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

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Abstract

The volatile components produced in wheat starch containing 1% soy protein isolate (SPI), and wheat starch/1% SPI 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/glucose/SPI and starch/glucose/SPI/aHVP extrudates obtained at 180 °C. In total, 94 compounds were identified in the eight extrudates. The smallest number (31) was found in the extrudate of the starch/glucose/SPI feedstock processed at 150 °C and the largest (64) in the extrudate of the starch/SPI feedstock 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. Strecker aldehydes were also present in all extrudates; however, in those extrudates containing aHVP, these compounds were quantitatively the dominant components. Maillard reaction products, such as pyrroles, pyrazines and oxazoles, were mainly found in extrudates containing aHVP whereas sulphur-containing aliphatic compounds were found in all extrudates. The production of the Maillard reaction products and sulphur-containing compounds was 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. In addition, SPI was found to have a modifying effect on the volatile content and odour of extrudates also containing glucose and aHVP.

Keywords: Extrusion; Soy protein isolate; Acid-hydrolysed vegetable protein; Glucose; Starch; Odour; Volatiles; GC–MS analyses

1. Introduction

Soy protein isolate (SPI) and hydrolysed vegetable protein (HVP) have become important ingredients in extruded foods as a result of their availability at reasonable cost and demonstrated functional and nutritional values (Messina, 1995; Lusas & Riaz, 1995). SPI is used for texturisation and to increase the protein content of foods (Lusas & Riaz, 1995). HVP is added to promote cooked and roasted odours through Maillard reactions (Aaslyng et al., 1998). Currently, little is known of the effects that SPI and HVP, as ingredients, have on the odour of extruded cereal-based foods. As manufactured, SPI has a slight green or bean-like odour (Solina, Baumgartner, Johnson, & Whitfield, 2005) whereas the odour of HVP varies, depending on its method of preparation. When HVP is produced by enzymic hydrolysis, its odour is described as bouillon/soy or malt/brown bread (Aaslyng et al., 1998) whereas the product obtained by acid hydrolysis is described as green, garlic and onion-like, and somewhat similar to chicken broth (Solina et al., 2005). Consequently, the retention, by extruded foods, of compounds responsible for these ingredient odours could influence the acceptability of the final product. Furthermore, the interaction of the cereal base, during extrusion, with non-volatile compo-

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nents, such as amino acids and fatty acids present in these ingredients (Solina et al., 2005), could lead to the production of additional odorous compounds that would also contribute to the odour of extruded foods.

We have recently reported on the effect that the addition of 1% acid-hydrolysed vegetable protein (aHVP), both in the presence and absence of 1% glucose, had on the odour of wheat starch extruded under mild (150 °C and 20% moisture) and extreme (180 °C and 16% moisture) conditions (Solina, Johnson, & Whitfield, 2007). The greatest effects were observed in the extrudates obtained at 180 °C. Under these conditions, the addition of aHVP alone produced a soy/malt-like odour of "medium" intensity whereas that containing both aHVP and glucose produced a bakery/cheese cracker odour of "strong" intensity. Some of the compounds responsible for these odours were identified by gas chromatography-mass spectrometry (GC–MS) coupled with gas chromatography olfactometry (GCO) (Solina et al., 2007). Lipid oxidation and Maillard reaction of amino acids and reducing sugars appeared to be the major source of these compounds. As part of a continuing study, we now report on the effects that the addition of 1% SPI alone, and in combination with 1% glucose, 1% aHVP and 1% glucose/1% aHVP, has on the odour of wheat starch extruded under mild and extreme conditions. The paper will consider the influence that the addition of such ingredients to 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, NSW, Australia) and was free of all 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 material also contained a significant level of unbound lipids, including free fatty acids, of 0.2% (Solina et al., 2007). Reducing sugars were not detected in the raw starch; however, extrusion of this material under mild and extreme conditions gave a reducing sugar content in the extrudates of 75 and 85 mg/10 g (Solina et al., 2007). The SPI was purchased from ADM Protein Specialists P/L (Decatur, IL) and had a moisture content of 10.3% and a pH of 6.6. This material had a protein content of 82.5% w/w but contained no detectable free amino acids or reducing sugars (Solina et al., 2005). The SPI had a bound lipid content of 3% w/w, and an unbound lipid content, including free fatty acids, of 0.5% w/w (Solina et al., 2005). The aHVP was purchased from Halcyon Protein P/L (Dandenong, VIC, Australia) and was derived from soy protein. This material had a moisture content of 6.4% w/w, a free amino acids content of 18.4% w/w and a unbound lipid content, including free fatty acids, of 0.4% w/w but was free of reducing sugars (Solina et al., 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. Extrusion processing

The flour feedstocks under investigation, starch/1% SPI, starch/1% glucose/1% SPI, starch/1% SPI/1% aHVP and starch/1% glucose/1% SPI/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 mild (150 °C and 20% moisture) and extreme (180 °C and 16% moisture) processing 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 screw section 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 26% and 27%. The die pressure was recorded in the die entrance area. This pressure was highest (240 psi) for wheat starch/SPI extruded under mild conditions and lowest (40–100 psi) for starch/glucose/SPI 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 conditions (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.

2.3. Sensory assessment of extrudate 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 agreed upon by the panellists. Panellists were chosen based on their enthusiasm and ability to recognise and describe a range of cooked food odours.

2.4. 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 P/L, 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. 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 GCO, volatile extracts from three different quantities (10, 1 and 0.1 g) of starch/glucose/SPI and starch/glucose/SPI/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.

2.5. Analysis of volatiles by gas chromatography–mass spectrometry

Analyses were performed on a Hewlett-Packard HP 5890 series II Plus 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 amu 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 all response factors were 1. These concentrations are reported as ng/10 g sample. Compounds described as "trace" were present at concentrations of <0.5 ng/10 g sample. The reported relative concentrations are the averages of three separate isolations collected from each sample.

2.6. 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, 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 GCO analyses.

3. Results and discussion

3.1. Volatile components of raw and extruded wheat starch and SPI

Analysis of the volatile components of the starch/SPI feedstock resulted in the identification of 33 compounds (Table 1), of which 17 were derived from the oxidation of the free fatty acids present in the starch and SPI (Solina et al., 2005; Solina et al., 2007). These compounds, principally alkanals (C_5–C_{10}), (*E*)-2-alkenals (C_7–C_9), (*E*,*E*)-2,4-alkadienals (C_9–C_{10}), 1-alkanols (C_5–C_8), and 2-pentylfuran, accounted for 71% of the volatiles (571 ng/10 g) isolated from the feedstocks. In addition, benzaldehyde, also a possible lipid oxidation product (Bruechert et al., 1988), and 2-butyl-2-octenal, an aldol condensation product of hexanal (Solina et al., 2005), were identified. Of the remaining 14 compounds, dimethyl disulphide, 1-*tert*-butoxy-2-methoxyethane and 1-nitrohexane had been found in SPI (Solina et al., 2005), and pyridine, toluene, octane, 1,4-dimethylbenzene, limonene and ethyl acetate had been identified in starch (Solina et al., 2007). With the exception of dimethyl disulphide, 1-nitrohexane and limonene, the other six compounds were all industrial solvents and, as such, were environmental contaminants. The remaining five compounds, all present in quantities of 1 ng/10 g or less, have not been found in either the starch or SPI used in this study. Four compounds, hexanal (220 ng/10 g), 2-pentylfuran (110 ng/10 g), pyridine (48 ng/10 g) and ethyl acetate (36 ng/10 g), dominated the profile of the volatile extract and accounted for 73% of the volatiles isolated from the feedstock.

