Available online at www.sciencedirect.com
SCIENCE DIRECT
Food Chemistry 100 (2007) 678–692
Food Chemistry
www.elsevier.com/locate/foodchem

Effects of glucose and acid-hydrolysed vegetable protein on the volatile components of extruded wheat starch

Marica Solina [a], Robert L. Johnson [b], Frank B. Whitfield [b,*]

[a] The University of Western Sydney, Centre for Advanced Food Research, Locked Bag 1797, Penrith South DC, NSW 1797, Australia
[b] Food Science Australia, P.O. Box 52, North Ryde, NSW 1670, Australia

Received 13 June 2005; accepted 11 October 2005

Abstract

The volatile components produced in wheat starch, and wheat starch combined with 1% glucose, 1% acid-hydrolysed vegetable protein (aHVP) or 1% glucose and 1% aHVP, extruded under different processing conditions (temperatures of 150 or 180 °C and moisture content of 16% or 20%) were identified by gas chromatography-mass spectrometry (GC-MS). Gas chromatography olfactometry (GCO) was used to assess the odour intensity of volatile components present in the starch and starch/glucose/aHVP extrudates obtained at 180 °C. In total, 70 compounds were identified in the eight extrudates. The smallest number (24) was found in the extrudate of the starch/glucose mixture and the largest number (67) in the extrudate of the starch/glucose/aHVP mixture, both processed at 180 °C. Lipid degradation products, such as alkanals, 2-alkanones, 2-alkenals and 2,4-alkadienals, were present in all extrudates in significant quantities. However, in those extrudates containing aHVP, Strecker aldehydes were quantitatively the dominant components. Maillard reaction products, such as pyrroles and pyrazines, were only found in extrudates containing both glucose and aHVP whereas sulphur-containing aliphatic compounds were found in all extrudates containing aHVP. The production of the Maillard reaction products and sulphur-containing compounds were favoured by extrusion at 180 °C. Sensory analyses showed that each of the eight extrudates had different odours, and that the extrudates containing both glucose and aHVP possessed the highest overall odour intensity.

Keywords: Extrusion; Glucose; Acid-hydrolysed vegetable protein; Starch; Odour; Volatiles; Non-volatiles

1. Introduction

The wide use of extruders in the production of foodstuffs has led to a number of reviews detailing the effects that extrusion has on odour generation and on odour retention in extruded products (Camire & Belbez, 1996; Riha & Ho, 1998; Villota and Hawkes, 1994). These authors stressed that the chemical reactions producing these odours remain obscure. Furthermore, the complex nature of the extrusion process has made it difficult for engineers and cereal chemists to describe odour production within the extruder in terms of product flow and energy input of the system. The extrusion process is characterised by rapid heating, resulting in chemical reactions within a relatively short time before the product leaves the die. The thermal generation of odour compounds in extruded cereals can therefore be considered as an open-ended series of reactions, as the rates and types of these reactions can be affected differently by the operating parameters of the extruder. Some recent studies in this field have led to a better understanding of the influences of different extruder conditions on odour development. Using maize, wheat and oat flours, it has been demonstrated that higher barrel temperatures and lower moisture contents give higher yields of Maillard reaction products so important in the development of baked and roasted odours (Bredie, Mottram, & Guy, 1998a; Bredie, Mottram, Hassell, & Guy, 1998b; Parker, Hassell, Mottram, & Guy, 2000). Barrel retention time, however, had a relatively small effect on the odour generated in

* Corresponding author. Fax: +61 2 9490 8499.
E-mail address: frank.whitfield@csiro.au (F.B. Whitfield).

0308-8146/$ - see front matter.
doi:10.1016/j.foodchem.2005.10.021

extruded maize but had a greater effect on the odour of extruded wheat flour. These studies also demonstrated the qualitative and quantitative differences between volatiles produced from extruded maize, wheat and oat flours.

Some progress has also been made on the role that non-volatile and volatile ingredients have in the formation of odour compounds during extrusion. Such studies have focussed on the qualitative and quantitative charges in the volatile components from the Maillard reaction through the addition of carbonyl and nitrogenous compounds to feedstocks before extrusion (Bredie, Hassell, Guy, & Mottram, 1997; Farouk, Pudil, Janda, & Porkornỳ, 2000; Ho & Riha, 1998; Riha, Hwang, Karwe, Hartman, & Ho, 1996). The majority of these studies involved the addition of amino acids and glucose to corn or wheat flour feedstocks before extrusion and showed that the addition of glucose or amino acids, or a mixture of both, gave an increase in the intensity of the odour of the extrudate. Greater concentrations of Maillard reaction products, particularly pyrazines, were formed by the addition of most amino acids (Farouk et al., 2000). The exception was cysteine which, when added to wheat starch, favoured the formation of sulphur compounds (Hwang et al., 1997).

In an effort to extend the current knowledge of odour production during extrusion we chose to investigate the effect that the addition of acid-hydrolysed vegetable protein (aHVP) to wheat starch feedstock could have on odour development during extrusion. As part of this study, we also chose to investigate the role that glucose could have on odour production when added to this mixture. Both ingredients were added at the 1% level, a quantity considered economically acceptable to the food industry. This paper will discuss the effect that the addition of such ingredients to wheat starch can have on the volatile content and odour of extruded products.

2. Materials and methods

2.1. Raw materials, reagents and reference chemicals

Commercial wheat starch was obtained from The Manildra Group (Auburn, Australia) and was free of any noticeable odours. This starch had a particle size of about 75 μm, a moisture content of 12.5% and a protein content of 0.3% w/w. The aHVP was purchased from Halcyon Protein Pty Ltd (Dandenong, Australia) and was derived from soy protein. This material had a moisture content of 6.4% w/w, a free amino acid content of 18.4% and a total lipid content of 0.4% w/w (Solina, Baumgartner, Johnson, & Whitfield, 2005). D-(+)-Glucose was purchased from Aldrich Chemical Co. Inc (Milwaukee, WI) and calcium triphosphate from Chemische Fabrik (Budenheim, Germany). Distilled water was purified through a Milli-Q purification system (Millipore Corp., Bedford, MA). All inorganic chemicals were of analytical reagent grade and were purchased from Merck KGaA (Darmstadt, Germany). Authentic samples of reference compounds were either purchased from a range of laboratory chemical suppliers or obtained as gifts from flavour laboratories. Chlorododecane and chlorotetradecane were purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI).

2.2. Lipid and free fatty acid analysis

Lipid and free fatty acid contents of the wheat starch were determined by BRI Australia (North Ryde, Australia) using the following methods: bound and unbound lipids were determined following acid hydrolysis of the sample and extraction with diethyl ether and petroleum ether (b.p. < 60 °C) according to the Official Methods of AOAC (1995) 922.06. Unbound lipids were determined by extraction of the sample with diethyl ether according to the Official Methods of AOAC (1995) 920.85. Free fatty acids were determined by titration, as oleic acid, using the Official Methods of AOAC (1995) 920.85 and 940.28. All analyses were performed in triplicate and results are reported as mg/10 g sample.

2.3. Fatty acid composition of bound and unbound lipids

The fatty acid composition of the lipid component of the wheat starch sample was determined by Silliker Microtech Ltd (Regents Park, Australia) as methyl esters, using the Official Methods of AOAC (1995) 963.22. The bound and unbound lipids were isolated as previously described and were hydrolysed with methanolic sodium hydroxide. The salts of the fatty acids were converted to their methyl esters with boron trifluoride in methanol using the Official Methods of AOAC (1955) 991.39 and the esters quantified by gas chromatography (GC). The analyses were performed in triplicate and the results are reported as mg/10 g sample.

2.4. Determination of reducing sugars in raw and extruded wheat starch

Reducing sugars were determined colorimetrically after reaction of aqueous extracts of the materials with 3,5-dinitrosalicylic acid (Aldrich Chemical Co. Inc., Milwaukee, W1), according to the method of Englyst and Hudson (1987). The absorbances of the solutions at 540 nm were measured using a Pharmacia LKB Biochrom 4060 UV–visible spectrometer (Pharmacia Biotech, Uppsala, Sweden). A calibration curve was plotted for standard solutions of glucose and the reducing sugar contents of the raw and extruded wheat starch were expressed as mg glucose/10 g sample. All analyses were performed in triplicate.

2.5. Extrusion processing

The flour feedstocks under investigation, wheat starch, wheat starch/1% glucose, wheat starch/1% aHVP and wheat starch/1% glucose/1% aHVP, were thoroughly mixed for 10 min and then sifted through a 2 mm sieve.

Calcium triphosphate (0.05% w/w) was added to each feedstock in order to improve the flow properties of the starch. The feedstocks were processed using an APV Baker MPF 40 co-rotating twin-screw extruder (APV Baker Ltd, Peterborough, UK).

Two extrusion temperatures and moisture combinations were chosen to cover intermediate (150 °C and 20% moisture) and extreme (180 °C and 16% moisture) conditions. A total of 15 kg of each feedstock was processed through the extruder using these conditions. The independent variables of water and feedstock feed rate were adjusted by microcomputer to control the chosen feed moisture level and overall feed rate. The screw rotation was held at 225 rpm. The dependent mass temperature along the screws was adjusted to the chosen profile by heating or cooling of the barrel sections. A measure of the mass temperature in the screw sections along the barrel was obtained from readings of six temperature probes in contact with the fluid mass. Adjustments to this barrel temperature profile were made to provide a constant mass temperature along each barrel section. Other dependent processing variables, such as torque and die pressure, were kept constant within each run. Motor torque was recorded and expressed as the specific mechanical energy (SME) input and, for the above feedstocks, the SME varied between 27% and 32%. The die pressure was recorded in the die entrance area. This pressure was highest (400 psi) for wheat starch extruded under mild conditions and lowest (20 psi) for wheat starch/1% aHVP extruded under extreme conditions. The overall length/diameter ratio (D) of the screws was 20D. Screws were made up from units of feed screws (FS), lead screws (LS) and paddle elements (P). The screw configuration (from feed section to die) used to process the extrudates were 3DFS, 1DLS, 3 forward P at 60°, 2DLS, 4 forward P at 60°, 2DLS, 4 reverse P at 60° and 1DLS. The standard screw configuration gave a median retention time of 60 s at a feed rate of 15 kg/h, as obtained from the residence time distribution of the marker compound Erythrosin B. A 6 mm diameter die was used and extrudates were collected over a period of 3–5 min, during which time the main extrusion variables showed least variation. Individual extrudates were collected, allowed to cool, then thoroughly mixed and milled to provide a homogeneous powder. The samples were packed in hermetically sealed laminate bags (polyethylene-foil-polyester laminate) and stored at −20 °C until required for analyses.

