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Comparison of volatiles in raw and boiled potatoes using a mild extraction technique combined with GC odour profiling and GC–MS

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Aromas of raw and boiled potatoes were compared using a mild extraction technique, ensuring preservation of the very labile composition of potato aroma during analysis. The extracts were evaluated by GC–MS and GC-sniffing using a panel of four judges. A total of 29 compounds were identified by GC–MS in raw potatoes and 25 in boiled. Twenty compounds were found in both raw and boiled potatoes, but most often in very different concentrations. During GC-sniffing, 33 odours were detected in boiled, and 27 in raw potatoes. Eight odours corresponded to compounds identified by GC–MS. Another four odours could be tentatively identified. It is concluded that the change in aroma during boiling of potatoes depends on compounds from lipid oxidation as well as compounds from other types of reactions, for instance the Strecker-degradation. © 1998 Elsevier Science Ltd. All right reserved

INTRODUCTION

The aroma of boiled potatoes is rather weak but distinct and very different from the aroma of raw potatoes. Raw potatoes have a very high content of lipoxygenase, which catalyzes the oxidation of unsaturated fatty acids (Galliard and Phillips, 1971). These reactions occur as soon as cells are disrupted (Galliard and Matthew, 1973), for instance by peeling or cutting, and may lead to the production of a number of potent aroma compounds (Hsieh, 1994). Enzymatic reactions can also occur during boiling of potatoes, probably in a moving zone of damaged tissue between the cool centre and the hot, outer layer where enzymes have been inactivated (Josephson and Lindsay, 1987).

In earlier studies on aroma of potatoes, the Likens–Nickerson method has often been used (Nursten and Sheen, 1974; Buttery *et al.*, 1970). However, this method includes boiling of the sample, often for 1 h or more, and differences between raw and boiled potato aroma will be difficult to detect. An alternative, often seen in more recent literature, is dynamic headspace sampling. This method, however, is reported to require either very long purge times (15 h at 21°C; Josephson and Lindsay, 1987) or purging at high temperature (1 h at 100°C; Salinas *et al.*, 1994), both enabling many different types of enzymatic and chemical processes to occur which disturb the differences in aroma pattern.

In the present study it was decided to use an extraction procedure, since it can be carried out at ambient temperature and does not require very long extraction times. When this procedure is combined with a sniffing technique like GC odour profiling, it is possible to describe the differences in aroma between raw and boiled potatoes.

The purpose of this study was therefore to identify and compare volatiles and odours in extracts of raw and boiled potatoes.

MATERIALS AND METHODS

All analyses were carried out on potatoes (*Solanum tuberosum*) of the variety Bintje grown in the same commercial field. From harvest till use (approximately 5 months) the tubers were stored at 4°C, either in a commercial store or in a 'Refritherm' in the lab without the use of sprout inhibitors. The potatoes had no visible sprouts at the time of analysis. The potatoes were analyzed raw and boiled (peeled and then boiled for 20 min at 100°C).

Extraction was carried out on watery suspensions of potatoes. Suspensions were prepared from 150 g of

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peeled shredded potato and 300 g of tap water to which was added internal standard (2 ml of a 50 μl litre^{-1} solution of 4-methyl-1-pentanol); this was homogenized for 30 s with an Ultra Turrax macerator. This ratio between potato and water ensured that both raw and boiled potatoes yielded suspensions of sufficiently low viscosity.

To ensure representativity of the sample, a minimum of five potatoes were shredded and mixed. Two hundred grams of suspension were gently treated with 100 ml diethyl ether/pentane (1:1), and extraction was carried out on a magnetic stirrer for 40 min. A 500 ml Erlenmeyer flask was used to increase surface area between the two phases. Stirring was done at a low rate (200 r.p.m.) to avoid mixing of the phases, since an emulsion would otherwise be created. After extraction the flask was put in the freezer overnight, and the non-frozen organic phase could then be easily poured off. Finally, the extract was dried by adding 1 g of Na_2SO_4, and concentrated to 50 mg by gently blowing nitrogen over the surface.