Extrusion of the starch/SPI feedstock under mild and extreme conditions increased the number of compounds identified; 38 were found in the material extruded at 150 °C and 64 in that extruded at 180 °C (Table 1). However, whereas the amount of volatiles recovered from the extrudate formed at 180 °C (1088 ng/10 g) increased, that obtained from the product formed at 150 °C (466 ng/10 g) was less than that found in the feedstock. Lipid-derived compounds again dominated, both qualitatively and quantitatively, the volatile profiles of these extrudates. In the material produced under mild conditions, 22 compounds, accounting for 86% of volatiles isolated, were derived from lipid oxidation, whereas the extrudate produced under extreme conditions had 27 compounds derived from this source and these accounted for 52% of the volatile content. Benzaldehyde was found in increased amounts in both extrudates but the levels of 2-butyl-2-octenal had decreased compared with that found in the feedstock. Of the remaining 14 compounds found in the extrudate produced at 150 °C, only the contaminant, 1-*tert*-butoxy-2-methoxyethane, was present in a quantity that exceeded 10 ng/10 g. By comparison, in the extrudate formed at 180 °C, 13 of the remaining compounds exceeded this quantity. Prominent among these 13 were three Strecker aldehydes, 3-methylbutanal (57 ng/10 g), 2-methylbutanal (16 ng/10 g) and phenylacetaldehyde (14 ng/10 g). A fourth Strecker aldehyde, 2-methylpropanal (5 ng/10 g) was also present. These compounds accounted for 9% of volatiles isolated. Other compounds that exceeded 10 ng/10 g were dimethyl disulphide, limonene and the contaminants, toluene, 1,4-dimethylbenzene, ethyl acetate, 1-*tert*-butoxy-2-methoxyethane and 1-*tert*-butoxy-2-ethoxyethane. Compounds present in greatest amounts in the extrudates obtained at 150 °C and 180 °C, excluding the contaminants, were hexanal (170 and 230 ng/10 g), 2-pentylfuran (36 and 110 ng/10 g), 3-methylbutanal (tr and 57 ng/10 g), 2-heptanone (24 and 48 ng/10 g), (*E*,*E*)-2,4-decadienal (36 and 29 ng/10 g) and dimethyl disulphide (2 and 23 ng/10 g), respectively.

All of the aliphatic aldehydes (alkanals, 2-alkenals and 2,4-alkadienals), 2-alkanones and 1-alkanols found in the extruded products were derived, either directly or indirectly, from the oxidative breakdown of oleic, linoleic and linolenic acids (Badings, 1970). These compounds are the dominant fatty acids present in starch (Solina et al., 2007) and SPI (Solina et al., 2005). Furthermore, such fatty acids are the likely source of the 2-alkylfurans (Frankel, Neff, & Selke, 1981).

Free amino acids are the only possible source of the Strecker aldehydes in the extrudates but no measurable quantities of these acids were found in either the starch (Solina et al., 2007) or the SPI (Solina et al., 2005). However, SPI has a protein content of 82%. Thermal or physical disruption of such proteins during extrusion at 180 °C could produce sufficient amino acids to account for the Strecker aldehydes found in the extrudate formed under extreme conditions. The amino acids valine, leucine, isoleucine and phenylalanine, the precursors of such Strecker aldehydes, were all major components of the protein fraction of SPI (Solina et al., 2005). In addition, cysteine and methionine from such protein would appear to be the source of the disulphides and trisulphide found in this extrudate (Table 1). Dicarbonyl compounds required to promote the Strecker degradation would be derived from reducing sugars formed by the thermal cleavage of the starch during extrusion (Solina et al., 2007).

Five compounds present in both extrudates had relative concentrations that exceeded their odour threshold concentrations (OTC) in water (Badings, 1970; Fors, 1983). These compounds were hexanal, (*E*)-2-nonenal, (*E*,*E*)-2,4-decadienal, 2-pentylfuran and dimethyl trisulphide. A further two compounds, 3-methylbutanal and dimethyl disulphide, exceeded their OTC in the extrudate obtained at 180 °C. Accordingly, it would be expected that all of these compounds could contribute to the odours of the extrudates obtained at 150 and 180 °C.

Table 1
Relative concentrations of headspace volatiles of starch/SPI and starch/glucose/SPI feedstocks extruded under different conditions of temperature and moisture content

Identity	LRI[a]	Starch/SPI						Starch/glucose/SPI						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	8	(1.7)	2	(2.7)	17	(4.9)	2	(1.1)	39	(8.1)	11	(2.0)	MS + LRI
Hexanal	817	220	(44)	170	(40)	230	(5.5)	150	(36.4)	280	(21)	250	(34)	MS + LRI
Heptanal	907	7	(1.7)	21	(1.0)	18	(4.2)	4	(2.9)	14	(2.9)	23	(5.4)	MS + LRI
Octanal	1008	3	(0.1)	2	(0.2)	5	(0.1)	3	(0.5)	3	(<0.1)	4	(1.2)	MS + LRI
Nonanal	1105	10	(2.6)	5	(0.1)	9	(<0.1)	12	(2.9)	–	–	–	–	MS + LRI
Decanal	1204	2	(0.7)	3	(0.6)	2	(0.3)	3	(0.7)	1	(0.2)	2	(0.6)	MS + LRI
(*E*)-2-Hexenal	858	–	–	1	(0.1)	1	(<0.1)	–	–	1	(0.2)	1	(0.2)	MS + LRI
(*E*)-2-Heptenal	961	3	(1.3)	5	(0.8)	3	(0.4)	2	(0.5)	5	(0.1)	6	(1.5)	MS + LRI
(*Z*)-2-Octenal	1062	6	(1.6)	10	(1.5)	15	(1.4)	6	(0.8)	9	(0.4)	11	(1.8)	MS + LRI
(*E*)-2-Nonenal	1162	10	(1.2)	12	(1.3)	10	(2.9)	12	(2.5)	8	(0.6)	16	(2.2)	MS + LRI
(*E*,*E*)-2,4-Octadienal	1120	–	–	1	(0.1)	1	(<0.1)	tr	(0.3)	–	–	–	–	MS + LRI
(*E*,*E*)-2,4-Nonadienal	1217	1	(0.3)	1	(0.1)	–	–	1	(0.2)	–	–	–	–	MS + LRI
(*E*,*Z* or *Z*,*E*)-2,4-Decadienal	1295	–	–	22	(3.0)	13	(1.0)	tr	(0.1)	30	(5.4)	52	(14)	MS
(*E*,*E*)-2,4-Decadienal	1317	2	(0.5)	36	(4.9)	29	(3.3)	3	(0.3)	59	(8.1)	60	(15)	MS + LRI
Ketones														
2-Pentanone	699	–	–	–	–	4	(<0.1)	–	–	–	–	–	–	MS + LRI
2-Hexanone	802	–	–	–	–	2	(0.1)	–	–	–	–	1	(0.2)	MS + LRI
3-Heptanone	886	–	–	–	–	1	(<0.1)	–	–	–	–	tr	(<0.1)	MS + LRI
2-Heptanone	898	12	(2.6)	24	(3.3)	48	(2.0)	6	(2.8)	22	(0.4)	35	(3.8)	MS + LRI
3-Octen-2-one	1045	–	–	3	(0.5)	4	(0.4)	–	–	2	(0.4)	4	(0.3)	MS + LRI
2-Nonanone	1093	–	–	2	(<0.1)	3	(0.1)	2	(1.5)	–	–	–	–	MS + LRI
(*E*,*E*)-3,5-Octadien-2-one	1100	–	–	–	–	1	(0.1)	–	–	–	–	–	–	MS + LRI
Alcohols														
1-Pentanol	783	2	(1.8)	3	(0.6)	4	(0.9)	3	(1.3)	2	(0.5)	3	(2.2)	MS + LRI
1-Hexanol	880	–	–	7	(0.2)	11	(1.2)	9	(4.5)	13	(2.2)	11	(3.1)	MS + LRI
1-Heptanol	974	2	(0.4)	–	–	–	–	2	(0.7)	–	–	–	–	MS + LRI
1-Octen-3-ol	984	5	(<0.1)	3	(0.3)	3	(0.7)	4	(0.8)	2	(0.3)	3	(0.6)	MS + LRI
1-Octanol	1071	2	(0.2)	–	–	–	–	1	(0.5)	–	–	–	–	MS + LRI
1-Nonanol	1160	–	–	–	–	–	–	1	(0.6)	–	–	–	–	MS + LRI
Furans														
2-Methylfuran	<650	–	–	–	–	1	(0.9)	–	–	–	–	–	–	MS + LRI
2-Ethylfuran	699	–	–	3	(2.5)	21	(6.0)	–		–	–	25	(5.7)	MS + LRI
2,5-Dimethylfuran	706	–	–	–	–	–	–	–	–	–	–	6	(1.2)	MS + LRI
2-Propylfuran	791	–	–	–	–	3	(0.7)	–	–	1	(0.9)	5	(1.3)	MS + LRI
2-Pentylfuran	995	110	(8.3)	64	(9.3)	110	(27)	74	(9.2)	92	(9.8)	150	(22)	MS + LRI
Sugar-derived														
Ketones														
2,3-Octanedione	991	–	–	–	–	7	(0.8)	–	–	–	–	5	(0.1)	MS + LRI
Furans														
2-Furfural	841	–	–	–	–	–	–	–	–	–	–	2	(0.4)	MS + LRI