2.6. Sensory assessment of sample odours

Individual powdered samples (10 g) of each raw material or extruded product were placed in screw-capped jars and, just before qualitative sensory assessment, were wetted with water (30 ml). Four panellists assessed the samples at room temperature using a range of descriptive terms nominated by the panellists. Panellists were chosen for their enthusiasm and ability to recognise and describe a range of cooked food odours.

2.7. Collection of volatile components

A powdered sample (10 g) of raw material or extruded product was transferred to a 250 ml conical flask fitted with a 30 mm screw joint, a Teflon seal, a Dreschel head and a magnetic stirrer bar. The sample was mixed with water (80 ml) and chlorododecane (100 ng in 100 μl ethanol) was added as an internal standard to estimate the recovery of the volatile compounds. A pre-conditioned, glass-lined stainless-steel tube (115 mm long × 0.75 mm i.d.) packed with 10 mg Tenax TA (Scientific Glass Engineering Pty Ltd, Melbourne, Australia) was attached by a stainless-steel reducing union fitted to the Dreschel head outlet. During collection of the volatile components, the aqueous mixture was stirred slowly and the volatiles were swept from the flask onto the absorbent in the trap using a flow of oxygen-free nitrogen (40 ml/min). The collection was continued for 1 h during which time the flask and sample were maintained at 37 °C in a water bath. The trap remained at room temperature. At the end of the collection, the trap was removed and connected directly to the nitrogen supply (40 ml/min) for 5 min to remove residual water. An internal standard, chlorotetradecane (100 ng in 1 μl pentane) was added for quantification purposes to the front of the trap just before analysis by GC-MS.

For the odour assessment of volatile components by gas chromatography olfactometry (GCO), volatile extracts from three different quantities (10, 1 and 0.1 g) of wheat starch, extruded under extreme conditions, and wheat starch/glucose/aHVP, extruded under extreme conditions, were used. The headspace technique was the same as that used for the GC-MS analyses except that chlorotetradecane was not added to the trap before olfactory analysis.

2.8. Analysis of volatiles by gas chromatography-mass spectrometry

Analyses were performed on a Hewlett-Packard HP 5890 series II gas chromatograph (Hewlett-Packard, Palo Alto, CA) fitted with a CHIS injection port (Scientific Glass Engineering, Melbourne, Australia) and coupled to a Hewlett-Packard HP 5972 mass spectrometer controlled by a G 1701 BA ChemStation. The GC was fitted with a Hewlett-Packard HP5-Trace Analysis column (25 m × 0.2 mm i.d. 1 μm film thickness) and a pre-column retention gap (30 cm × 0.32 mm i.d.) uncoated but deactivated (Fisons Instruments, Mainz, Germany). The absorbed volatiles were desorbed onto the front of the pre-column by heating the Tenax trap for 10 min at 280 °C and cooling the pre-column to −78 °C with solid carbon dioxide. During the desorption, the GC oven was held at 40 °C then heated at 5 °C/min to 280 °C and held at this temperature for 5 min. A series of *n*-alkanes (C_5–C_{24}) was analysed under the same conditions to obtain the linear retention index (LRI) values for the volatile components of the isolates.

The MS was operated in the electron impact mode with an electron energy of 70 eV and an emission current of 50 μA. The ion source temperature was 250 °C. A continuous scan mode was employed over a mass range of 35–400 anu at a rate of 1 s/decade. Compounds were identified by first comparing their mass spectra with those contained in the NIST/EPA/NIH and Wiley Mass Spectral Databases or in previously published literature, followed by comparison of LRI values with either those of authentic compounds or published values. The relative concentrations of individual compounds were determined by comparing the peak area of the compound in each chromatogram with that of the chlorotetradecane internal standard (100 ng) and assuming that all response factors were 1. The relative concentrations of these compounds are reported as ng/10 g sample. Compounds described as "trace" were present at concentrations of <0.5 ng/10 g sample. The reported concentrations are the averages of three separate isolations collected from each sample.

2.9. Gas chromatography olfactometry

A Hewlett-Packard HP 5890 series II Plus gas chromatograph equipped with a CHIS injection port and a humidified odour port (Scientific Glass Engineering, Melbourne, Australia) was used for all odour evaluations. The pre-column, column and GC oven conditions were the same as those used for the GC-MS analyses. The column effluent (0.6 ml/min) was split at a ratio of 1:8 (v/v) between the flame ionization detector and the odour port. Both the detector and the connecting line to the port were held at 250 °C and the make-up gas for the detector and the port was nitrogen (30 ml/min). Humidified air (40 ml/min) was added to the GC effluent at the odour port.

Five pre-screened assessors separately evaluated the odours of the eluted components from each of three extracts (10, 1 and 0.1 g samples). The assessors described, in their own words, the odours perceived and these descriptors were recorded alongside the retention time of the odour. All odours reported were described by at least three assessors. The assessors rated the intensity of each odour according to a scale, including "low", "moderate", "strong" and "very strong". Retention data of the eluted compounds were obtained as LRI values by the analysis of a solution of *n*-alkanes (C_5–C_{24}) at the beginning and end of the days of olfactory analyses.

3. Results and discussion

3.1. Non-volatile components of wheat starch and aHVP

Data from the analyses of the non-volatile components of raw and extruded starch are recorded in Tables 1–3. Results in Table 1 show that the defatting step used by the manufacturers to convert wheat flour to starch had failed to remove all lipid components. The starch contained significant levels of unbound lipids (20 mg/10 g), including a proportion of free fatty acids (<10 mg/10 g), levels greater than normally found in such material. However, no bound lipids were detected. Analysis of the fatty acid composition of the lipid fraction (Table 2) showed that the wheat starch contained 11 fatty acids, of which 34.5% were saturated, 20.1% monosaturated and 45.4% polyunsaturated. The major fatty acid present was linoleic acid. Reducing sugars were not detected in the raw starch (Table 3). However, extrusion of this material under mild conditions gave a product with 75 mg/10 g reducing sugars whereas, under extreme conditions, the level was 85 mg/10 g. The formation of such reducing sugars from starch during extrusion has been reported by others (Camire, Camire, & Krumhar, 1990; Politz, Timpa, White, & Wasserman, 1994). Our results are consistent with these findings. Data provided by the manufacturers showed that the starch contained 0.3% protein but no free amino acids.

By comparison, previous studies (Solina et al., 2005) had shown that the aHVP contained 40 mg/10 g of unbound lipids, principally non-saponifiable material, and <10 mg/10 g of free fatty acids. The aHVP contained 18.4% free amino acids made up of 19 amino acids, of which the major ones were glutamic acid, alanine, proline, leucine, serine

Table 1
Lipid content of wheat starch

Lipid	Conc. (mg/10 g)
Free fatty acids	<10
Unbound lipids	20
Bound lipids	nd[a]

[a] nd, not detected at a detection limit of 1 mg/10 g.

Table 2
Fatty acid content of wheat starch

Fatty acids	Conc. (mg/10 g)
Myristic acid (14:0)	0.28
Palmitic acid (16:0)	4.82
Stearic acid (18:0)	0.60
Arachidic acid (20:0)	0.04
Behenic acid (22.0)	0.04
Palmitoleic acid (16:1)	0.14
Oleic acid (18:1)	2.96
Eloidic acid (18:1)	0.18
Eicosenoic acid (20:1)	0.10
Linoleic acid (18:2)	7.22
Linolenic acid (18:3)	0.38

Table 3
Reducing contents of raw and extruded wheat starch

Sample (extrusion temperature/moisture)	Reducing sugar as glucose (mg/10 g)
Raw starch	nd[a]
Starch extruded under mild conditions (150 °C/20%)	75
Starch extruded under extreme conditions (180 °C/16%)	85

[a] nd, not detected at a detection limit of 1 mg/10 g.

and phenylalanine. Neither protein nor reducing sugars were found in the aHVP (Solina et al., 2005).

3.2. Volatile components of raw and extruded wheat starch

Analysis of the volatile components of raw starch led to the identification of 22 compounds (Table 4) of which 15 were derived from the oxidation of the free fatty acids present in this material. These 15 compounds, principally *n*-alkanals (C_5–C_{10}), accounted for 35% of the total volatiles detected (302 ng/10 g). Of the remaining seven compounds all, with the exception of limonene and furfural, appeared to be contaminants. Three compounds, limonene (88 ng/10 g), ethyl acetate (68 ng/10 g) and hexanal (52 ng/10 g) dominated the profile of the volatile extract and accounted for 69% of the total concentration of volatiles isolated from the starch.

Extrusion of the wheat starch under mild and extreme conditions resulted in an increase of the number of compounds identified; 32 were found in the material extruded under mild conditions and 33 under extreme conditions (Table 4). Also increased were the amounts of volatiles recovered (535 and 534 ng/10 g). Lipid-derived compounds again dominated the volatile profiles of those extrudates, both qualitatively and quantitatively. In the material produced under mild conditions 20 compounds (75% of total volatiles) were derived from lipids whereas that produced under extreme conditions had 21 compounds (79% of total volatiles) derived from this source. Of the remaining compounds, dimethyl disulphide and the Strecker aldehydes, 3-and 2-methylbutanal were quantitatively the most important of those formed during extrusion. Compounds present in greatest amounts were hexanal (190 and 150 ng/10 g), (*E*,*E*)-2,4-decadienal (48 and 130 ng/10 g), 2-pentylfuran (34 and 31 ng/10 g), pentanal (31 and 22 ng/10 g), dimethyl disulphide (20 and 27 ng/10 g) and (*E*)-2-nonenal (17 and 24 ng/10 g). Limonene, the major volatile component in the raw material, was present at much lower levels in the extrudates (13 and 13 ng/10 g) whereas those compounds, probably contaminants, were present at either similar levels or at decreased levels.