Separation and identification of volatiles in the extract was carried out on a Hewlett-Packard G1800A GCD System (GC–MS), while sniffing was done on a Hewlett-Packard 5890 GC equipped with an SGE Olfactory Detector Outlet ODO-1. Both instruments were equipped with Hewlett-Packard INNOWax columns (30 m×0.25 mm i.d., 0.25 μm film thickness). Two μl extract was injected and the temperature program was: 10 min at 40°C, increased to 240°C at 6°C min^{-1}, and held constant at 240°C for 25 min. The GC–MS system had a split ratio of 15:1 while splitless injection was used for sniffing.

For the analyses, four extracts of raw and four extracts of boiled potatoes were prepared. To obtain higher sensitivity the extracts were combined four and four and concentrated to 50 mg.

Each of the two combined extracts (raw and boiled potatoes) was analyzed twice by GC–MS, and sniffed by four judges using the GC odour profiling technique (Tønder *et al.*, 1997). The judges were familiar with aroma analysis, but not trained for potato aroma. They were instructed to note start time of each odour, description of the odour quality (using descriptors of their own choice) and to evaluate the intensity of the odour on a scale from 1 to 5. Each sniffing session continued for 40 min.

Since the FID-detector was detached on the sniffing-GC, standard mixtures containing a total of 20 aroma compounds were sniffed and analyzed by GC–MS. From the GC–MS runs retention indices were calculated, and the 20 compounds could then be used as references for calculation (linear interpolation) of retention indices of the odour signals detected by the judges.

From GC–MS data, compounds cannot readily be quantified, since different compounds in the same amount do not necessarily produce the same peak area in the 'Total Ion Chromatogram' (TIC). Nevertheless, relative areas were calculated from the TIC's (peak area divided by internal standard peak area), yielding expressions that can be compared within compounds, but not between compounds.

RESULTS AND DISCUSSION

Table 1 lists 29 compounds identified in the extracts from raw and boiled potatoes. All of the compounds identified with a high degree of certainty have already been found in potatoes (Josephson and Lindsay, 1987; Nursten and Sheen, 1974; Buttery *et al.*, 1970; Salinas *et al.*, 1994). The highest number of compounds was identified in the raw potatoes (25 vs 20 in boiled) and, of those appearing in both raw and boiled potatoes, the concentration was in general highest in the raw. The exceptions from this were: ethanol, pentanal, hexanal and (E)- 9-octadecene. Nine compounds (1-penten-3-one, heptanal, 2-methyl-1-butanol, 2-nonenal, propanoic acid, (E,Z)-2,6-nonadienal, phenylacetaldehyde, 2,4-nonadienal and benzyl alcohol) were found only in raw potatoes, while four compounds (nonanal, methional, heptadecane and nonadecane) were found only in boiled potatoes.

Josephson and Lindsay (1987) analyzed raw and boiled potatoes, using a dynamic headspace technique. It was found, in good agreement with the present study, that raw shredded potatoes contained relatively high amounts of the two isomers of 2,4-decadienal, of (E)-2-octenal and of hexanal, all being products of lipoxygenase-initiated reactions of unsaturated fatty acids, taking place soon after disruption of cells. Also in agreement with the present study, Josephson and Lindsay (1987) found that, after boiling, the concentrations of 2,4-decadienal and (E)-2-octenal decreased, while hexanal increased. These changes are due to degradation reactions where 2,4-decadienal is first broken down to (E)-2-octenal, which is subsequently converted to hexanal (Josephson and Lindsay, 1987).

Also, the following compounds, which all are found in highest concentration in raw potatoes, are reported to be products of lipoxygenase-initiated reactions in general: 1-penten-3-one (Gardner *et al.*, 1996), heptanal (Schieberle and Grosch, 1981), 2-pentyl furan (Ho and Chen, 1994), 1-pentanol (Sok and Kim, 1994), (E,E)-2,4-heptadienal (Ho and Chen, 1994) and (E,Z)-2,6-nonadienal (Josephson and Lindsay, 1987).

When concentration of a compound is lower in boiled potatoes it may be due to degradation during heat treatment or to less enzymatic activity since, in boiled potatoes, shredding was done after boiling, that is with enzymes inactivated.