Amino acid-derived														
Aldehydes														
2-Methylpropanal	<650	–	–	–	–	5	(1.2)	–	–	–	–	7	(1.3)	MS + LRI
3-Methylbutanal	669	–	–	tr	(0.5)	57	(5.0)	–	–	17	(0.9)	46	(13)	MS + LRI
2-Methylbutanal	677	–	–	–	–	16	(0.2)	–	–	3	(0.2)	33	(5.3)	MS + LRI
Benzaldehyde[f]	979	5	(0.6)	7	(1.1)	15	(2.0)	5	(0.7)	10	(0.3)	16	(2.1)	MS + LRI
Phenylacetaldehyde	1063	–	–	–	–	14	(0.7)	–	–	–	–	–	–	MS + LRI
Maillard reaction-derived														
Pyrroles														
1-*H*-Pyrrole	771	–	–	–	–	–	–	–	–	–	–	1	(0.2)	MS + LRI
Pyridines														
Pyridine	765	48	(17)	7	(1.5)	88	(14)	18	(7.9)	41	(3.6)	9	(0.5)	MS + LRI
2-Propylpyridine	1201	–	–	–	–	1	(<0.1)	–	–	–	–	–	–	MS
Pyrazines														
Pyrazine	736	–	–	–	–	5	(1.1)	–	–	–	–	1	(0.1)	MS + LRI
Methylpyrazine	839	–	–	–	–	3	(0.6)	–	–	–	–	8	(2.6)	MS + LRI
Sulphur-containing														
Aliphatic compounds														
Dimethyl disulphide	756	3	(1.1)	2	(0.4)	23	(3.3)	–	–	4	(1.2)	30	(3.1)	MS + LRI
Dimethyl trisulphide	975	1	(<0.1)	1	(0.3)	3	(0.1)	–	–	–	–	1	(0.1)	MS + LRI
Methyl pentyl disulphide	1137	–	–	1	(<0.1)	2	(<0.1)	–	–	–	–	–	–	MS
Thiazoles														
Benzothiazole	1257	–	–	–	–	–	–	1	(0.1)	–	–	–	–	MS + LRI
Thiophenes														
Thiophene	<650	–	–	–	–	4	(0.6)	–	–	–	–	–	–	MS + LRI
3-Methylthiophene	805	–	–	–	–	tr	(<0.1)	–	–	–	–	tr	(0.1)	MS
2-Pentylthiophene	1164	–	–	–	–	4	(0.8)	–	–	–	–	–	–	MS + LRI
Thiapyrans														
2-Pentylthiapyran	1324	–	–	–	–	1	(<0.1)	–	–	–	–	–	–	MS + LRI
Derived from other sources														
Aldehydes														
2-Butylacrolein	847	–	–	–	–	5	(0.2)	–	–	–	–	3	(0.7)	MS
2-Butyl-2-octenal	1367	4	(0.2)	2	(0.3)	2	(0.4)	4	(0.5)	1	(0.3)	–	–	MS + LRI
4-Pentylbenzaldehyde	1505	–	–	–	–	1	(<0.1)	–	–	–	–	2	(0.3)	MS
Ketones														
3-Cyclohepten-1-one	823	–	–	–	–	2	(0.5)	–	–	–	–	2	(0.6)	MS
5-Decanone	1179	1	(<0.1)	–	–	–	–	–	–	–	–	–	–	MS
(*E,E*)-6,10-Dimethyl-5,9-undecadien-2-one	1443	1	(0.2)	1	(0.1)	1	(0.9)	2	(0.1)	–	–	–	–	MS
2,6-bis(1,1-Dimethyl)-2,5-cyclohexadiene-1,4-dione	1461	1	(0.1)	1	(1.1)	1	(0.2)	1	(0.1)	–	–	–	–	MS
2-Tridecanone	1475	–	–	1	(0.1)	–	–	–	–	–	–	–	–	MS
Alcohols														
3-Methylbutanol	722	–	–	–	–	–	–	tr	(0.1)	–	–	–	–	MS + LRI
Furans														
2,2,4,4-Tetramethyltetrahydrofuran	783	–	–	–	–	10	(0.1)	–	–	–	–	–	–	MS

(*continued on next page*)

Table 1 (*continued*)

Identity	LRI[a]	Starch/SPI						Starch/glucose/SPI						Method of Identification[b]
		RM[c]		150/20[d]		180/16		RM		150/20		180/16		
		ng/10 g sample[e] (SD)												
Phenols														
Phenol	756	–	–	–	–	1	(<0.1)	–	–	–	–	2	(0.2)	MS + LRI
Hydrocarbons														
Toluene	784	11	(11)	4	(0.6)	15	(0.9)	4	(3.3)	7	(0.3)	17	(2.1)	MS + LRI
Octane	800	4	(2.9)	1	(0.3)	3	(2.1)	tr	(0.2)	–	–	7	(3.5)	MS + LRI
1,4-Dimethylbenzene	878	18	(6.2)	8	(2.8)	15	(2.1)	7	(4.9)	8	(3.2)	11	(6.2)	MS + LRI
α-Pinene	937	tr	(0.2)	–	–	1	(0.1)	–	–	–	–	–	–	MS + LRI
Limonene	1034	4	(2.4)	9	(1.7)	26	(1.1)	4	(1.0)	3	(0.3)	10	(1.3)	MS + LRI
Miscellaneous														
Ethyl acetate	<650	36	(53)	–	–	13	(2.1)	5	(4.6)	–	–	–	–	MS + LRI
Propyl acetate	707	–	–	–	–	2	(<0.1)	–	–	–	–	–	–	MS + LRI
1,1-Diethoxyethane	738	–	–	–	–	–	–	1	(0.5)	–	–	–	–	MS + LRI
Butyl acetate	816	–	–	–	–	1	(0.2)	–	–	–	–	–	–	MS + LRI
1-*tert*-Butoxy-2-methoxyethane	844	22	(15)	14	(1)	120	(27)	3	(0.3)	64	(16.3)	54	(12)	MS
Hexanenitrile	882	–	–	–	–	2	(0.3)	–	–	2	(<0.1)	2	(0.5)	MS
1-*tert*-Butoxy-2-ethoxyethane	904	–	–	–	–	40	(17)	–	–	16	(6.3)	20	(5.8)	MS
1-Nitropentane	947	–	–	–	–	2	(0.2)	–	–	–	–	2	(0.5)	MS
1-Nitrohexane	1050	7	(0.9)	7	(0.3)	–	–	8	(0.4)	9	(2.2)	8	(1.4)	MS

[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 the Tenax trap after volatile collection; the averages 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 either lipid- or amino acid-derived. (The GC–MS response factors for each component are assumed to be 1:1. Consequently, the reported quantities are considered as approximate values).