All of the aliphatic aldehydes (alkanals, 2-alkenals and 2,4-alkadienals) were derived from the oxidation of oleic, linoleic and linolenic acids (Badings, 1970). In particular, hexanal and (*E*,*E*)-2,4-decadienal would be derived from the oxidation of linoleic acid, the principal fatty acid present in the starch lipids (Table 2). Oxidation of this fatty acid is also the likely source of 2-pentylfuran a known oxidation product of methyl linoleate (Frankel, Neff, & Selke, 1981; Neff, Frankel, Selke, & Weisleder, 1983). (*E*)-2-Nonenal would be derived from the oxidation of either oleic acid, another major fatty acid of the starch lipid or linoleic acid (Badings, 1970). The small quantities of benzaldehyde found in the extruded products (Table 4) can also be attributed to lipid oxidation (Bruechert et al., 1988). Although no free amino acids were reported to be present in the raw starch this material does contain 0.3% protein (30 ng/10 g). Thermal and, or physical disruption of this protein accordingly appears to be the most likely source of the significant quantities of dimethyl disulphide and dimethyl trisulphide found in these extrudates (Table 4).

Five compounds, present in both extrudates, had relative concentrations that exceeded their odour threshold concentrations (OTC) in water (Badings, 1970; Fors, 1983). The compounds were hexanal, (*E*)-2-nonenal, (*E*,*E*)-2,4-decadienal, 3-methylbutanal and dimethyl disulphide. The relative concentration of another compound, nonanal, exceeded its OTC in the extrudate obtained at 150 °C, and a further compound, dimethyl trisulphide, exceeded its OTC in the extrudate obtained at 180 °C. All of these compounds could be expected to contribute to the perceived odour of the extrudates.

3.3. Volatile components of raw and extruded starch and glucose

Analysis of the volatile components of the starch/glucose feedstock resulted in the identification of 28 compounds, six more than found in the raw starch (Table 4). Ten additional compounds were found in the feedstock but four compounds previously identified in the starch were absent. None of these absent compounds had been present at levels >5 ng/10 g. Five of the additional compounds found in the starch/glucose feedstock were lipid-derived, four were amino acid derived and the other compound was a possible contaminant. Of the compounds not detected in this feedstock, three were lipid-derived and one sugar-derived. Lipid derived compounds accounted for 60% of the total volatiles detected (393 ng/10 g), in the starch/glucose extrudate. Three compounds hexanal (110 ng/10 g), ethyl acetate (88 ng/10 g) and 2-pentylfuran (49 ng/10 g) dominated the volatile profile and accounted for 63% of the volatiles isolated. But limonene, a major component in raw starch (88 ng/10 g), was present in only a minor quantity (3 ng/10 g). The reduction in the level of this monoterpene, coupled with the significant increase in the levels of lipid oxidation products, 35% in raw starch to 60% in the starch/glucose feedstock, suggests that this mixture is more susceptible to oxidation than is starch alone.

Extrusion of the starch/glucose feedstock under mild and extreme conditions had either no effect or little effect on the number of volatile compounds identified. Under mild conditions, 28 compounds were identified whereas, under extreme conditions, 24 compounds were found (Table 4). The quantity of total volatiles recovered under mild conditions was about the same as that for the feedstock (409 ng/10 g); however, under extreme conditions this quantity was significantly increased (543 ng/10 g). Lipid-derived compounds again dominated the volatile profiles of these extrudates. Such compounds accounted for 86% of the total volatiles identified in each product. Surprisingly, sugar-derived compounds were not found in quantities greater than found in extruded starch. In addition, the levels of sulphur-containing aliphatic compounds were less than those found in the starch extrudates. However, the level of 3-

Table 4
Relative concentrations of headspace volatiles of starch and starch/glucose feedstocks extruded under different conditions of temperature and moisture content

Identity	LRI[a]	Starch						Starch/glucose						Method of identification[b]
		RM[c]		150/20[d]		180/16		RM		150/20		180/16		
		ng/10 g sample[e] (SD)												
Lipid-derived aldehydes														
Pentanal	722	4	(0.8)	31	(14)	22	(4.5)	6	(1.3)	17	(2.6)	6	(1.2)	MS + LRI
Hexanal	817	52	(7.9)	190	(11)	150	(8.5)	110	(2.9)	140	(2.3)	98	(2.1)	MS + LRI
Heptanal	907	4	(1.5)	11	(5.3)	13	(1.5)	7	(1.2)	12	(0.9)	15	(0.7)	MS + LRI
Octanal	1008	2	(0.6)	3	(1.3)	2	(0.6)	5	(2.9)	2	(0.5)	2	(0.5)	MS + LRI
Nonanal	1105	9	(2.1)	11	(3.3)	9	(0.7)	15	(3.4)	–	–	6	(0.9)	MS + LRI
Decanal	1204	3	(0.7)	5	(1.4)	2	(0.1)	5	(3.7)	1	(0.1)	1	(0.1)	MS + LRI
(*E*)-2-Hexenal	858	tr	–	1	(0.4)	1	(0.1)	–	–	–	–	1	(0.1)	MS + LRI
(*E*)-2-Heptenal	961	tr	–	12	(3.3)	4	(0.9)	2	(0.2)	4	(0.9)	1	(0.1)	MS + LRI
(*E*)-2-Octenal	1062	–	–	13	(4.2)	14	(1.1)	5	(0.7)	9	(1.0)	12	(1.8)	MS + LRI
(*E*)-2-Nonenal	1162	5	(1.9)	17	(7.0)	24	(3.3)	11	(1.6)	13	(2.0)	19	(2.0)	MS + LRI
(*E*)-2-Decenal	1269	–	–	–	–	1	(<0.1)	–	–	–	–	–	–	MS + LRI
(*E*,*E*)-2,4-Nonadienal	1217	–	–	1	(0.5)	1	(<0.1)	1	(0.3)	–	–	–	–	MS + LRI
(*E*,*Z* or *Z*,*E*)-2,4-Decadienal	1295	–	–	–	–	–	–	–	–	49	(14)	56	(3.3)	MS + LRI
(*E*,*E*)-2,4-Decadienal	1317	–	–	48	(7.3)	130	(5.5)	–	–	44	(5.0)	95	(7.5)	MS + LRI
Benzaldehyde[f]	979	1	(0.8)	2	(1.0)	2	(<0.1)	2	(0.1)	–	–	1	(0.1)	MS + LRI
Ketones														
2-Butanone[g]	<650	–	–	10	(4.5)	9	(3.0)	5	(3.2)	–	–	–	–	MS + LRI
2-Pentanone	699	2	(1.1)	6	(2.4)	4	(0.7)	–	–	tr	–	1	(0.1)	MS + LRI
2-Heptanone	898	2	(1.2)	4	(2.9)	4	(0.2)	1	(0.1)	3	(0.8)	4	(0.1)	MS + LRI
2-Nonanone	1093	2	(0.4)	tr	–	1	(<0.1)	–	–	–	–	–	–	MS + LRI
Alcohols														
1-Pentanol	783	–	–	3	(1.0)	1	(0.7)	2	(0.2)	2	(0.2)	–	–	MS + LRI
1-Hexanol	880	9	(3.5)	–	–	–	–	5	(2.0)	8	(2.1)	9	(0.8)	MS + LRI
1-Octen-3-ol	984	–	–	–	–	–	–	4	(1.2)	–	–	–	–	MS + LRI
Furans														
2-Butylfuran	889	–	–	–	–	–	–	1	(0.1)	2	(0.7)	–	–	MS + LRI
2-Pentylfuran	995	10	(2.8)	34	(5.7)	31	(5.6)	49	(4.5)	51	(12)	140	(10)	MS + LRI
Sugar-derived furans														
2-Furfural	841	1	(0.5)	1	(0.2)	1	(0.4)	–	–	1	(0.1)	1	(0.1)	MS + LRI
Amino acid-derived aldehydes														
2-Methylpropanal	<650	–	–	1	(0.8)	–	–	–	–	–	–	–	–	MS + LRI
3-Methylbutanal	669	–	–	8	(2.2)	8	(1.5)	1	(0.1)	7	(1.4)	40	(0.8)	MS + LRI
2-Methylbutanal	677	–	–	5	(2.2)	8	(1.0)	tr	–	5	(0.4)	7	(1.0)	MS + LRI
Alcohols														
3-Methylbutanol	772	–	–	–	–	–	–	3	(1.1)	–	–	–	–	MS + LRI
Maillard reaction-derived Pyridines														
Pyridine	765	14	(2.4)	–	–	–	–	17	(5.8)	3	(0.4)	–	–	MS + LRI
Sulphur-containing aliphatic compounds														
Dimethyl disulphide	756	–	–	20	(6.5)	27	(8.2)	–	–	5	(3.0)	12	(1.4)	MS + LRI
Dimethyl trisulphide	975	–	–	–	–	7	(0.1)	–	–	–	–	–	–	MS + LRI
Methyl pentyl disulphide	1137	–	–	–	–	1	(<0.1)	–	–	–	–	–	–	MS
Derived from other sources *Ketones*														
3-Cyclohepten-1-one	823	–	–	1	(0.5)	1	(0.2)	–	–	2	(0.1)	2	(0.1)	MS
Furans														
Tetrahydro-2-methylfuran	<650	–	–	2	(0.6)	–	–	–	–	–	–	–	–	MS
Hydrocarbons														
Toluene	784	15	(4.6)	16	(7.0)	15	(0.2)	19	(4.3)	5	(2.5)	3	(0.1)	MS + LRI
Octane	800	–	–	–	–	–	–	–	–	1	(0.1)	–	–	MS + LRI
1,4-Dimethylbenzene	878	10	(1.3)	14	(2.0)	10	(1.0)	20	(2.3)	10	(0.1)	–	–	MS + LRI
Limonene	1034	88	(7.3)	13	(4.7)	13	(3.2)	3	(0.1)	5	(1.1)	11	(1.0)	MS + LRI

(*continued on next page*)

Table 4 (*continued*)

Identity	LRI[a]	Starch						Starch/glucose						Method of identification[b]
		RM[c]		150/20[d]		180/16		RM		150/20		180/16		
		ng/10 g sample[e] (SD)												
Miscellaneous														
Ethyl acetate	<650	68	(18)	43	(10)	10	(1.0)	88	(35)	–	–	–	–	MS + LRI
Hexanenitrile	882	–	–	1	(0.5)	1	(0.2)	tr	–	1	(0.2)	–	–	MS
1-Nitrohexane	1050	1	(0.8)	8	(2.5)	7	(0.6)	6	(0.5)	7	(1.4)	–	–	MS

The GC-MS response factors for each component are assumed to be 1:1. Consequently, the reported quantities are considered as approximate values.

