis of flavor compounds. Relative amounts (RA) of all monitored compounds are given in Table 3. Amounts of Strecker aldehydes and sulfur compounds did not differ sig-

TABLE 1
Temperature (°C) of Palmolein and Silicone Fluid During Frying[a]

	Time (s)					
	0	30	60	90	120	150
Palmolein	180.3	166.2	163.6	162.1	161.3	161.0
Silicone fluid	180.3	168.7	164.4	161.8	159.8	158.5
Level of significance[b]	NS	**	NS	NS	*	**

[a] Standard deviation <6% for 10 replicate experiments.
[b] Level of significance determined using Students *t*-test; NS, not significant; *$P < 0.05$; **$P < 0.01$.

TABLE 2
Heat Transfer Coefficient, *h* (W/m^2 °C) of Palmolein and Silicone Fluid in the Temperature Range 160–180°C[a]

	Temperature (°C)		
	160	170	180
Palmolein	250.72	249.40	258.60
Silicone fluid	238.90	242.65	241.85

[a]No significant difference ($P > 0.05$) between frying media or temperatures (Students *t*-test). Three replicate experiments. Standard deviation <11%.

nificantly between the frying media. Therefore, the potato provided all the precursors required for the formation of these compounds. Theoretically, α-dicarbonyls formed by lipid degradation could participate in the Strecker degradation of amino acids. If this did happen in the palmolein system, the effect on yields of Strecker aldehyes was not significant. The palmolein and silicone fluid acted as heat transfer media, and the different heating characteristics of the two oils had no significant effect on levels of the monitored Strecker aldehydes and sulfur compounds.

RA of all of the pyrazines were significantly lower when potato slices were fried in silicone fluid (Table 3), the total RA being 41.5% of that for chips fried in palmolein. However, yields of 6 of the 10 pyrazines, as a percentage of the total pyrazine amount (%RA), were more similar in the two frying media, significant differences being obtained for only four of them (Fig. 1). The data suggest that the reaction pathways leading to pyrazine formation in palmolein and silicone fluid are the same, and palmolein does not provide a source of flavor precursors. However, the kinetics of pyrazine formation appear to be different, probably due to differences in heat transfer experienced by the potato slices. Temperature greatly affects the rate of formation of pyrazines (13), and frying temperature greatly affects yields of pyrazines in potato chips (14). Therefore, a lower potato temperature in the silicone fluid, due to a lower *h* during frying, could account for the lower RA values obtained for pyrazines in this frying medium (Table 3). Also, the temperature of silicone oil was lower than that of palmolein during the last minute of frying (Table 1). Thus, it appears that small differences in the thermal properties of the frying medium can have a significant effect on levels of pyrazines in potato chips while not signifiantly affecting levels of Strecker aldehydes and sulfides. Parker *et al.* (15) reported that amounts of pyrazines in extruded debranned oat flours increased ~3.5–5.0-fold when the extrusion temperature was increased from 150 to 180°C, while levels of Strecker aldehydes increased ~1.4–2.6-fold over the same temperature range.

Levels of three products of lipid oxidation were monitored (Table 3). Chips fried in silicone fluid contained hexanal, whereas (*E,Z*)- and (*E,E*)-2,4-decadienal, in addition to hexanal, were identified in palmolein-fried chips. Potato contains 0.2% lipid on a fresh weight basis (16), and linoleic acid accounts for 52–60% of the total fatty acids (17). Lipoxygenase-mediated oxidation of linoleic acid in potato tissue (which would occur in potato slices before frying) yields the 9- and 13-hydroperoxides in the ratio 95:5 (18). These hydroperox-

TABLE 3
Relative Amounts[a] **of Selected Flavor Compounds Formed in Potato Slices Fried in Palmolein or Silicone Fluid**