However, very similar reactions take place due to autoxidation (not enzymatically catalyzed oxidation) of linoleate or linolenate (Sok and Kim, 1994). Products from autoxidation would be expected to be present in the highest concentration in boiled potatoes since the

Table 1. Compounds identified in extracts of raw and boiled potatoes

Retention time	Retention index	Compound	Identification MS[a]	Ref.[b]	Sniff[c]	Relative area[d] Raw	Boiled
3.63	950	Ethanol	*			.01	.03
3.89	963	2-Ethylfuran	vis	x		trace	trace
4.41	983	Pentanal	**	x		.03	.06
5.57	1019	1-Penten-3-one	**	x		.04	—
8.20	1079	Hexanal	**	x		.37	.49
13.88	1186	Heptanal	(*)	x	x	.02	—
15.16	1212	2-Methyl-1-butanol	**			.10	—
15.82	1233	2-Pentylfuran	**	x	x	.14	.02
16.72	1260	1-Pentanol	**			.13	.02
18.62	1317	(E)-2-heptenal	**	x	x	.09	.02
20.60	1390	Nonanal	*	x		—	.03
20.82	1398	?, m/z: 83 (100%), 70 (66%), 55 (56%),41 (52%), 29 (43%), 39 (33%)				.69	.01
21.47	1426	(E)-2-octenal	**	x	x	.65	.02
22.03	1450[e]	Methional	vis	x	x	—	.01
22.05	1451[e]	Acetic acid	**	x	x	.06	.03
22.97	1489	(E,E)-2,4-heptadienal	*	x		.03	.01
23.94	1535	2-Nonenal	vis	x		.02	—
24.26	1550	Propanoic acid	*	x		.005	—
25.02	1585	(E,Z)-2,6-nonadienal	vis	x	x	.01	—
26.11	1639	Phenylacetaldehyde	vis	x	x	.01	—
26.25	1646	(E)-9-Octadecene	**			.09	.24
26.91	1679	1-Methyl-2-pyrrolidinone	**			.51	.07
27.29	1698	Heptadecane	**	x		—	.16
27.33	1700	2,4-nonadienal	*	x		.03	—
28.55	1767	2,4-decadienal	*	x		.14	.03
29.37	1811	2,4-decadienal	**	x		.17	.04
30.04	1849	Hexanoic acid	*	x		.23	.05
30.59	1880	Benzyl alcohol	**			.15	—
30.95	1900	Nonadecane	**	x		—	.07

[a]** Quality index > 90, *quality index between 80 and 90, (*) quality index between 70 and 80, vis: agreement between largest peaks in mass spectrum by visual comparison with mass spectrum in library.
[b]Known reference compound gives same mass spectrum and retention index.
[c]An odour corresponding to descriptions of the suggested compound percieved by sniffing.
[d]Peak area relative to internal standard peak area in Total Ion Chromatogram (GC–MS).
[e]Methional and acetic acid can be separated during GC-sniffing, but coelute during GC–MS.The values given under 'relative area' are therefore not relative areas, but height of base peak in mass spectrum divided by height of base peak of internal standard.

higher temperature will accelerate the processes. This is reported to be the case with pentanal (Sok and Kim, 1994), and may well be the case for other compounds found in highest concentrations in boiled potatoes.

A third type of reaction is the Strecker-degradation of amino acids, leading to the corresponding aldehydes. For instance, phenylalanine and methionine will be converted to phenylacetaldehyde and methional, especially during heat treatment (Josephson and Lindsay, 1987). This fits well for methional, which is only found in boiled potatoes, and has a characteristic odour of boiled potato. Oppositely, phenylacetaldehyde is only found in raw potatoes, and this cannot readily be explained. Maga (1994) reports that phenylacetaldehyde has been found in both raw and boiled potatoes.

To our knowledge, no other studies have been conducted where a panel of judges evaluated the odour quality and intensity of potato extracts after separation on a GC-column. Josephson and Lindsay (1987), Nursten and Sheen (1974), and Mazza and Pietrzak (1990) carried out GC-sniffing on potato extracts, but no intensities were determined and the number of judges used was not reported.

Figure 1 shows that a total of 51 odour impressions were detected by two, three or all four of the judges. The highest number of odour impressions was seen in the extract from boiled potatoes (33 vs 27 in the raw). Nine odours were detected in both raw and boiled potatoes.