[a] Linear Retention Index.

[b] MS + LRI: identified by comparison of mass spectra and LRI with those of an authentic compound or previously published data; MS: mass spectrum agrees with the reference spectrum from the NIST/EPS/NIH Mass Spectral Database.

[c] Raw material.

[d] Extrusion variables, temperature °C/moisture content (%).

[e] Concentration (ng/10 g) obtained by comparing GC-MS peak area with that from 100 ng chlorotetradecane internal standard added to the Tenax trap after volatile collection; the average of triplicate analyses are shown; (–) not detected (limit of detection 0.1 ng/10 g sample); (tr) volatiles in concentrations of <0.5 ng/10 g.

[f] Benzaldehyde may be ether lipid- or amino acid-derived.

[g] 2-Butane may be either lipid or sugar-derived.

methylbutanal (40 ng/10 g) found in the starch/glucose extrudate at 180 °C was greater than found in the starch extrudate (Table 4). The presence of Strecker aldehydes in all extrudates, either starch alone or those containing added glucose, indicated that the raw starch originally contained some levels of free amino acids, presumably below their detection limit of 50 μg/10 g. Compounds present in greatest quantities in the extrudates containing added glucose were hexanal (140 and 98 ng/10 g), 2-pentylfuran (51 and 140 ng/10 g), (*E*,*E*)-2,4-decadienal (44 and 98 ng/10 g) and (*E*,*Z* or *Z*,*E*)-2,4-decadienal (49 and 56 ng/10 g).

Compounds present in both extrudates with relative concentrations that exceeded their OTC in water were the same five compounds as identified in the starch extrudates (Section 3.2). In addition, 2-pentylfuran exceeded its OTC in the starch/glucose extrudate obtained at 180 °C whereas dimethyl trisulphide exceeded its OTC in the extrudate obtained at 150 °C (Table 4). Admittedly, these OTC in water are likely to be far lower than the corresponding thresholds in the extrudate; however, they do provide some guidance as to the relative importance of individual volatile compounds in the solid material. Based on these data, it could be expected that the odours of the starch and starch/glucose extrudates obtained at either temperature would be very similar provided no trace odour components, not detected by the GC-MS, were present in the extrudates.

Accordingly, the addition of glucose to wheat starch apparently had little effect on the volatile composition of the extrudates obtained at either 150 or 180 °C.

3.4. Volatile components of raw and extruded starch and aHVP

Twenty-two compounds were identified in the starch/aHVP feedstock (Table 5), the same number as previously found in raw starch (Table 4). However, the total quantity of volatiles found (268 ng/10 g) was slightly less. Four compounds found in starch in minor quantities were not found in the feedstock; however, the feedstock contained four different compounds, 2-and 3-methylbutanal, 2-butanone and 2-furanmethanol. The Strecker aldehydes, previously identified as major components of aHVP (Solina et al., 2005) were found at levels of 5 and 15 ng/10 g. The aHVP was the likely source of these compounds in the feedstock.

Forty-one compounds were identified in the starch/aHVP extrudate obtained at 150 °C, whereas 55 compounds were found in that extruded at 180 °C (Table 5). These numbers were significantly greater than those found in the feedstock. Lipid-derived compounds dominated both extrudates (23 and 21), followed by sulphur-containing aliphatic compounds (4 and 6) and Strecker aldehydes (4 and 5 compounds). The product extruded at 180 °C also contained minor quantities of Maillard reaction products (7). The remaining compounds found in these extrudates (9 and 16) were either derived from unidentified sources or were possible contaminants (Table 5). With few exceptions these compounds were present in minor quantities (<10 ng/10 g).

The quantities of volatiles found in the extrudates were also far greater than those found in the feedstock; 482 ng/10 g in the extrudate formed at 150 °C and 1987 ng/10 g in that produced at 180 °C. In the material extruded under mild conditions, lipid-derived compounds accounted for 68% of the total volatiles found but, under extreme conditions, such compounds accounted for only 20% of the volatiles, although the quantities found in each extrudate were similar (326 and 404 ng/10 g). Strecker aldehydes, and in particular 3-methylbutanal, dominated the volatile compounds found in the material extruded at 180 °C, totalling 71% of the total volatiles. The major compounds found in the extrudate produced at 150 °C were hexanal (110 ng/10 g), (*E*,*E*)-2,4-decadienal, (60 ng/10 g), 2-pentylfuran (49 ng/10 g) and 3-methylbutanal (47 ng/10 g). By compar-

Table 5
Relative concentrations of headspace volatiles of starch/aHVP and starch/glucose/aHVP feedstocks extruded under different conditions of temperature and moisture content

Identity	LRI[a]	Starch/aHVP						Starch/glucose/aHVP						Method of identification[b]
		RM[c]		150/20[d]		180/16		RM		150/20		180/16		
		ng/10 g sample[e] (SD)												
Lipid-derived aldehydes														
Pentanal	722	4	(2.8)	1	(0.4)	12	(3.8)	7	(4.9)	25	(4.1)	5	(0.9)	MS + LRI
Hexanal	817	48	(6.4)	110	(20)	110	(13)	92	(6.4)	160	(8.9)	100	(13)	MS + LRI
Heptanal	907	2	(1.0)	11	(2.1)	17	(2.6)	4	(2.0)	17	(1.3)	17	(2.9)	MS + LRI
Octanal	1008	2	(1.1)	3	(1.5)	4	(0.6)	2	(1.2)	6	(2.3)	4	(1.9)	MS + LRI
Nonanal	1105	8	(1.4)	8	(1.3)	8	(1.1)	9	(4.4)	12	(3.7)	13	(0.8)	MS + LRI
Decanal	1204	3	(0.7)	2	(0.7)	2	(0.5)	2	(1.5)	3	(1.3)	5	(1.3)	MS + LRI
(*E*)-2-Hexenal	858	–	–	1	(0.2)	1	(0.1)	tr	–	1	(0.7)	1	(0.3)	MS + LRI
(*E*)-2-Heptenal	961	1	(0.5)	7	(2.4)	3	(0.3)	2	(0.8)	11	(3.1)	3	(0.9)	MS + LRI
(*E*)-2-Octenal	1062	–	–	14	(2.1)	15	(1.5)	3	(0.7)	18	(1.7)	11	(2.8)	MS + LRI
(*E*)-2-Nonenal	1162	4	(1.0)	15	(1.7)	16	(1.7)	9	(2.2)	19	(1.4)	19	(2.7)	MS + LRI
(*E*)-2-Decenal	1269	–	–	2	(0.6)	1	(0.1)	–	–	1	(0.9)	–	–	MS + LRI
(*E*,*E*)-2,4-Heptadienal	1018	–	–	1	(0.2)	–	–	–	–	1	(0.2)	–	–	MS + LRI
(*E*,*E*)-2,4-Octadienal	1120	–	–	1	(0.6)	–	–	–	–	tr	–	–	–	MS + LRI
(*E*,*E*)-2,4-Nonadienal	1217	–	–	1	(0.8)	1	(0.2)	1	(0.6)	1	(0.4)	2	(0.5)	MS + LRI
(*E*,*Z* or *Z*, *E*)-2,4-Decadienal	1295	–	–	23	(6.3)	33	(0.6)	1	(0.2)	47	(4.2)	48	(5.0)	MS + LRI
(*E*,*E*)-2,4-Decadienal	1317	–	–	60	(5.0)	69	(5.3)	–	–	84	(5.4)	78	(8.7)	MS + LRI
Ketones														
2-Butanone[f]	<650	5	(2.1)	–	–	1	(0.1)	2	(0.8)	tr	–	–	–	MS + LRI
2-Pentanone	699	3	(2.3)	1	(0.2)	3	(1.4)	4	(0.9)	3	(1.2)	3	(0.7)	MS + LRI
2-Heptanone	898	1	(0.1)	3	(0.6)	5	(2.0)	1	(0.1)	8	(1.2)	5	(1.3)	MS + LRI
1-Octen-3-one	980	–	–	–	–	–	–	–	–	1	0.7	–	–	MS + LRI
2-Nonanone	1093	–	–	–	–	–	–	–	–	1	0.8	2	0.2	MS + LRI
3-Nonen-2-one	1140	–	–	4	(0.4)	–	–	1	(0.9)	2	(0.6)	1	(0.3)	MS + LRI
Alcohols														
1-Pentanol	783	–	–	1	(0.4)	tr	–	2	(0.4)	2	(0.4)	–	–	MS + LRI
1-Hexanol	880	–	–	6	(1.0)	8	(1.2)	12	(1.1)	5	(2.2)	7	(3.6)	MS + LRI
1-Octen-3-ol	984	–	–	2	(0.6)	–	–	3	(1.7)	3	(1.5)	1	(0.8)	MS + LRI
Furans														
2-Ethylfuran	699	–	–	–	–	4	(1.3)	–	–	19	(4.1)	–	–	MS + LRI
2-Pentylfuran	995	–	–	49	(5.7)	91	(9.7)	55	(8.9)	44	(8.3)	56	(8.6)	MS + LRI
Sugar-derived ketones														
2,3-Pentanedione	711	–	–	–	–	–	–	–	–	1	(0.9)	14	(2.7)	MS + LRI
Furans														
2-Furfural	841	3	(<0.1)	1	(0.5)	1	(0.9)	tr	–	2	(0.5)	11	(4.4)	MS + LRI
2-Furanmethanol	864	1	(0.1)	–	–	–	–	–	–	–	–	tr	–	MS + LRI
1-(2-Furanyl)-1-ethanone	916	–	–	tr	–	1	(0.2)	–	–	1	(0.4)	1	(0.5)	MS
Amino acid-derived aldehydes														
2-Methylpropanal	<650	–	–	–	–	15	(4.4)	1	(0.9)	tr	–	–	–	MS + LRI
3-Methylbutanal	669	15	(2.4)	47	(5.0)	1200	(66)	21	(3.9)	650	(54)	2900	(180)	MS + LRI
2-Methylbutanal	677	5	(0.5)	19	(6.9)	76	(9.5)	8	(3.3)	150	(17)	100	(3.7)	MS + LRI
Benzaldehyde[g]	979	2	(0.1)	7	(1.9)	4	(1.8)	3	(0.7)	10	(1.8)	14	(4.7)	MS + LRI
Phenylacetaldehyde	1063	–	–	24	(1.1)	76	(6.8)	–	–	150	(15)	260	(17)	MS + LRI
Maillard reaction-derived														
Pyrroles														
1-Methyl-1*H*-pyrrole	731	–	–	–	–	–	–	–	–	–	–	6	(1.7)	MS + LRI
1*H*-Pyrrole	771	–	–	–	–	2	(0.4)	–	–	–	–	7	(2.0)	MS + LRI
1-Ethyl-1*H*-pyrrole	829	–	–	–	–	tr	–	–	–	tr	–	8	(2.2)	MS + LRI
2-Methyl-1*H*-pyrrole	853	–	–	–	–	1	(0.2)	–	–	tr	–	2	(0.8)	MS + LRI
Pyridines														
Pyridine	765	–	–	9	(1.5)	19	(1.8)	10	(2.7)	–	–	–	–	MS + LRI
Pyrazines														
Pyrazine	736	–		–		–		–		3	(1.0)	49	(4.3)	MS + LRI
Methylpyrazine	839	–		–		–		–		5	(0.4)	36	(5.0)	MS + LRI
2,5- or 2,6-Dimethylpyrazine	916	–		–		–		–		1	(0.5)	6	(2.2)	MS + LRI
Ethylpyrazine	919	–		–		–		–		4	(2.1)	42	(3.9)	MS + LRI
2,3-Dimethylpyrazine	930	–		–		–		–		–	–	3	(1.3)	MS + LRI
Ethenyl pyrazine	934	–		–		–		–		1	(0.5)	8	(1.6)	MS + LRI
2-Ethyl-6-methylpyrazine	995	–		–		–		–		–	–	4	(0.9)	MS + LRI
2-Ethyl-5-methylpyrazine	1000	–		–		–		–		–	–	5	(0.9)	MS + LRI
2-Vinyl-6-methylpyrazine	1016	–		–		–		–		tr	–	6	(1.3)	MS + LRI
2-(Methylpropyl)-pyrazine	1068	–		–		–		–		–	–	2	(0.2)	MS
2,6-Diethylpyrazine	1080	–		–		–		–		–	–	2	(0.6)	MS + LRI
2-(3-Methylbutyl)-6-methylpyrazine	1248	–		–		–		–		–	–	2	(0.1)	MS