3.2. Volatile components of raw and extruded starch, glucose and SPI

Analysis of the volatile components of the starch/glucose/SPI feedstock led to the identification of 37 compounds, four more than were found in the starch/SPI feedstock (Table 1). Lipid oxidation products (22) were again both qualitatively and quantitatively the dominant components of the volatile profile of the feedstock and accounted for 83% of the volatile content (363 ng/10 g). In addition, benzaldehyde and 2-butyl-2-octenal were present in amounts similar to those found in the starch/SPI feedstock (Table 1). Of the remaining 13 compounds, only three, benzothiazole, 3-methylbutanol and 1,1-diethoxyethane had not been found previously in the starch/SPI feedstock and were present in quantities not greater than 1 ng/10 g (Table 1). Three compounds, hexanal (150 ng/10 g), 2-pentylfuran (74 ng/10 g) and pyridine (18 ng/10 g), accounted for 67% of the volatiles isolated from the starch/glucose/SPI feedstock.

Extrusion of this feedstock under mild conditions led to a reduction in the number of volatiles detected; 31 compounds, compared with 37 found in the feedstock. However, in the extrudate obtained at 180 °C, the number detected was 48 compounds. Thus, in both of the extrudates, the numbered compounds detected were considerably fewer than the numbers found in the extrudates of the starch/SPI feedstock . However, the quantities of volatiles found in the two corresponding pairs of extrudates were comparable. The volatile content of the starch/glucose/SPI extrudate obtained at 150 °C was 768 ng/10 g and that obtained at 180 °C was 978 ng/10 g. Lipid-derived compounds (18 and 22) dominated the volatile profile of both extrudates and accounted for 76% and 69% of the volatiles obtained. Increased levels of benzaldehyde were found in both extrudates but that of 2-butyl-2-octenal was less than that found in the feedstock (Table 1). Two Strecker aldehydes, 3-methylbutanal and 2-methylbutanal, were found in the volatiles of the extrudate obtained under mild conditions and three, the previous two aldehydes and 2-methylpropanal, in the extrudate obtained at 180 °C. These aldehydes accounted for 3% and 9% of the total volatiles isolated. Dimethyl disulphide was found in minor quantities in the extrudate obtained at 150 °C but accounted for 4% of the volatiles in the extrudate obtained under extreme conditions. The only other compounds found in both extrudates in relatively high concentrations were the contaminants 1-*tert*-butoxy-2-methoxyethane and 1-*tert*-butoxy-2-ethoxyethane. Compounds present in greatest amounts in the extrudates obtained under mild and extreme conditions were hexanal (280 and 250 ng/10 g), 2-pentylfuran (92 and 150 ng/10 g), (*E*,*E*)-2,4-decadienal (59 and 60 ng/10 g), (*E*,*Z* or *Z*,*E*)-2,4-decadienal (30 and 52 ng/10 g), 3-methylbutanal (17 and 46 ng/10 g) and 2-heptanone (22 and 35 ng/10 g).

Five compounds, found in the both starch/glucose/SPI extrudates, were present in quantities that exceeded their OTC in water (Badings, 1970; Fors, 1983). These compounds were hexanal, (*E*)-2-nonenal, (*E*,*E*)-2,4-decadienal, 2-pentylfuran and 3-methylbutanal. The quantity of a sixth compound, dimethyl disulphide, also exceeded its OTC in water in the extrudate obtained at 180 °C. The first four of these compounds also exceeded their OTC in both starch/SPI extrudates and, as a consequence, they could be expected to provide a common background odour to all four extrudates.

The volatile contents of the starch/glucose/SPI and starch/SPI extrudates were both qualitatively and quantitatively very similar (Table 1). Thus the addition of glucose at the 1% level had little effect on the principal chemical reactions occurring in the starch/SPI system. However, the apparent absence of glucose decomposition products and the absence of increased levels of Strecker aldehydes is somewhat perplexing.

3.3. Volatile components of raw and extruded starch, SPI and aHVP

Some 39 volatile compounds were identified in the starch/SPI/aHVP feedstock (Table 2). Lipid-derived compounds (21) dominated the volatile profile of the feedstock and accounted for 74% of the total volatile content (541 ng/10 g). Three compounds, hexanal (210 ng/10 g), 2-pentylfuran (100 ng/10 g) and the probable contaminant, ethyl acetate (72 ng/10 g), were present in the highest quantities with only four other compounds, (*E*)-2-nonenal, 2-heptanone, 1-hexanol and 1,4-dimethylbenzene, exceeding 10 ng/10 g.

Thirty eight compounds were identified in the starch/SPI/aHVP extrudate obtained at 150 °C and 51 were found in that obtained at 180 °C (Table 2). Lipid-derived compounds qualitatively dominated the volatile profile of both extrudates (20 and 20), followed by the Strecker aldehydes (4 and 5). Benzaldehyde has been included among these aldehydes as, in the presence of aHVP, an amino acid becomes a likely additional source of this compound (Solina et al., 2007). In addition, eight Maillard reaction products were identified in the extrudate obtained under extreme conditions; however, none of these compounds were detected in the extrudate obtained at 150 °C (Table 2).

The quantity of volatiles found in the extrudate obtained at 150 °C (576 ng/10 g) was similar to that as in the feedstock but, under extreme conditions, the quantity obtained was far greater (2885 ng/10 g). In the material extruded at 150 °C, lipid-derived compounds (444 ng/10 g) accounted for 77% of the total volatile content. By comparison, in the extrudate obtained at 180 °C, the quantity of such compounds was far greater (709 ng/10 g) but only accounted for 25% of the total volatiles. Quantitatively, the major volatile compounds found in the extrudate obtained under extreme conditions were the Strecker aldehydes (1879 ng/10 g), that accounted for 65% of the volatiles obtained from this material. In the extrudate obtained at 150 °C, these aldehydes accounted for only

Table 2
Relative concentrations of headspace volatiles of starch/SPI/aHVP and starch/glucose/SPI/aHVP feedstocks extruded under different conditions of temperature and moisture content