Eight odours could (by retention index and odour quality) be related to compounds identified in the potato extracts (2-ethyl furan, hexanal, heptanal, (E)-2-heptenal, acetic acid, methional, (E,Z)-2,6-nonadienal and phenylacetaldehyde) and one odour was probably an artifact (2-(2-butoxyethoxy)-ethanol acetate). When comparing intensities in raw and boiled potatoes for these odours, the same differences as above are seen, except for (E,Z)-2,6-nonadienal. This may be explained by the very low concentration of this compound, making detection and quantitation of peaks difficult.

For the rest of the odours, no peaks with corresponding retention index could be found by GC–MS, indicating that the odours stem from compounds with

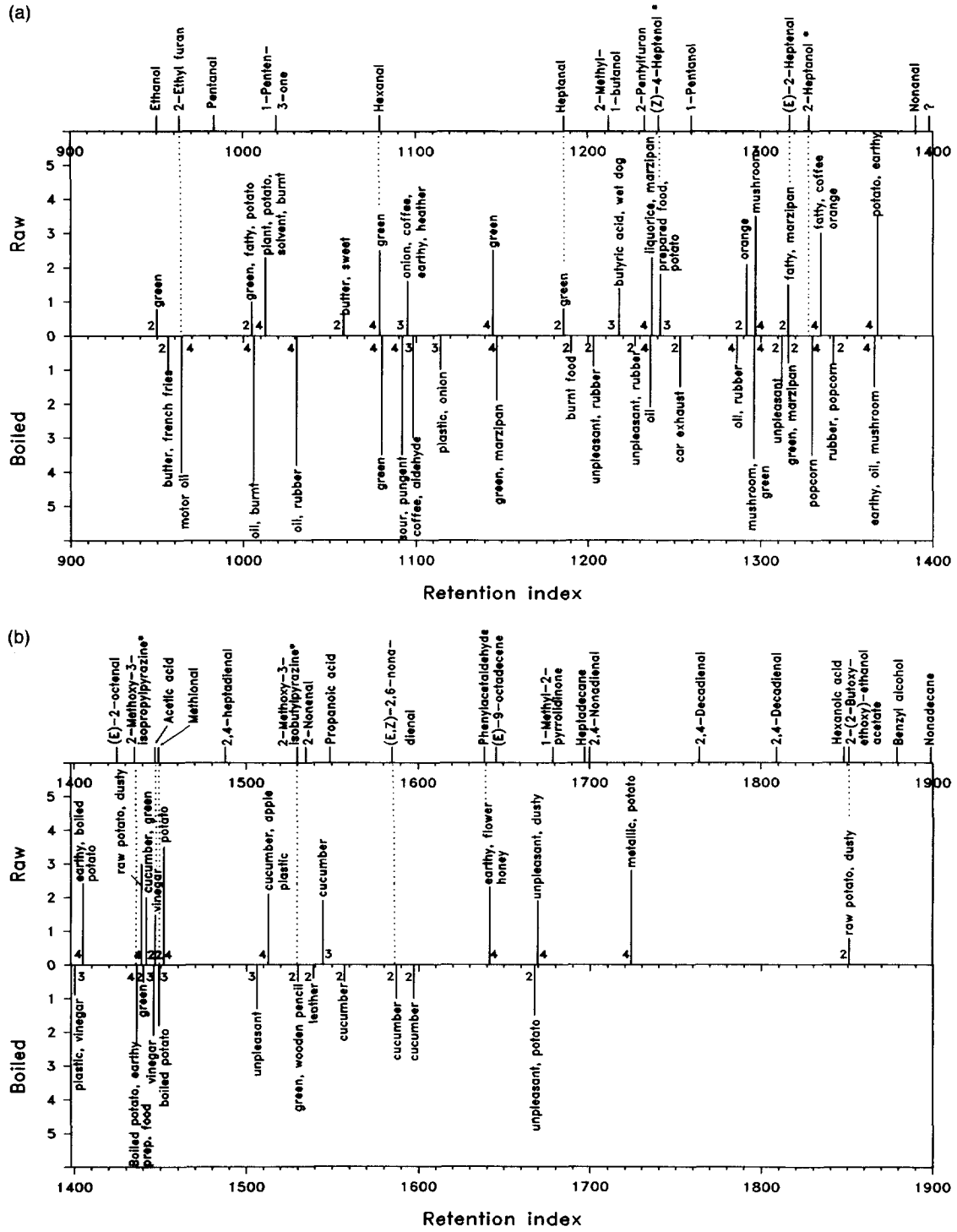

Fig. 1. (a) GC odour profiling of raw and boiled potatoes. Bars indicate intensity of odours averaged over four judges. If a judge did not perceive an odour, intensity was set to zero and included in the average. Numbers at the base of the bars indicate number of judges actually perceiving the odour. '*' indicates correspondence with a known reference, i.e. the compound was not found in the extracts. (b) Figure 1(a) continued.