(*continued on next page*)

Table 5 (*continued*)

Identity	LRI[a]	Starch/aHVP						Starch/glucose/aHVP						Method of identification[b]
		RM[c]		150/20[d]		180/16		RM		150/20		180/16		
		ng/10 g sample[e] (SD)												
2-Butyl-3,5-dimethylpyrazine	1314	–		–		–		–		–		1	(0.4)	MS
Oxazoles														
2,4,5-Trimethyloxazole	848	–		–		–		–		–		tr	–	MS + LRI
Sulphur-containing aliphatic compounds														
Methanethiol	<650	–	–	tr	–	–	–	–	–	–	–	–	–	MS
Dimethyl disulphide	756	3	(1.2)	22	(3.5)	65	(5.4)	3	(0.7)	64	(11)	210	(26)	MS + LRI
Methyl ethyl disulphide	861	–	–	–	–	1	(0.1)	–	–	–	–	1	(0.7)	MS + LRI
1-(Methylthio)-pentane	902	–	–	–	–	1	(0.1)	–	–	–	–	–	–	MS
3-(Methylthio)-propanal	910	–	–	–	–	1	(0.7)	–	–	tr	–	2	(0.7)	MS + LRI
Dimethyl trisulphide	975	–	–	5	(0.7)	20	(2.7)	1	(0.4)	13	(1.1)	64	(3.3)	MS + LRI
Methyl pentyl disulphide	1137	–	–	1	(0.2)	–	(0.5)	–	–	1	(0.4)	1	(0.1)	MS
Dimethyl tetrasulphide	1240	–	–	–	–	–	–	–	–	–	–	1	(0.4)	MS + LRI
Thiazoles														
Benzothiazole	1257	–	–	1	(0.2)	1	(0.2)	tr	–	1	(0.3)	–	(0.2)	MS + LRI
Thiophenes														
2-Methylthiophene	805	–	–	–	–	tr	–	–	–	–	–	–	–	MS + LRI
2-Vinylthiophene	927	–	–	–	–	1	(0.2)	–	–	–	–	–	–	MS + LRI
Thiopyrans														
2-Pentylthiopyran	1324	–	–	–	–	2	(0.2)	–	–	–	–	–	–	MS + LRI
Derived from other sources														
Aldehydes														
3-Methyl-2-butenal	806	–	–	–	–	–	–	–	–	1	(0.2)	1	(0.4)	MS + LRI
2-Phenyl-2-propenal	1156	–	–	–	–	1	(0.1)	–	–	1	(0.1)	2	(0.4)	MS + LRI
5-Methyl-2-phenyl-2-hexenal	1486	–	–	–	–	–	–	–	–	–	–	5	(1.8)	MS
Ketones														
4,4-Dimethyl-2-cyclopenten-1-one	795	–	–	–	–	–	–	–	–	–	–	8	(3.7)	MS
3-Cyclopenten-1-one	823	–	–	1	(0.3)	1	(0.3)	–	–	–	–	–	–	MS
5-Methyl-2-hexanone	857	–	–	–	–	1	(0.1)	tr	–	1	(0.4)	8	(1.9)	MS + LRI
Acetophenone	1063	–	–	–	–	–	–	1	(0.1)	1	(0.5)	1	(0.1)	MS + LRI
5-Decanone	1179	–	–	–	–	1	(0.6)	–	–	–	–	1	(0.2)	MS
Furans														
3-Phenylfuran	1228	–	–	1	(0.4)	3	(0.4)	–	–	8	(2.0)	70	(6.9)	MS
Hydrocarbons														
Toluene	784	14	(2.6)	6	(0.4)	14	(2.9)	14	(2.0)	15	(1.2)	10	(1.3)	MS + LRI
Octane	800	–	–	–	–	–	–	1	(0.5)	–	–	–	–	MS + LRI
1,4-Dimethylbenzene	878	8	(1.3)	7	(4.3)	3	(1.0)	8	(3.8)	8	(1.4)	4	(3.0)	MS + LRI
Limonene	1034	100	(12)	4	(1.2)	14	(2.1)	67	(7.4)	23	(4.0)	7	(1.8)	MS + LRI
Miscellaneous														
Ethyl ethanoate	<650	36	(5.1)	–	–	15	(3.2)	84	(7.4)	2	(1.5)	–	–	MS + LRI
Phenol	756	–	–	–	–	–	–	–	–	–	–	2	(1.6)	MS + LRI
Butyl ethanoate	816	–	–	tr	–	tr	–	–	–	1	(0.5)	–	–	MS + LRI
Hexanenitrile	882	tr	–	1	(0.4)	1	(0.1)	1	(0.5)	1	(0.8)	1	(0.3)	MS
1-Nitrohexane	1050	–	–	–	–	39	(4.2)	4	(2.5)	–	–	–	–	MS
2,3-Dihydro-1*H*-indole	1114	–	–	–	–	1	(0.1)	–	–	1	(0.1)	4	(1.2)	MS

The GC-MS response factors for each component are assumed to be 1:1. Consequently, the reported quantities are considered as approximate values.

[a] Linear Retention Index.

[b] MS + LRI: identified by comparison of mass spectra and LRI with those of an authentic compound or previously published data; MS: mass spectrum agrees with the reference spectrum from the NIST/EPA/NIH Mass Spectral Database.

[c] Raw material.

[d] Extrusion variables, temperature °C/moisture content (%).

[e] Concentration (ng/10 g) obtained by comparing GC-MS peak area with that from 100 ng chlorotetradecane internal standard added to Tenax trap after volatile collection; the average of triplicate analyses are shown; (–) not detected (limit of detection 0.1 ng/10 g sample); (tr) volatiles in concentrations <0.5 ng/10 g.

[f] 2-Butanone may be either lipid- or sugar-derived.

[g] Benzaldehyde may be either lipid- or amino acid-derived.

ison, in the extrudate formed at 180 °C, the major compounds were 3-methylbutanal (1200 ng/10 g), hexanal (110 ng/10 g), 2-pentylfuran (91 ng/10 g), 2-methylbutanal (76 ng/10 g),phenylacetaldehyde (76 ng/10 g), (*E*,*E*)-2,4-decadienal (69 ng/10 g) and dimethyl disulphide (65 ng/10 g). The principal source of the Strecker aldehydes was the added aHVP (18.4% free amino acid), through the interaction of some of these amino acids with reducing sugars formed during the extrusion of the starch (Table 1). The precursors of the Strecker aldehydes listed in Table 5 are the amino acids valine, isoleucine, leucine and phenylalanine. These amino acids are all present in significant amounts in aHVP (Solina et al., 2005). Benzaldehyde may be either lipid- or amino acid-derived (Solina et al.,

2005), and it is possible that some of the benzaldehyde found in these extrudates could also be derived from amino acids (Solina et al., 2005). The increased levels of dimethyl disulphide (22 and 65 ng/10 g) and dimethyl trisulphide (5 and 20 ng/10 g) found in these extrudates can be attributed to the presence of cysteine (16.8 ng/10 g) in the added aHVP (Solina et al., 2005).