Identity	LRI [a]	Starch/SPI/aHVP						Starch/Glucose/SPI/ 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	3	(1.5)	17	(2.4)	12	(1.0)	13	(4.4)	38	(6.9)	6	(0.5)	MS + LRI
Hexanal	817	210	(12)	180	(29)	250	(35)	210	(10)	310	(6.7)	310	(39)	MS + LRI
Heptanal	907	7	(0.3)	17	(0.8)	48	(11)	7	(1.4)	24	(0.6)	41	(7.7)	MS + LRI
Octanal	1008	3	(0.2)	2	(0.3)	17	(4.8)	2	(1.2)	4	(0.2)	14	(3.8)	MS + LRI
Nonanal	1105	8	(2.2)	3	(0.4	14	(3.5)	10	(2.5)	6	(0.8)	15	(1.9)	MS + LRI
Decanal	1204	1	(0.2)	1	(0.1)	3	(0.3)	2	(0.4)	2	(0.3)	–	–	MS + LRI
(*E*)-2-Hexenal	858	–	–	1	(0.1)	4	(0.3)	–	–	1	(<0.1)	–	–	MS + LRI
(*E*)-2-Heptenal	961	3	(0.4)	4	(0.2)	3	(0.8)	3	(0.4)	5	(0.2)	4	(0.9)	MS + LRI
(*E*)-2-Octenal	1062	7	(0.3)	12	(1.8)	23	(4.2)	6	(0.8)	11	(0.8)	32	(5.9)	MS + LRI
(*E*)-2-Nonenal	1162	14	(0.6)	12	(1.3)	21	(4.9)	13	(2.1)	16	(3.2)	24	(5.1)	MS + LRI
(*E*)-2-Decenal	1269	–	–	tr	(0.1)	–	–	–	–	–	–	–	–	MS + LRI
(*E*,*E*)-2,4-Octadienal	1120	–	–	1	(<0.1)	–	–	–	–	–	–	–	–	MS + LRI
(*E*,*E*)-2,4-Nonadienal	1217	1	(<0.1)	1	(0.1)	2	(0.3)	1	(0.1)	–	–	–	–	MS + LRI
(*E*,*Z* or *Z*,*E*)-2,4-Decadienal	1295	1	(0.2)	–	–	14	(6.1)	1	(0.1)	32	(3.0)	31	(9.0)	MS
(*E*,*E*)-2,4-Decadienal	1317	4	(0.3)	79	(3.3)	59	(9.2)	4	(0.5)	63	(5.4)	69	(16)	MS + LRI
Ketones														
3-Heptanone	886	–	–	–	–	2	(0.5)	–	–	–	–	1	(0.3)	MS + LRI
2-Heptanone	898	12	(1.8)	21	(1.3)	68	(12)	15	(2.4)	27	(0.3)	41	(7.3)	MS + LRI
3-Octen-2-one	1045	–	–	3	(0.2)	–	–	–	–	3	(0.2)	–	–	MS + LRI
2-Nonanone	1093	2	(0.1)	–	–	4	(0.6)	3	(0.3)	–	–	4	(0.7)	MS + LRI
3-Nonen-2-one	1140	–	–	1	(0.1)	–	–	–	–	–	–	–	–	MS + LRI
Alcohols														
1-Pentanol	783	3	(0.5)	–	–	2	(1.8)	4	(0.7)	7	(1.6)	5	(1.0)	MS + LRI
1-Hexanol	880	11	(2.2)	7	(1.5)	20	(5.7)	15	(2.7)	6	(1.3)	19	(4.9)	MS + LRI
1-Heptanol	974	2	(<0.1)	–	–	–	–	2	(0.4)	–	–	–	–	MS + LRI
1-Octen-3-ol	984	6	(0.3)	2	(0.5)	3	(0.6)	6	(0.7)	2	(0.5)	–	–	MS + LRI
1-Octanol	1071	1	(0.1)	–	–	–	–	2	(1.6)	–	–	–	–	MS + LRI
1-Nonanol	1160	1	(<0.1)	–	–	–	–	1	(0.1)	–	–	–	–	MS + LRI
Furans														
2-Ethylfuran	699	–	–	–	–	–	–	–	–	41	(10)	–	–	MS + LRI
2-Propylfuran	791	–	–	–	–	–	–	–	–	5	(1.2)	4	(0.8)	MS + LRI
2-Pentylfuran	995	100	(2.2)	80	(13)	140	(25)	86	(14)	120	(10)	170	(40)	MS + LRI
Sugar-derived														
Ketones														
2,3-Octanedione	991	–	–	–	–	5	(1.1)	–	–	–	–	4	(1.0)	MS + LRI
Furans														
1-(2-Furanyl)-ethanone	916	–	–	–	–	3	(0.6)	–	–	–	–	3	(0.9)	MS

Amino acid-derived															
Aldehydes															
2-Methylpropanal	<650	–	–	–	–	120	(8.2)	–	–	–	–	150	(40)	MS + LRI	
3-Methylbutanal	669	2	(1.8)	44	(11)	1420	(210)	5	(0.2)	2960	(310)	1200	(320)	MS + LRI	
2-Methylbutanal	677	–	–	17	(4.1)	99	(1.4)	–	–	147	(40)	110	(30)	MS + LRI	
Benzaldehyde[f]	979	6	(1.1)	8	(1.8)	29	(6.0)	7	(0.8)	14	(2.1)	26	(4.2)	MS + LRI	
Phenylacetaldehyde	1063	–	–	16	(0.8)	240	(63)	–	–	76	(5.9)	220	(31)	MS + LRI	
Maillard reaction-derived															
Pyrroles															
1-*H*-Pyrrole	771	–	–	–	–	9	(2.5)	–	–	–	–	5	(0.4)	MS + LRI	
1-Ethyl-1*H*-pyrrole	829	–	–	–	–	4	(0.5)	–	–	–	–	4	(0.6)	MS + LRI	
Pyridines															
Pyridine	765	9	(4.6)	8	(0.7)	4	(7.2)	21	(5.8)	–	–	–	–	MS + LRI	
Pyrazines															
Methylpyrazine	839	–	–	–	–	28	(6.1)	–	–	3	–	34	(10)	MS + LRI	
2,5- or 2,6-Dimethylpyrazine	916	–	–	–	–	6	(1.5)	–	–	–	–	23	(4.3)	MS + LRI	
Ethylpyrazine	919	–	–	–	–	19	(4.3)	–	–	–	–	22	(4.9)	MS + LRI	
Ethenylpyrazine	934	–	–	–	–	3	(0.7)	–	–	–	–	3	(0.6)	MS + LRI	
2-Vinyl-6-methylpyrazine	1016	–	–	–	–	6	(1.2)	–	–	–	–	5	(1.4)	MS + LRI	
3-Ethyl-2,5-dimethylpyrazine	1081	–	–	–	–	11	(2.7)	–	–	–	–	–	–	MS + LRI	
2-(3-Methylbutyl)-6-methylpyrazine	1248	–	–	–	–	5	(1.2)	–	–	–	–	–	–	MS	
Oxazoles															
2,4,5-Trimethyloxazole	848	–	–	–	–	3	(0.5)	–	–	–	–	–	–	MS + LRI	
Sulphur-containing															
Aliphatic compounds															
Dimethyl disulphide	756	1	(0.8)	12	(1.3)	–	–	3	(1.3)	100	(15)	47	(2.6)	MS + LRI	
Dimethyl trisulphide	975	1	(0.2)	2	(0.2)	16	(4.2)	2	(0.7)	–	–	16	(3.4)	MS + LRI	
Methyl pentyl disulphide	1137	–	–	1	(<0.1)	–	–	–	–	–	–	–	–	MS	
Thiazoles															
Benzothiazole	1257	1	(0.1)	1	(0.1)	–	–	1	(<0.1)	–	–	–	–	MS + LRI	
Derived from other sources															
Aldehydes															
3-Methyl-2-butenal	806	–	–	–	–	8	(1.5)	–	–	–	–	–	–	MS + LRI	
2-Butyl-2-octenal	1367	4	(0.8)	2	(0.2)	3	(0.7)	5	(0.6)	–	–	5	(1.2)	MS + LRI	
Ketones															
5-Methyl-2-hexanone	857	–	–	–	–	–	–	–	–	1	(0.1)	11	(2.7)	MS + LRI	
(*E,E*)-6,10-Dimethyl-5,9-undecadien-2-one	1443	1	(0.1)	1	(0.3)	–	–	1	(0.2)	–	–	–	–	MS	
2,6-bis(1,1-Dimethyl)-2,5-cyclohexadiene-1,4-dione	1461	1	(0.2)	–	–	–	–	1	(0.3)	tr	(0.2)	–	–	MS	
Furans															
2,5-Dihydrofuran	918	–	–	–	–	–	–	–	–	–	–	10	(1.0)	MS	
3-Phenylfuran	1228	–	–	1	(0.1)	15	(4.1)	–	–	8	(0.2)	40	(7.5)	MS	