			Frying medium		
Compound	LRI exptl.[b]	LRI lit.[c]	Palmolein	Silicone fluid	Level of significance[d]
Methylpropanal		552	649.8	548.9	NS
3-Methylbutanal	671	655	941.6	948.5	NS
2-Methylbutanal	680	665	1227.2	1156.2	NS
Phenylacetaldehyde	1063	1066	50.7	57.3	NS
Methional		924	3.6	2.9	NS
Dimethyl disulfide	753	744	196.5	167.8	NS
Dimethyl trisulfide	989	990	13.0	20.5	NS
Pyrazine			1.1	0.6	**
Methylpyrazine	836	833	53.7	19.1	**
2,5(6)-Dimethylpyrazine	924	925	74.8	28.0	**
Ethylpyrazine	927	930	22.9	10.4	**
2,3-Dimethylpyrazine	930	932	9.0	4.0	***
Vinylpyrazine	946	948	3.8	2.1	*
2-Ethyl-6-methylpyrazine	1009	1010	16.9	6.2	**
2-Ethyl-5(3)-methylpyrazine	1014	1016	54.8	24.2	**
2-Vinyl-6-methylpyrazine	1033	1034	9.2	5.5	
3-Ethyl-2,5-dimethylpyrazine	1086	1086	32.4	15.5	***
Hexanal	808	795	40.1	62.2	NS
(*E,Z*)-2,4-Decadienal			40.2	0.4	***
(*E,E*)-2,4-Decadienal	1335	1317	105.6	ND[e]	***

[a]Amounts of components are quoted in gas chromatographic (GC) peak area units relative to an internal standard (see the Experimental Procedure section). Figures quoted are the means of triplicate analyses. Coefficient of variation: <25%.
[b]Calculated linear retention indices (LRI) for identified components.
[c]LRI values obtained for authentic compounds analyzed on the same GC column or from the literature (9,18).
[d]See Table 1, footnote *b*.
[e]Not detected.

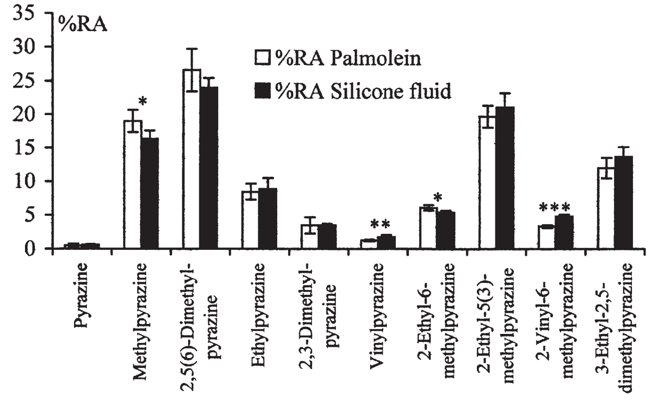

FIG. 1. Percentage relative amount (%RA) values for pyrazines in chips fried in palmolein or silicone fluid. Error bars represent the standard deviation. Significant differences indicated by *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$.

ides will continue to form nonenzymatically from linoleic acid, once frying has begun. Hexanal is formed from linoleic acid *via* the 13-hydroperoxide (19), and potato lipid must be the source of hexanal in the silicone fluid-fried chips. 2,4-Decadienal is also formed from linoleic acid, but *via* the 9-hydroperoxide (19), and its virtual absence in the chips fried in silicone fluid requires an explanation. Hexanal is the predominant product of autoxidized 2,4-decadienal (20), and it would appear that 2,4-decadienal, formed from linoleic acid in potato tissue, is converted to hexanal during frying of potato slices. The rate of oxidation of 2,4-decadienal to hexanal would be expected to be greater than that of linoleic acid to 2,4-decadienal (21), accounting for only trace levels of 2,4-decadienal in the chips fried in silicone fluid. The presence of linoleic acid in palmolein at 11.8% (mass/mass) of the total fatty acids (22) accounts for the significantly higher levels of (*E,Z*)- and (*E,E*)-2,4-decadienal in chips fried in that medium.

The vastly reduced amounts of 2,4-decadienals in the potato slices fried in silicone fluid would be expected to result in much less intense "fried" odors, including those relating to fried potato products, such as chips. Differences in levels of alkylpyrazines between chips fried in the two media were less pronounced, and odor threshold values of pyrazines are often several orders of magnitude greater than those of the 2,4-decadienals (2). Nevertheless, the lower levels of pyrazines in chips fried in silicone fluid would be expected to result in less intense notes, such as "baked" and "nutty." Thus, the higher observed levels of 2,4-decadienals and pyrazines in the palmolein-fried chips would be expected to result in a considerable flavor improvement, compared to chips fried in silicone fluid, the effect being most marked for the 2,4-decadienals.

ACKNOWLEDGMENTS

Lisa Bates and Ian Steedman (United Biscuits) are thanked for many helpful discussions and suggestions. We thank Pedro Bouchon for advice and assistance and Andrew Dodson for expert technical assistance. The Biotechnology and Biological Sciences Research Council (UK) and United Biscuits (UK) funded this project *via* a studentship (to FLM).