Compounds present in both extrudates that had relative concentrations that exceeded their OTC in water (Badings, 1970; Fors, 1983) were hexanal, (*E*)-2-nonenal, (*E*,*E*)-2,4-decadienal, 3-methylbutanal, dimethyl disulphide and dimethyl trisulphide. 2-Pentylfuran exceeded its OTC in the extrudate obtained at 180 °C. Accordingly, most of these compounds were the same as previously identified as possible odour impact compounds in the starch and starch/glucose extrudates. It would therefore appear that these compounds provide the background odour of these extrudates and that as yet unidentified compounds are responsible for any difference in odour observed between these extrudates.

Accordingly, the addition of aHVP to starch had a more noticeable effect on the volatile composition of the extrudates than had been previously observed when glucose was the added ingredient. The most striking effect was the formation of the greater quantities of the four Strecker aldehydes and the increased levels of dimethyl disulphide and dimethyl trisulphide.

3.5. Volatile components of raw and extruded starch, glucose and aHVP

Thirty-eight compounds were identified in the starch/glucose/aHVP feedstock (Table 5), a greater number than previously found in the starch/glucose feedstock (Table 4) or the starch/aHVP feedstock (Table 5). Surprisingly, the additional compounds were mainly lipid-derived, reinforcing the observation that mixtures containing glucose were more susceptible to oxidation (Section 3.3). The quantity of volatile compounds found in this feedstock (439 ng/10 g) was also similar to that found in the starch/glucose feedstock (393 ng/10 g) but was far greater than found in the feedstock containing aHVP as the ingredient (268 ng/10 g).

Sixty compounds were identified in the starch/glucose/aHVP extrudate obtained at 150 °C and 67 were found in that obtained at 180 °C (Table 5). As previously observed for other extrudates, these numbers are far greater than found in the feedstocks. Lipid-derived compounds again dominated both extrudates (27 and 20), followed by Maillard reaction products (8 and 18), sulphur containing aliphatic compounds (4 and 6) and Strecker aldehydes (5 and 4). The remaining compounds found in these extrudates (16 and 19) were derived from sugar degradation, unidentified sources or were possible contaminants (Table 5). The relative concentrations of these compounds were all <11 ng/10 g with the exception of limonene (23 ng/10 g) in the extrudate obtained at 150 °C and 3-phenylfuran (70 ng/10 g) in the extrudate obtained at 180 °C (Table 5).

The quantities of volatiles found in the extrudates were again far greater than those found in the feedstock 1614 ng/10 g in the extrudate formed at 150 °C and 4274 ng/10 g in that produced at 180 °C. In the material extruded under mild conditions, lipid-derived compounds accounted for 30% of the total volatiles found but, under extreme conditions, such compounds only accounted for 9% of the volatile components. However, the quantities of lipid derived compounds found in each extrudate were quite similar (494 and 381 ng/10 g). As with the other extrudates containing aHVP, Strecker aldehydes, and in particular 3-methylbutanal, dominated the volatile profile found in the material extruded at both 150 and 180 °C (59% and 77% of the total volatiles). The major compounds found in the extrudate produced at 150 °C were 3-methylbutanal (150 ng/10 g), hexanal (160 ng/10 g), 2-methylbutanal (150 ng/10 g), phenylacetaldehyde (150 ng/10 g) (*E*,*E*)-2,4-decadienal (84 ng/10 g), dimethyl disulphide (64 ng/10 g) (*E*,*Z* or *Z*,*E*)-2,4-decadienal (47 ng/10 g) and 2-pentylfuran (44 ng/10 g). By comparison, in the extrudate formed at 180 °C, the major compounds were 3-methylbutanal (2900 ng/10 g), phenylacetaldehyde (260 ng/10 g), dimethyl disulphide (210 ng/10 g), 2-methylbutanal (100 ng/10 g), hexanal (100 ng/10 g), (*E*,*E*)-2,4-decadienal (78 ng/10 g), 3-phenylfuran (70 ng/10 g) and dimethyl trisulphide (64 ng/10 g). The source of the Strecker aldehydes and sulphur-containing aliphatic compounds has been discussed previously (Section 3.4) but the origin of 3-phenylfuran requires some explanation. A likely pathway to this compound, as shown in Fig. 1, would involve an aldol condensation between phenylacetaldehyde and hydroxyacetaldehyde, a recognised retro-aldol decomposition product of glucose (Vernin & Párkányi, 1982).

The remaining compounds found in large numbers in the extrudates were the Maillard reaction products, and in particular pyrroles and alkylpyrazines (Table 5). The formation of these compounds was favoured by the higher temperature of extrusion with only 2 pyrroles and 6 alkylpyrazines found in the extrudate produced at 150 °C compared with 4 pyrroles and 13 alkylpyrazines found in the material extruded at 180 °C. However the quantity of these compounds produced during extrusion was relatively small, only 1% of the total volatiles found in the extrudate obtained at 150 °C and 4.4% of that found in the extrudate obtained at 180 °C. In the product formed at 180 °C, the major Maillard reaction products were pyrazine (49 ng/10 g), ethylpyrazine (42 ng/10 g) and methylpyrazine (36 ng/10 g). The relative concentrations of the remaining 15 Maillard reaction products varied between trace (<0.5 ng/10 g) and 8 ng/10 g (Table 5). All of these Maillard reaction products can be formed by the combined interaction of retro-Aldol degradation products of glucose, and in certain cases Strecker aldehydes, with ammonia derived from the Strecker degradation of free amino acids (Vernin & Párkányi, 1982). It is important to note that these Maillard reaction products were not found in extrudates produced from starch/aHVP feedstock, although

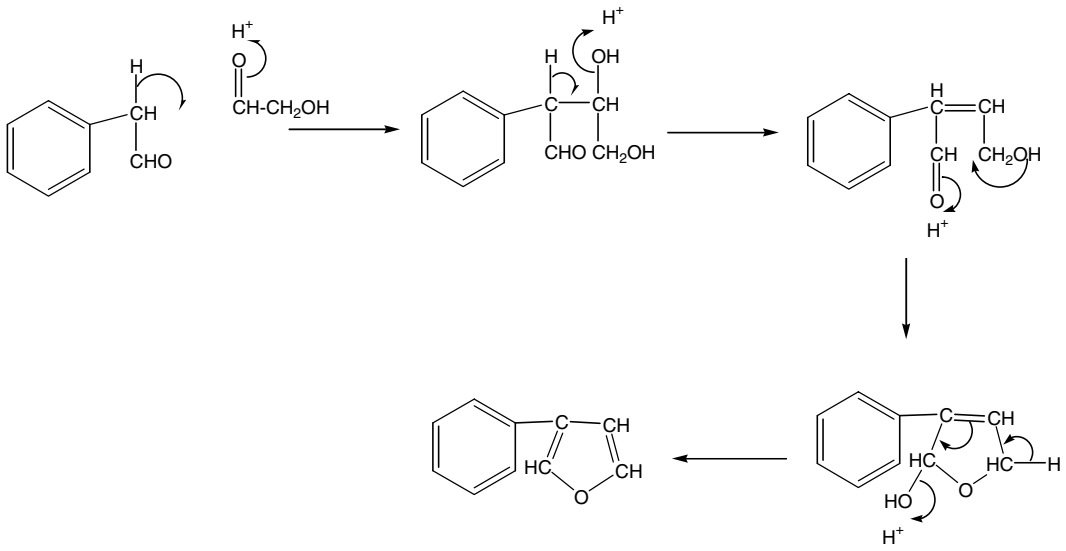

Fig. 1. Possible reaction pathway to 3-phenylfuran.

some reducing sugars were known to be formed during the extrusion process (Section 3.1). As the concentrations of the reducing sugars formed in the extrudates at 150 °C (75 ng/10 g) and at 180 °C (85 ng/10 g) were comparable with the quantity of glucose (100 ng/10 g) added to the feedstock, it would appear that the structure of these reducing sugars restricts their involvement in the formation of Maillard reaction products. However, this explanation is difficult to support, as these same reducing sugars were apparently involved in the Strecker degradation of amino acids during the extrusion of the starch/aHVP feedstock (Section 3.4).

Ten compounds, present in the extrudate obtained at 150 °C, had relative concentrations that exceeded their OTC in water. These were, hexanal, nonanal, (*E*)-2-nonenal, (*E*,*E*)-2,4-decadienal, 1-octen-3-ol, 3-methylbutanal, 2-methylbutanal, phenylacetaldehyde, dimethyl disulphide and dimethyl trisulphide. However, in the extrudate obtained at 180 °C two of these compounds, 1-octen-3-ol and 2-methylbutanal, did not exceed their OTC in water (Table 5). Four of these compounds, nonanal, 1-octen-3-ol, 2-methylbutanal and phenylacetaldehyde had not been previously identified as possible odour impact components in the starch, starch/glucose or starch/aHVP extrudates. Accordingly, these compounds could be expected to modify the odour of the starch/glucose/aHVP extrudate so that they would be appreciably different from the extrudates of the other three feedstocks. Interestingly, none of the identified Maillard reaction products, either pyrroles or alkylpyrazines, found in the extrudate obtained at 180 °C, exceeded their OTC in water.

The combined addition of glucose and aHVP to starch produced a significant effect on the volatile composition of both extrudates and, in particular, that obtained at 180 °C. In the material extruded under extreme conditions, the greatest effects were the formation of greater quantities of three Strecker aldehydes, the increased number and quantity of the sulphur-containing compounds and the production of Maillard reaction products.