(*continued on next page*)

Table 2 (*continued*)

Identity	LRI [a]	Starch/SPI/aHVP						Starch/Glucose/SPI/ aHVP						Method of Identification[b]
		RM[c]		150/20[d]		180/16		RM		150/20		180/16		
		ng/10 g sample[e] (SD)												
Hydrocarbons														
Toluene	784	5	(3.1)	3	(1.7)	12	(2.4)	11	(5.5)	5	(0.8)	26	(5.0)	MS + LRI
Octane	800	1	(1.3)	–	–	1	(1.9)	1	(0.2)	–	–	–	–	MS + LRI
1,4-Dimethylbenzene	878	13	(11)	5	(2.9)	36	(15)	9	(2.5)	10	(5.0)	40	(12)	MS + LRI
α-Pinene	937	–	–	–	–	–	–	tr	(0.1)	–	–	–	–	MS + LRI
Limonene	1034	4	(0.2)	4	(0.4)	5	(0.7)	2	(0.5)	5	(0.4)	5	(1.7)	MS + LRI
Miscellaneous														
Ethyl acetate	<650	72	(23)	–	–	–	–	14	(13)	–	–	–	–	MS + LRI
Propyl acetate	707	–	–	–	–	4	(0.8)	–	–	–	–	2	(1.8)	MS + LRI
1,1-Diethoxyethane	738	tr	(0.3)	–	–	–	–	–	–	–	–	–	–	MS + LRI
1-*tert*-Butoxy-2-methoxyethane	844	8	(1.5)	5	(2.0)	54	(7.0)	12	(1.7)	8	(2.2)	42	(8.4)	MS
Hexanenitrile	882	–	–	–	–	4	(0.7)	2	(2.7)	2	(0.3)	3	(0.1)	MS
1-Nitropentane	947	3	(0.4)	2	(0.4)	–	–	3	(0.3)	–	–	2	(0.4)	MS
1-Nitrohexane	1050	9	(0.5)	–	–	–	–	7	(0.3)	–	–	–	–	MS
2,3-Dihydro-1*H*-indole	1114	–	–	tr	(<0.1)	4	(0.9)	–	–	–	–	–	–	MS

[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 the Tenax trap after volatile collection; the averages 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 either lipid- or amino acid-derived. (The GC–MS response factors for each component are assumed to be 1:1. Consequently, the reported quantities are considered as approximate values).

15% of the volatiles. Volatiles from the material extruded at 180 °C also contained Maillard reaction products, mainly pyrroles, pyrazines and oxazoles (94 ng/10 g), that made up a further 3% of the volatile content. Compounds present in greatest amounts in these extrudates were 3-methylbutanal (44 and 1420 ng/10 g), hexanal (180 and 250 ng/10 g), phenylacetaldehyde (16 and 240 ng/10 g), 2-pentylfuran (80 and 140 ng/10 g), 2-methylbutanal (17 and 99 ng/10 g), 2-heptanone (21 and 68 ng/10 g) and (*E*,*E*)-2,4-decadienal (79 and 59 ng/10 g).

Six compounds, present in both extrudates, exceeded their OTC in water (Badings, 1970; Fors, 1983). These compounds were hexanal, (*E*)-2-nonenal, (*E*,*E*)-2,4-decadienal, 2-pentylfuran, 3-methylbutanal and dimethyl trisulphide. A further six compounds, heptanal, octanal, nonanal, 2-methylpropanal, phenylacetaldehyde and 3-ethyl-2,5-dimethylpyrazine, present in the extrudate obtained at 180 °C, also exceeded their OTC in water. These six compounds could be expected to greatly modify the perceived odour of the extrudate obtained under extreme conditions. However, all 12 compounds could be expected to contribute to the odours of the extrudates obtained under either mild or extreme conditions.

The apparent absence of Maillard reaction products in the volatiles of the starch/SPI/aHVP feedstock indicates that, although such compounds were present in the aHVP, and accounted for 11% of the volatile content of this ingredient (Solina et al., 2005), at the 1% level of addition they were insufficient to be detected by the GC–MS. Furthermore, the fact that such compounds accounted for 3% of the volatile content in the extrudate obtained at 180 °C shows that the quantity and type of reducing sugars produced in the thermal breakdown of the starch were appropriate for reaction with the aHVP amino acids to form Maillard reaction products.

3.4. Volatile components of raw and extruded starch, glucose, SPI and aHVP

Forty volatile compounds were identified in the starch/glucose/SPI/aHVP feedstock (Table 2). Lipid-derived compounds (21) again dominated the volatile profile of the feedstock and accounted for 79% of the volatile content (406 ng/10 g). Two compounds hexanal (210 ng/10 g) and 2-pentylfuran (86 ng/10 g) were present in greatest quantities, and eight other compounds, including five lipid oxidation products, pentanal, nonanal, (*E*)-2-nonenal, 2-heptanone and 1-hexanol, exceeded 10 ng/10 g.

Thirty four compounds were identified in the starch/glucose/SPI/aHVP extrudate obtained at 150 °C and 44 were found in that obtained at 180 °C (Table 2). Lipid-derived compounds qualitatively dominated the volatile profile of both extrudates (17 and 20), followed by the Strecker aldehydes (4 and 5). Five Maillard reaction products were identified in the extrudate obtained at 180 °C but only one of these compounds was detected in the extrudate obtained at 150 °C (Table 2). Of interest, the number of these compounds found in the extrudate formed under extreme conditions was less than that of the corresponding product produced from starch/SPI/aHVP (Section 3.3).

The quantity of volatiles obtained from the extrudate formed at 150 °C (4062 ng/10 g) was far greater than that found in the feedstock (513 ng/10 g) and was considerably greater than that found in the extrudate obtained at 180 °C (2840 ng/10 g). Lipid-derived compounds accounted for only 18% and 28% of the volatile contents. However, the quantities of these compounds (722 and 790 ng/10 g) were appreciably greater than those found in the feedstocks. Quantitatively, the major compounds found in these extrudates were the Strecker aldehydes (3183 and 1680 ng/10 g) that accounted for 78% and 59% of the total volatiles found in these materials. Volatiles obtained from the extrudate formed at 180 °C also contained Maillard reaction products (87 ng/10 g) that made up a further 3% of the total volatile content. Compounds present in greatest amounts were 3-methylbutanal (2960 and 1200 ng/10 g), hexanal (310 and 310 ng/10 g), phenylacetaldehyde (76 and 220 ng/10 g), 2-pentylfuran (140 and 170 ng/10 g), 2-methylbutanal (147 and 110 ng/10 g), dimethyl disulphide (160 and 47 ng/10 g) and (*E*,*E*)-2,4-decadienal.

Seven compounds, present in both extrudates, exceeded their OTC in water (Badings, 1970; Fors, 1983). These compounds were hexanal, (*E*)-2-nonenal, (*E*,*E*)-2,4-decadienal, 2-pentylfuran, 3-methylbutanal, phenylacetaldehyde and dimethyl disulphide. In the extrudate obtained at 150 °C, 2-methylbutanal exceeded its OTC in water and in the material obtained at 180 °C six additional compounds, heptanal, octanal, nonanal, (*E*)-2-octenal, 2-methylpropanal and dimethyl trisulphide, exceeded their OTC in water. All 14 compounds could be expected to contribute to the odours of the extrudates obtained under either mild or extreme conditions. However, the additional six compounds that exceeded their OTC in the extrudate obtained at 180 °C would be expected to greatly modify the perceived odour of this extrudate.