low threshold values present in concentrations below detection limit of the GC–MS. However, retention indices and odour qualities were also compared for a total of 27 reference compounds that were analyzed by GC–MS and GC-sniffing in our laboratory. From this, four odours could additionally be identified by having the same retention index and same odour quality as the following reference compounds: (Z)-4-heptenal, 2-heptanol, 2-methoxy-3-isopropylpyrazine and 2-methoxy-3-isobutylpyrazine. Of these, (Z)-4-heptenal was found only in raw potatoes while 2-heptanol and the two methoxypyrazines were found only in the boiled potatoes. Other pyrazines tested (2,5- dimethylpyrazine, 2,6-dimethylpyrazine and 2-ethyl-3,6-dimethylpyrazine

could not be related to odour signals in the samples. Also Josephson and Lindsay (1987), Nursten and Sheen (1974) and Mazza and Pietrzak (1990) found areas with unidentified odours (retention index 1430–1460), that could very well be caused by pyrazines in concentrations below the detection limit of the GC–MS.

Though rather few of the detected odours could be identified, the total change during boiling can be described as follows: methional, 2-ethyl furan, 2-heptanol, (E,Z)-2,6-nonadienal, probably 2-methoxy-3-isopropylpyrazine and 2-methoxy-3-isobutylpyrazine, were produced, giving rise to two potato odours, an oily odour, a popcorn odour, a cucumber odour and a green odour. Heptanal, (Z)-4-heptenal and perhaps phenylacetaldehyde disappeared, leading to loss of plant odour, a prepared food/potato odour and an earthy or flowery odour. Concentration of hexanal increased by 33% and the intensity of the corresponding green odour increased. Concentration of (E)-2-heptenal decreased by a factor 5, and a small decrease in intensity of the corresponding marzipan-like odour was seen. Concentration of acetic acid also decreased, but the intensity of the vinegar odour was almost unchanged. Furthermore, during boiling, two unidentified orange odours were lost together with five potato-like odours and three cucumber odours. On the other hand, four oily odours were produced together with a sour, pungent odour and two boiled potato odours.

Comparison of the present method with others is difficult since different potato varieties have been used and since potatoes were stored for different periods of time before analyses were carried out. Furthermore, it is known that the extraction methods employed give higher yields of higher boiling compounds such as 2,4-decadienal, which is important for evaluating how far lipid oxidation has progressed. Therefore it is almost impossible to determine whether differences found are due to the raw material used, to the choice of methodology (extraction vs headspace), or to reactions occurring during analysis.

One important feature in the development of the present method was that it should be able to handle both raw and boiled potatoes. Few studies have been conducted on aroma of raw potatoes and even fewer have compared the levels found with the levels in boiled potatoes. One exception is Josephson and Lindsay (1987) who supplemented their headspace analyses of boiled potatoes with some analyses of shredded raw potatoes and reported concentrations of hexanal, (E)-2-octenal and 2,4-decadienal. The patterns of changes of those three compounds during boiling are in good agreement with the present study, taking the above reservations into account, but there is an important difference: in the study of Josephson and Lindsay, hexanal totally dominated the chromatograms of both raw and boiled potatoes. In the present study this is not the case in raw potatoes, indicating that the lipid oxidation processes have not progressed as far. This would also be expected since time of analysis was 40 min in the present study and 15 h in the study of Josephson and Lindsay (both at ambient temperature).

In a study by Khan *et al.* (1977), raw potatoes were analyzed using a headspace method (purging for 2 h at ambient temperature) in combination with an enzyme inhibitor (Na_2SO_3). As in the present study this resulted in chromatograms with moderate hexanal peaks.