3.6. Sensory analysis of volatile components of extrudates obtained at 180 °C

Preliminary qualitative sensory assessment of the eight extrudates obtained at 150 and 180 °C showed that, for each feedstock, the extrudates obtained at 180 °C had relatively "stronger" odours. As a consequence, only those materials that were obtained by extrusion under extreme conditions will be discussed. The extruded starch had an odour of very "low" intensity that resembled wet paper with a sweet overtone. That of the starch/glucose extrudate was also of "low" intensity with an odour reminiscent of rice crispbread. By comparison, the odour of the starch/aHVP extrudate was of "moderate" intensity and was described as savoury with malty notes. That associated with the starch/glucose/aHVP extrudate was "moderate" to "strong" in intensity and was described as a pleasant sweet bakery odour, reminiscent of cheese cracker. Of these four extrudates, the qualitative sensory assessment indicated that the material containing both ingredients, glucose and aHVP, had the most interesting and complex odour. Accordingly, this extrudate was chosen for further sensory assessment using gas chromatography olfactometry (GCO), together with the starch extrudate as a base reference material. In an attempt to identify those compounds contributing to the odours of these extrudates, these materials were analysed by GCO at three dilutions. Those compounds detected at the greatest dilution could be expected to most influence the odours of the two extrudates.

3.7. GCO profile of starch extrudate

The GCO analyses of the volatile components of the starch extrudate processed at 180 °C led to the detection

of 16 odour points of which 11 had LRI values that corresponded to identified compounds (Table 6). Accordingly, it would appear that some of the odorous components were present at concentrations below their GC-MS detection limits. None of the odours were described as "very strong" but four were described as "strong". These odours corresponded to the LRI values of three identified compounds, 2-furfural, heptanal, 1-octen-3-ol and an unidentified compound. Another five odours were described as "moderate" in their intensities. Four of these odour points corresponded to the LRI values of dimethyl disulphide, hexanal, 2-pentylfuran, octanal and an unidentified compound. Descriptors used by the panel for most of these compounds were in agreement with those reported in the literature (Aldrich, 1998; Badings, 1970; Fors, 1983). However, it is accepted that, for some odours, the compounds identified might not be responsible for the perceived odour. At one tenth dilution, nine odours were detected, of which two had intensities described as "moderate" (Table 6). One of the odour points had the same LRI value as 2-furfural and the other corresponded to that of an unidentified component. Another seven odours were described as "weak" and, of these, six had retention indices that corresponded to the LRI values of hexanal, (*E*)-2-heptenal, benzaldehyde, 1-octen-3-ol, 2-pentylfuran and nonanal. No odours were detected at one hundredth dilution.

All nine odorous compounds detected at the one tenth dilution could be expected to influence the odour of the starch extrudate. Of these, 2-furfural could contribute to the sweet overtone of this odour although its relative concentration in this extrudate is well below its OTC in water, of 30 ng/10 g (Fors, 1983). Other compounds, such as (*E*)-2-heptenal, octanal and nonanal could also contribute to the "wet paper" odour associated with this extrudate. However, further studies are required to identify the two unidentified odour components detected at the one tenth dilution.

3.8. GCO profile of the starch, glucose and aHVP extrudate

Some 54 odour points were detected in the GCO analyses of the volatile components of the starch/glucose/aHVP extrudate processed at 180 °C, of which 31 had LRI values that corresponded to identified compounds (Table 7). Accordingly, it would appear that many of the odorous compounds in this extrudate were also present in quantities below their GC-MS detection limited. Four of these odours were described as "very strong" and 26 as "strong". Of the odours with "very strong" intensities, only one had an LRI value that corresponded to an identified compound, namely 2-heptanone. By comparison, 21 of the 26 odour points with "strong" intensities had the same LRI values as identified compounds (Table 7). At one tenth dilution, 46 odours were detected, of which, 15 had intensities described as "strong". Ten of these odours had LRI values that corresponded to identified compounds. Prominent among these compounds were hexanal, methylpyrazine, 2,4,5-trimethyloxazole, hexanol, 2-heptanone, 2,5- or 2,6-dimethylpyrazine, ethylpyrazine, dimethyl trisulphide, 1-octen-3-ol and 2-pentylfuran. At one hundredth dilution, 30 odours were detected, of which 17 had LRI values that corresponded to identified compounds (Table 7). Only three of these odours were described as "strong", whereas another 12 were of "medium" intensity. One of the "strong" odours had the same LRI value as 2,5- or 2,6-dimethylpyrazine. Of those odours with "medium" intensity, 9 had the same LRI values as dimethyl disulphide, methylpyrazine, methyl ethyl disulphide, hexanol, 2-heptanone, dimethyl trisulphide, 1-octen-3-ol, 2-pentylfuran and 5-methyl-2-phenyl-2-hexanal.

Table 6
GCO analysis of volatile components at different concentrations of wheat starch extruded under extreme conditions

LRI[a]	Odour description	Odour intensity[b]			Major compound in region of odour[c]
		10 g	1 g	0.1 g	
<650	Apples	W	–	–	Unknown
756	Fried onions	M	–	–	Dimethyl disulphide
817	Green	M	W	–	Hexanal
841	Bread-like, sweet on dilution	S	M	–	2-Furfural
860	Caramel, toffee	M	–	–	Unknown
907	Burnt toast	S	–	–	Heptanal
924	Sweet apples, caramel-like on dilution	S	M	–	Unknown
961	Musty, putty like	W	W	–	(*E*)-2-Heptenal
979	Burnt sugar	W	W	–	Benzaldehyde
984	Fresh mushrooms	S	W	–	1-Octen-3-ol
989	Savoury, mustard-like	M/W	W	–	Unknown
995	Metallic	M	W	–	2-Pentylfuran
1008	Dough-like	M	–	–	Octanal
1105	Fatty	W	W	–	Nonanal
1129	Vegemite	W	–	–	Unknown
1162	Fried fat	W	–	–	(*E*)-2–Nonenal

[a] LRI, Linear Retention Index.
[b] S, "strong"; M, "moderate"; W, "weak"; – not present.
[c] Odour description need not necessarily relate to compound(s) identified in this region of the chromatogram.

Table 7
GCO analysis of volatile components at different concentrations of wheat starch/aHVP/glucose extruded under extreme conditions

LRI[a]	Odour description	Odour intensity[b]			Major compound in region of odour[c]
		10 g	1 g	0.1 g	
669	Acrid, toffee-like after dilution	S	W	W	3-Methylbutanal
677	Toast	W	–	–	2-Methylbutanal
711	Sharp, buttery	S	–	–	2,3-Pentanedione
756	Sulphur, boiled cabbage	S	S/M	M	Dimethyl disulphide
805	Cabbage, vegetable-like	S	M	–	3-Methylthiophene
817	Green beans, sweet on dilution	S	S	W	Hexanal
829	Burnt, buttered crust, bread, malt on dilution	M	M	–	1-Ethyl-1*H*-pyrrole
832	Cabbage, vegetable, pickle, vinegar	M	M	W	Unknown (acetic acid)
835	Ester-like, apple	VS	S	M	Unknown
839	Potato-like	S	S	M	Methylpyrazine
841	Bread-crust, sweet	S	M	–	2-Furfural
845	Sickly sweet, crushed ants, floral on dilution	VS	S	S	Unknown
848	Vegetable, burnt, cabbage-like	S	S	W	2,4,5-Trimethyloxazole
858	Cut grass	S	–	–	(*E*)-2-Hexenal
861	Sharp, sulphurous, onion-like on dilution	S/M	M	M	Methyl ethyl disulphide
863	Broccoli	M	W	–	Unknown
876	Broccoli-like, onion, peppery on dilution	S	S/M	W	Unknown
880	Burnt	S	S	M	1-Hexanol
892	Putrid, crushed ant	M	M	–	Unknown
989	Sweet, apple-like on dilution	VS	S	M	2-Heptanone
907	Sweet, metallic, fruity on dilution	M	W	–	Heptanal
910	Boiled cabbage, sulphury	S	W	–	3-(Methylthio)propanal
916	Sweet, buttered popcorn, wheat biscuit	S	S	S	2,5- or 2,6-Dimethylpyrazine
919	Biscuit, buttery	S	S	W	Ethylpyrazine
944	Sweet, baked bread	W	–	–	Unknown
955	Amine-like, baked fish	VS	S	M	Unknown
961	Putty, malt	W	W	–	(*E*)-2-Heptenal
975	Sweet, meaty, burnt	S	S	M	Dimethyl trisulphide
984	Mushroom	S	S	M	1-Octen-3-ol
995	Rubbery, metallic	S	S	M	2-Pentylfuran
1000	Baked bread	S	–	–	2-Ethyl-5-methylpyrazine
1021	Cooked battered fish	M	W	–	Unknown
1034	Sweet citrus	S	W	–	Limonene
1053	Sweet, musk, vanilla	M	M	–	Unknown
1063	Floral	S	M	–	Phenylacetaldehyde
1093	Floral	S	–	–	2-Nonanone
1126	Biscuit, peanut butter, bread	M	M	W	3,5-Dimethyl-2-methylpyrazine
1137	Burnt, biscuit-like	S	W	–	Unknown
1171	Biscuit, chocolate-like on dilution	M	W	W	Unknown
1179	Floral, daisy-like	W	–	–	Unknown
1215	Green, floral	W	W	–	2-Decanone
1257	Rubber-like, acrid, bread crust	W	–	–	Benzothiazole
1295	Buttered biscuit	M	W	W	(*E*,*Z*- or *Z*,*E*)-2,4-Decadienal
1317	Biscuit, floral, chocolate	M	M	W	(*E*,*E*,)-2,4-Decadienal
1378	Dough-like, baked potatoes	W	W	–	Unknown
1407	Raw potatoes	M	M	–	Unknown
1431	Sweet biscuit, malty on dilution	M	W	W	Unknown
1486	Sweet coffee, malt biscuit on dilution	S	M	M	5-Methyl-2-phenyl-2-hexenal
1525	Biscuit, roasted coffee, malty on dilution	S	S	S	Unknown
1543	Biscuit, shortbread-like on dilution	W	W	W	Unknown
1651	Biscuity, sweet meat-like on dilution	M	W	W	Unknown
1725	Biscuity, coffee, crushed ant on dilution	S	W	W	Unknown
1761	Biscuity, savoury cracker-like	M	M	W	Unknown
1781	Roast meat, savoury cracker	S	S	M	Unknown

[a] LRI, Linear retention index.
[b] VS, "very strong"; S, "strong"; M, "moderate"; W, "weak"; – not present.
[c] Odour description need not necessarily relate to the compound(s) identified in this region of the chromatogram.