REFERENCES

1. Smith, O., Potato Chips, in *Potato Processing,* 3rd edn., edited by W.F. Talburt and O. Smith, AVI, Westport, CT, 1975, pp. 305–402.
2. Whitfield, F.B., and J.H. Last, Vegetables, in *Volatile Compounds in Foods and Beverages*, edited by H. Maarse, Marcel Dekker, New York, 1991, pp. 223–281.
3. Maga, J.A., Potato Flavor, *Food Rev. Int. 10*:1–48 (1994).
4. Hawrysh, Z.J., M.K. Erin, and R.T. Hardin, Quality and Stability of Potato Chips Fried in Canola, Partially Hydrogenated Canola, Soybean, and Cottonseed Oils, *J. Food Qual. 19*: 107–120 (1996).
5. Warner, K., P. Orr, and M. Glynn, Effect of Fatty Acid Composition on Flavor and Stability of Fried Foods, *J. Am. Oil. Chem. Soc. 74*:347–356 (1997).
6. Miller, K.S., R.P. Singh, and B.E. Farkas, Viscosity and Heat-Transfer Coefficients for Canola, Corn, Palm, and Soybean Oils, *J. Food Process. Preserv. 18*:461–472 (1994).
7. NIST/EPA/MSDC, Mass Spectral Database (versions for PC and for Mass Spectrometer Database Systems), Office of Standard Reference Data of the National Institute of Standards and Technology, Gaithersburg, 1992.
8. Adams, R.P., *Identification of Essential Oil Components by Gas Chromatography–Mass Spectroscopy*, Allured Publishing Corporation, Carol Stream, IL, 1995.
9. Kondjoyan, N., and J.-L. Berdague, *A Compilation of Relative Retention Indices for the Analysis of Aromatic Compounds,* edited by Laboratoire Flaveur, 1st edn., INRA, Dijon, France, 1996.
10. Sahin, S., S.K. Sastry, and L. Bayindirli, The Determination of Convective Heat-Transfer Coefficient During Frying, *J. Food Eng. 39*:307–311 (1999).
11. Costa, R.M., F.A.R. Oliviera, O. Delaney, and V. Gekas, Analysis of the Heat-Transfer Coefficient During Potato Frying, *J. Food Eng. 39*:293–299 (1996).
12. Sahin, S., S.K. Sastry, and L. Bayindirli, Heat Transfer During Frying of Potato Slices, *Lebensm. Wiss. Technol. 32*:19–24 (1999).
13. Jusino, M.G., C.T. Ho, and C.H. Tong, Formation Kinetics of 2,5-Dimethylpyrazine and 2-Methylpyrazine in a Solid Model System Consisting of Amioca Starch, Lysine and Glucose, *J. Agric. Food Chem. 45*:3164–3170 (1997).
14. Maga, J.A., and C.E. Sizer, Flavour Preferences for Potato Chips as Influenced by Time and Temperature of Chipping and Total Pyrazine Concentration, *Lebensm. Wiss. Technol. 11*:181–182 (1978).
15. Parker, J.K., G.M.K. Hassell, D.S. Mottram, and R.C.E. Guy, Sensory and Instrumental Analyses of Volatiles Generated During the Extrusion Cooking of Oat Flours, *J. Agric. Food Chem. 48*:3497–3506 (2000).
16. Paul, A.A., and D.A.T. Southgate (eds.), *McCance and Widdowson's The Composition of Foods*, HMSO, London, United Kingdom, 1978.
17. Galliard, T., Lipids of Potato Tubers I. Lipid and Fatty Acid Composition of Tuber from Different Varieties of Potato, *J. Sci. Food Agric. 24*:617–622 (1973).
18. Galliard, T., and D.R. Phillips, Lipoxygenase from Potato Tubers, *Biochem. J. 124*:431–438 (1971).
19. Frankel, E.N., Lipid Oxidation, *Prog. Lipid. Res. 22*:1–22 (1980).
20. Matthews, R.F., R.A. Scanlan, and L.M. Libbey, Autoxidation Products of 2,4-Decadienal, *J. Am. Oil Chem. Soc. 48*:745–747 (1971).
21. Lilliard, D.A., and E.A. Day, Degradation of Monocarbonyls from Autoxidizing Lipids, *Ibid. 41*:549–552 (1964).
22. Hammond, E.W., *Chromatography for the Analysis of Lipids*, CRC Press, Boca Raton, FL, 1993.

[Received March 5, 2001; accepted May 3, 2001]