No other studies have allowed for similar comparisons, since aroma compounds have not been quantified or raw and boiled potatoes have not been analysed together. The above comparisons indicate, however, that time of analysis in the present study is so short, that lipid oxidation is limited compared to other studies.

Josephson and Lindsay (1987) and Mazza and Pietrzak (1990) analysed freshly boiled potatoes using dynamic headspace methods and obtained aroma patterns very similar to that in the present study (largely dominated by hexanal and with low levels of 2,4-alkadienals). In the present study, the choice of extraction would be expected to lead to higher levels of the longer chained 2,4-alkadienals but, in contrast, the shorter time of analysis would prevent formation of these aldehydes, which has been shown to occur within hours when boiled potatoes are stored (unpublished data).

In conclusion, it must be noted that only few methods have reported comparisons of aroma compounds in raw and boiled potatoes. There are indications that the present method has some advantages, mainly when raw potatoes are analysed. One element that probably could be used to improve the present method is the use of an appropriate enzyme inhibitor.

Much work is still to be done to identify the compounds causing the reported odours but, from the ones identified at present, it is seen that the change in aroma during boiling of potatoes depends both on compounds from lipid oxidation and compounds from other types of reactions, for instance the Strecker-degradation.

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REFERENCES

Buttery, R. G., Seifert, R. M. and Ling, L. C. (1970) Characterization of some volatile potato components. *Journal of Agricultural and Food Chemistry* **18**(3), 538–539.

Galliard, T. and Matthew, J. A. (1973) Lipids of potato tubers. II. Lipid-degrading enzymes in different varieties of potato tuber. *Journal of the Science of Food and Agriculture* **24**, 623–627.

Galliard, T. and Phillips, D. R. (1971) Lipoxygenase from potato tubers. *Biochemical Journal* **124**, 431–438.

Gardner, H. W., Grove, M. J. and Salch, Y. P. (1996) Enzymic pathway to ethyl vinyl ketone and 2-pentenal in soybean preparations. *Journal of Agricultural and Food Chemistry* **44**, 882–886.

Hsieh, R. J. (1994) Contribution of lipoxygenase pathway to food flavors. In *Lipids in Food Flavors*, eds C. T. Ho and T. G. Hartmann, pp. 38–48. American Chemical Society, Washington, DC.

Ho, C. T. and Chen, Q. (1994) Lipids in food flavors. An overview. In *Lipids in Food Flavors*, eds C. T. Ho and T. G. Hartmann, pp. 2–14. American Chemical Society, Washington, DC.

Josephson, D. B. and Lindsay, R. C. (1987) c4-Heptenal: an influential volatile compound in boiled potato flavour. *Journal of Food Science* **52**(2), 328–331.

Maga, J. A. (1994) Potato flavor. *Food Reviews International* **10**(1), 1–48.

Mazza, G. and Pietrzak, E. M. (1990) Headspace volatiles and sensory characteristics of earthy, musty flavoured potatoes. *Food Chemistry* **36**, 97–112.

Nursten, H. E. and Sheen, M. R. (1974) Volatile flavour components of cooked potato. *Journal of the Science of Food and Agriculture* **25**, 643–663.

Salinas, J. P., Hartman, T. G., Karmas, K., Lech, J. and Rosen, R. T. (1994) Lipid-derived aroma compounds in cooked potatoes and reconstituted dehydrated potato granules. In *Lipids in Food Flavors*, eds C. T. Ho and T. G. Hartmann, pp. 108–129. American Chemical Society, Washington, DC.

Schieberle, P. and Grosch, W. (1981) Model experiments about the formation of volatile carbonyl compounds. *Journal of the American Oil Chemists' Society* **May**, 602–607.

Sok, D. E. and Kim, M. R. (1994) Conversion of alpha-linolenic acid to dihydro(pero)xyocta- decatrienoic acid isomers by soybean and potato lipoxygenases. *Journal of Agricultural and Food Chemistry* **42**, 2703–2708.

Tønder, D., Petersen, M. A., Poll, L. and Olsen, C. E. (1997) Discrimination between freshly made and stored reconstituted orange juice using GC Odour Profiling and aroma values. (Accepted for publication in *Food Chemistry*).