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

Preliminary qualitative sensory assessment of the eight extrudates obtained at 150 °C and 180 °C showed that, for each feedstock, the extrudates obtained at 180 °C had relatively "stronger" odours. Accordingly, only those materials that were obtained by extrusion under extreme conditions will be discussed. The starch/SPI, starch/glucose/SPI and starch/SPI/aHVP extrudates all had odours of "low" intensity. That of the starch/SPI was described as reminiscent of bread dough. That of starch/glucose/SPI as malty and fatty, and that of starch/SPI/aHVP as cheese-like. However, the starch/glucose/SPI/aHVP extrudate had an odour of "moderate" intensity that was described as savoury and like melted cheese on bread. As a consequence of these assessments the starch/glucose/SPI and starch/glucose/SPI/aHVP extrudates were selected

for further sensory analysis using GCO. In the opinion of the panel, these two extrudates possessed the more interesting and complex odours. In an attempt to identify those compounds contributing to the odours of these extrudates, both 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.

3.6. GCO profile of starch, glucose and SPI extrudate

The GCO analyses of the volatile components of the starch/glucose/SPI extrudate processed at 180 °C led to the detection of 25 odour points of which 18 had LRI values that corresponded to identified compounds (Table 3). Accordingly, some of the odorous compounds were present at concentrations below their GC–MS detection limits. Two of the odours were described as "very strong", eight as "strong" and three as "strong/medium". Of the odours with "very strong" intensities only one had a LRI value that corresponded to an identified compound, namely (*E*,*Z* or *Z*,*E*)-2,4-decadienal. By comparison, seven of the eight odour points described as "strong" and all three odour points described as "strong/medium" had the same LRI values as identified compounds (Table 3). All six compounds, that were present in the undiluted extrudate in quantities that exceeded their OTC in water (Section 3.2), were detected at odour points of the corresponding LRI values. However, it should be noted, both here and elsewhere, that the OTC values in the extrudate may be very different from those in water, due to the different nature of the matrix. At one tenth dilution, 21 odours were detected, of which three had intensities described as "strong" and five described as "medium". Seven of these odours had LRI values that corresponded to identified compounds. Two of the odours with "strong" intensities corresponded to pyrrole and 1-octen-3-ol and those with "medium" intensities corresponded to 2-methylbutanal, heptanal, octanal, (*E*,*Z* or *Z*,*E*)-2,4-decadienal and (*Z*,*Z*)-2,4-decadienal. Of these, the relatively weak odorant 1-*H*-pyrrole, could not be responsible for the "strong" odour at LRI 771. At one hundredth dilution, only four odours were detected, of which two had intensities described as "medium" and two described as "weak". One of the odours of "medium" intensity had the same LRI value as 1-octen-3-ol and those of "weak" intensities corresponded to 2-methylbutanal and (*E*,*Z* or *Z*,*E*)-2,4-decadienal. All four odours detected at one hundredth dilution are likely to play important roles in the malty and fatty odour of the starch/glucose/SPI extrudate. However, although the three compounds with LRI values that correspond with these odour points could influence the odour of the undiluted extrudate, their OTC would preclude their detection at this low dilution. Consequently, the compounds respon-

Table 3
GCO analysis of volatile components at different concentrations of starch/glucose/SPI extrudates processed under extreme conditions

LRI[a]	Odour description	Odour intensity[b]			Major compound in region of odour[c]
		10 g	1 g	0.1 g	
585	Cooked meat, sweet	M/W	W	–	Unknown
625	Caramel, fruity	M	–	–	Unknown
645	Over-ripe apple, musty on dilution	W	W	–	2-Methylpropanal
669	Burnt toffee, caramel on dilution	M	W	–	3-Methylbutanal
677	Toffee apple, toffee, fruity on dilution	S	M	W	2-Methylbutanal
682	Crushed insect	VS	S	M	Unknown
690	Caramel, stale biscuit on dilution	M	W	–	Unknown
699	Apple, pear, caramel, toffee on dilution	M	W	–	2-Ethylfuran
756	Sulphury, rubber-like on dilution	S/M	W	–	Dimethyl disulphide
771	Solvent-like, apple, sweet and piercing on dilution	S	S	–	1-H-Pyrrole
817	Unpleasant, acrid crushed ant-like grassy on dilution	M	W	–	Hexanal
825	Unpleasant, sulphur-like, sweet oil	M	–	–	Unknown
877	Acrid, crushed ants, sweet and berry-like on dilution	S	W	–	Unknown
898	Acrid, egg-like, sweet, wine, cheese-like on dilution	S/M	W	–	2-Heptanone
907	Woody, leather	S	M	–	Heptanal
961	Putty	W	W	–	(*E*)-2-Heptenal
984	Mushroom-like	S/M	S	M	1-Octen-3-ol
995	Metallic, green	S	W	–	2-Pentylfuran
1008	Sweet, citrus, honey-like	M	M	–	Octanal
1062	Crushed ants, green and capsicum-like on dilution	S	W	–	(*E*)-2-Octenal
1103	Green, ant-like, slightly rancid	M	–	–	Unknown
1162	Fried vegetables	W	–	–	(*E*)-2-Nonenal
1204	Sweaty rubber, sweet on dilution	S	W	–	Decanal
1295	Fatty	VS	M	W	(*E*,*Z* or *Z*,*E*)-2,4-Decadienal
1317	Sweet, citrus	S	M	–	(*E*,*E*)-2,4-Decadienal

[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 compound(s) identified in this region of the chromatogram.

sible for the odours detected at one hundredth dilution are probably yet to be identified.

3.7. GCO profile of the starch, glucose, SPI and aHVP extrudate

The GCO analyses of the volatile components of the starch/glucose/SPI/aHVP extrudate processed at 180 °C led to the detection of 28 odour points, of which 21 had LRI values that corresponded to identified compounds (Table 4). Again, some of the compounds responsible for the odours were present in quantities below their GC–MS detection limit. Three of the odours were described as "very strong" and had LRI values that corresponded to heptanal, dimethyl trisulphide and 2-pentylfuran. A further 11 compounds had odours described as "strong", of which 10 had LRI values that corresponded to identified compounds (Table 4). Twelve of the 13 compounds, that were present in the undiluted extrudate in quantities that exceeded their OTC in water (Section 3.4), were detected at odour points of the corresponding LRI values. The compound not detected was phenylacetaldehyde. At one tenth dilution, 22 odours were detected, of which seven had intensities described as "strong" and six of these odours had LRI values that corresponded to identified compounds. These were, 3-methylbutanal, 2-methylbutanal, heptanal, 2,5 or 2,6-dimethylpyrazine, dimethyl trisulphide and (*E*)-2-octenal. At one hundredth dilution, 15 odours were detected, of which 11 had LRI values that corresponded to identified compounds (Table 4). Only one of these odours was described as "strong", another two as "medium" and the remainder were described as "weak". The odour with the "strong" intensity had the same LRI value as 3-methylbutanal and one of the two odours of "medium" intensity had the same LRI as heptanal. Of the 12 odours of "weak" intensity, nine had LRI values that corresponded to those of identified compounds (Table 4) and most of the odour descriptions were in general agreement with those reported for the identified compounds (Aldrich, 1998).