All 30 odorous compounds detected at one hundredth dilution could be expected to influence the odour of the starch/glucose/aHVP extrudate, previously described by panellists as a "sweet bread-like" odour reminiscent of "cheese crackers". However, of these, the three odours with the strongest intensities at this dilution would appear to contribute most to the perceived odour of the extrudate. One of these odour points had an LRI that corresponded

to either 2,5- or 2,6-dimethylpyrazine but the odour threshold values in water of these compounds, 18 and 15 μg/10 g (Fors, 1983), are far too high for such compounds to be responsible for the detected odour. As the LRI values of the other two odour points did not correspond to any identified compounds, the compounds responsible for all three ''strong'' odours must be considered unidentified. Of the 12 odour points of ''medium' intensity detected at one hundredth dilution, the compounds responsible for only five of these odours appear to have been identified. The likely sources of these odours were dimethyl disulphide, methyl ethyl disulphide, dimethyl trisulphide, 1-octen-3-ol and 5-methyl-2-phenyl-2-hexanal. Another four odour points had LRI values that corresponded to identified components, but it is unlikely that any of these compounds could be responsible for the odours described (Table 7). The remaining two odour points of ''medium'' intensity did not correspond to the LRI values of any of the identified components. Accordingly, the majority of compounds responsible for the odour of the extrudate have yet to be identified. Further studies involving the use of increased quantities of glucose and aHVP, possibly to the 5% level, would appear to be necessary to achieve these identifications.

3.9. Role of glucose and aHVP in odour development of extruded products

Studies by Bredie and co-workers (1997) had shown that extruded wheat starch had a very weak odour. As a consequence, starch was an ideal feedstock to study the effect of added ingredients on odour development during extrusion. Our studies confirmed this observation. A similar ''low'' intensity odour was also observed for our starch/glucose extrudate. However, the odour of the starch/glucose extrudate was different from that of starch alone although the volatile profiles of the two extrudates obtained at 180 °C were very similar (Table 4). Odorous compounds not detected by the GC-MS would be responsible for this difference. Accordingly, it would appear that the addition of 1% glucose to starch only slightly modified the odour of the resultant extrudate. This result is in agreement with that previously reported by Farouk and co-workers (2000). By comparison, the addition of aHVP to the starch feedstock gave a ''moderately'' intense odour that was significantly different from that of either the starch or starch/glucose extrudates. The volatile profile of the extrudate containing aHVP was also more complex than those of the other two, with almost double the number of components detected. The most striking differences between these extrudates were the presence of large levels of Strecker aldehydes and sulphur-containing aliphatic compounds in the extrudate containing aHVP (Table 5). As such, the addition of aHVP to starch, even at the 1% level, achieved an appreciable increase in volatile content and odour, compared with those associated with the starch and starch/glucose extrudates.

The addition of both glucose and aHVP to the starch feedstock gave extrudates with the most complex volatile profiles and strongest odours. The increase in volatile content was principally due to the presence of Maillard reaction products in the extrudate obtained at 180 °C. However, it would appear that none of these additional compounds were responsible for the increase in odour (Table 7). Evidence would indicate that the important odour-active components are yet to be identified (Section 3.8). Even so, the results obtained in this study demonstrate that the addition of 1% glucose and 1% aHVP to starch has a profound effect on the volatile content of extruded products, particularly those processed at 180 °C.

Acknowledgements

The authors thank Mr. C. Chessari, D. Raynor, J. Sellahewa and Dr. R. Sleigh for valuable advice and assistance during the operation of the extruder.

References

Aldrich (1998). *Flavours and Fragrances*. Sigma-Aldrich: Milwaukee, pp. 1–115.

Badings, H. T. (1970). Cold-storage defects in butter and their relation to the autoxidation of unsaturated fatty acids. *Nederlands Melk en Zuiveltijdschr, 24*, 147–256.

Bredie, W. L. P., Hassell, G. M., Guy, R. C. E., & Mottram, D. S. (1997). Aroma characteristics of extruded wheat flour and wheat starch containing added cysteine and reducing sugars. *Journal of Cereal Science, 25*, 57–63.

Bredie, W. L. P., Mottram, D. S., & Guy, R. C. E. (1998a). Aroma volatiles generated during extrusion cooking of maize flour. *Journal of Agricultural and Food Chemistry, 46*, 1479–1487.

Bredie, W. L. P., Mottram, D. S., Hassell, G. M., & Guy, R. C. E. (1998b). Sensory characterisation of the aromas generated in extruded maize and wheat flour. *Journal of Cereal Science, 28*, 97–106.

Bruechert, L. J., Zhang, Y., Huang, T.-C., Hartman, T. G., Rosen, R. T., & Ho, C.-T. (1988). Contribution of lipids to volatile generation in extruded corn-based model systems. *Journal of Food Science, 53*, 1444–1447.

Camire, M. E., & Belbez, E. O. (1996). Flavor formation during extrusion cooking. *Cereals Foods World, 41*, 734–736.

Camire, M. E., Camire, A., & Krumhar, K. (1990). Chemical and nutritional changes in foods during extrusion. *CRC Critical Reviews in Food Science and Nutrition, 29*, 35–57.

Englyst, H. N., & Hudson, G. J. (1987). Colorimetric method for routine measurement of dietary fibre as non-starch polysaccharides. A comparison with gas-liquid chromatography. *Food Chemistry, 24*, 63–76.

Farouk, A., Pudil, F., Janda, V., & Porkornỳ, J. (2000). Effect of amino acids on the composition and properties of extruded mixtures of wheat flour and glucose. *Nahrung, 44*, 188–192.

Fors, S. (1983). Sensory properties of volatile Maillard reaction products and related compounds: A literature review. In *The Maillard reaction in foods and nutrition*. In G. R. Waller & M. S. Feather (Eds.). *ASC Symposium Series* (215, pp. 185–286). Washington, DC: American Chemical Society.

Frankel, E. N., Neff, W. E., & Selke, E. (1981). Analysis of autoxidized fats by gas chromatography – mass spectrometry: VII. Volatile thermal decomposition products of pure hydroperoxides from autoxidized and photosensitized oxidized methyl oleate, linoleate and linolenate. *Lipids, 16*, 279–285.

Ho, C.-T., & Riha, W. E. (1998). Formation of Maillard aromas during extrusion cooking. In J. O'Brien, H. E. Nursten, M. J. C. Crabbe, & J. M. Ames (Eds.), *The Maillard reaction in foods and medicine* (pp. 187–196). Cambridge, UK: The Royal Society of Chemistry.

Hwang, C.-F., Riha, W. E., Jin, B., Karwe, M. V., Hartman, T. G., Daun, H., et al. (1997). Effect of cysteine addition on the volatile compounds released at the die during twin-screw extrusion of wheat flour. *Lebensmittel Wissenschaft und Technologie, 30*, 411–416.

Neff, W. E., Frankel, E. N., Selke, E., & Weisleder, D. (1983). Photosensitized oxidation of methyl linoleate monohydroperoxides: hydroperoxy cyclic peroxides dehydroperoxides, keto esters and volatile thermal decomposition products. *Lipids, 18*, 868–876.

Official Methods of AOAC International, (1995). Supplement March 1996 (16th ed.), Official Methods 920.85, 922.06, 940.28, 963.22, 991.39 Gaithersburg: AOAC International.

Parker, J. K., Hassell, G. M. E., Mottram, D. S., & Guy, R. C. E. (2000). Sensory and instrumental analyses of volatiles generated during the extrusion cooking of oat flours. *Journal of Agricultural and Food Chemistry, 48*, 3497–3506.

Politz, M. L., Timpa, J. D., White, A. R., & Wasserman, B. P. (1994). Non-aqueous gel permeation chromatography of wheat starch in dimethylacetamide (DMAC) and LiCl: extrusion-induced fragmentation. *Carbohydrate Polymers, 24*, 91–99.

Riha, W. E., & Ho, C.-T. (1998). Flavour generation during extrusion cooking. In *Advances in experimental medicine and biology*. In F. Shahidi, C.-T. Ho, & N. van Chuyen (Eds.). *Process-induced chemical changes in food* (vol. 434, pp. 297–306). New York: Plenum Press.

Riha, W. E., Hwang, C.-F., Karwe, M. V., Hartman, T. G., & Ho, C.-T. (1996). Effect of cysteine addition on volatiles of extruded wheat flour. *Journal of Agricultural and Food Chemistry, 44*, 1847–1850.

Solina, M., Baumgartner, P., Johnson, R. L., & Whitfield, F. B. (2005). Volatile aroma compounds of soy protein isolate and acid-hydrolysed vegetable protein. *Food Chemistry, 90*, 861–873.

Vernin, G., & Párkányi, C. (1982). Mechanisms of formation of heterocyclic compounds in Maillard and pyrolysis reactions. In G. Vernin (Ed.), *Chemistry of heterocyclic compounds in flavours and aromas* (pp. 151–207). Chichester: Ellis Horwood Limited.

Villota, R., & Hawkes, J. G. (1994). Flavouring in extrusion: An overview. In T. H. Parliament, T. H. Morello, & M. J. McGorrin (Eds.). *Thermally Generated Flavours; Maillard, Microwave and Extrusion Processes. ACS Symposium Series* (543, pp. 280–295). Washington DC: American Chemical Society.