All 15 odours detected at one hundredth dilution are likely to have an important role in the melted cheese on bread odour of the starch/glucose/SPI/aHVP extrudate. However, although most of the 11 compounds identified at these odour points could influence the odour of the diluted material, the OTC values of some of these compounds would appear to preclude their detection by odour at the lower dilution. Notable exceptions would be 3-methylbutanal and dimethyl trisulphide. Unidentified compounds,

Table 4
GCO analysis of volatile components at different concentrations of starch/glucose/SPI/aHVP extrudates processed under extreme conditions

LRI[a]	Odour description	Odour intensity[b]			Major compound in region of odour[c]
		10 g	1 g	0.1 g	
560	Sweet cabbage	M	–	–	Unknown
620	Tomato	S/M	M	W	Unknown
645	Vegetable-like, tomato	M	W	W	2-Methylpropanal
669	Sweet, caramel, condensed milk, golden syrup-like on dilution	S/M	S	S	3-Methylbutanal
677	Sweet, nail varnish, pear-like on dilution	S	S	W	2-Methylbutanal
681	Crushed ants	S/M	M	M	Unknown
707	Vegetable, rubber, onion-like	W	W	W	Propyl acetate
722	Sweet caramel	S	W	W	Pentanal
753	Fried onions, sulphury	S/M	–	–	Unknown
756	Pungent, flue gas, sweaty, vegetable on dilution	M	M	W	Dimethyl disulphide
771	Fruity, apple, cinnamon, biscuits	M	–	–	1-H-Pyrrole
800	Sweet green, green apples	M	M	W	Unknown
817	Green, rancid	S	W	–	Hexanal
903	Curried apple, onion-like	W	–	–	Unknown
907	Sweet biscuits	VS	S	M	Heptanal
916	Gravy, meat stew	S	S	–	2,5 or 2,6-Dimethylpyrazine
919	Oasts, biscuits, tobacco-like on dilution	S	M	W	Ethylpyrazine
961	Cut grass	S	–	–	(*E*)-2-Heptenal
975	Roast beef	VS	S	W	Dimethyl trisulphide
984	Mushrooms	M	M	W	1-Octen-3-ol
995	Metallic, vegetable	VS	M	–	2-Pentylfuran
1008	Stink bug, citrus-like	S	M	-	Octanal
1016	Biscuit	W	–	–	2-Vinyl-6-methylpyrazine
1062	Savoury, pizza, cheese cracker	S	S	W	(*E*)-2-Octenal
1105	Soft, floral, citrus, fatty	S	M	–	Nonanal
1115	Toasted cheese, burger ring, onion-and garlic-like on dilution	S	S	W	Unknown
1162	Cracker cheese biscuit	M	M	–	(*E*)-2-Nonenal
1317	Fried vegetables	S	M	–	(*E*,*E*)-2,4-Decadienal

[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.

and in particular that responsible for the toasted cheese odour at LRI 1115, would appear to be responsible for a proportion of the odours detected at one hundredth dilution.

The GC–MS analytical data of the starch/glucose/SPI/aHVP extrudate indicated that 13 compounds were present in relative concentrations that exceeded their OTC in water (Section 3.4). At one tenth dilution, odour points occurred at LRI values that corresponded to 12 of the compounds and, at one hundredth dilution, six of the compounds. These six compounds were heptanal, (*E*)-2-octenal, 2-methylpropanal, 3-methylbutanal, dimethyl disulphide and dimethyl trisulphide. All of these compounds could be expected to contribute to the perceived melted cheese on bread odour of the starch/glucose/SPI/aHVP extrudate.

3.8. Role of SPI in odour development of extruded products containing starch, glucose and/or aHVP

The addition of 1% SPI to starch had little effect on the volatile content of the extrudate produced at 150 °C compared with that obtained with starch extruded under the same conditions (Solina et al., 2007). However, there was a major difference between extrudates obtained at 180 °C; that containing SPI had almost double the number of volatile compounds (64) and more than twice the quantity (1088 ng/10 g) of that previously found in the corresponding starch extrudate (33 and 534 ng/10 g). These differences were due to the increased number and quantity of lipid-derived compounds, and the presence of Strecker aldehydes and sulphur-containing compounds in the volatiles from the extrudate containing SPI (Section 3.1). The formation of these compounds can be explained by the relatively high lipid content of the SPI (300 ng/10 g), and the decomposition of protein during extrusion to give free amino acids, which in turn would yield the Strecker aldehydes and sulphur compounds (Solina et al., 2005; Solina et al., 2007). The two extrudates obtained at 180 °C also had slightly different odours, both of "low" intensity, with the odour of the starch extrudate described as like "wet paper" (Solina et al., 2007) whereas the odour of that containing SPI was like "bread dough" (Section 3.5). This difference in odour is possibly due to the presence of the Strecker aldehydes and sulphur compounds in the extrudate containing the SPI.

Similarly, the addition of SPI to the starch/glucose feedstock had little effect on the volatile content of the extrudate obtained at 150 °C compared with the starch/glucose extrudate obtained under the same conditions (Solina et al., 2007). However, major differences did exist between the extrudates obtained at 180 °C. That containing the SPI had a greater number of volatile compounds and in larger quantity, the effects being similar to those observed when SPI was added to starch. Greater numbers and higher levels of lipid-derived compounds, Strecker aldehydes and sulphur-containing compounds were found in the extrudate containing the SPI. Both extrudates obtained at 180 °C had odours of "low" intensity. The odour of the starch/glucose extrudate was like that of rice crispbread (Solina et al., 2007) whereas that containing SPI had an odour described as malty and fatty (Section 3.5). Compounds with fatty odours were detected in the GCO analysis of the starch/glucose/SPI extrudate (Table 3). However, no single odour was described as malty. The closest odour descriptions were for two odour points described as caramel-like (Table 3). The compounds responsible for these odours were not identified. It would appear, however, that (*E*)-2-nonenal and (*E*,*Z* or *Z*,*E*)-2,4-decadienal could contribute to the fatty odour of this extrudate (Section 3.6). The greater numbers and larger quantity of Strecker aldehydes present in the extrudate containing SPI could also account for the difference in odours of the two extrudates.

The addition of SPI to the starch/aHVP feedstock also had little effect on the volatile content of the extrudate obtained at 150 °C compared with that of the starch/aHVP extrudate obtained under the same conditions (Solina et al., 2007). Although the quantities of volatiles obtained were slightly higher in the extrudate containing SPI, the volatile contents of the corresponding extrudates obtained at 180 °C were qualitatively similar, except for the addition of a small number (7) of pyrroles and pyrazines in the starch/SPI/aHVP extrudate (Table 2). The absence of such compounds in the volatiles of the starch/aHVP extrudate was unexpected (Solina et al., 2007), particularly as aHVP contains 18.4% free amino acids, and pyrroles and pyrazines are prominent components of the volatiles of aHVP (Solina et al., 2005). Once again, there was an increase in the quantity of volatiles (45%) in the extrudate containing SPI. This increase was due to the higher levels of Strecker aldehydes, principally 3-methylbutanal, phenylacetaldehyde and lipid-derived compounds (Table 2). The odour of the starch/aHVP extrudate obtained at 180 °C was described as savoury and malty and was of "moderate" intensity (Solina et al., 2007), whereas the corresponding extrudate containing SPI had a cheese-like odour and was of "low" intensity (Section 3.5). Based on the analytical data currently available, it is not possible to account for the differences in odours of the two extrudates. However, the sensory data showed that the addition of SPI had a modifying effect on the odour of the starch/aHVP extrudate obtained at 180 °C.

Some 34 compounds were identified in the volatile content of the starch/glucose/SPI/aHVP extrudate obtained at 150 °C and 44 in that obtained at 180 °C (Section 3.4). By comparison, 60 compounds were identified in the corresponding starch/glucose/aHVP extrudate obtained at 150 °C and 67 in that obtained at 180 °C (Solina et al., 2007). Accordingly, the addition of SPI to the starch/glucose/aHVP feedstock greatly reduced the numbers of compounds formed during extrusion. The major reason for this reduction in numbers was the presence of fewer Maillard reaction products, particularly pyrroles, pyrazines and

sulphur-containing compounds, in the extrudates containing SPI. Quantitatively, no obvious trend was apparent. For the extrudates obtained at 150 °C, the feedstock containing SPI gave more than twice the levels of volatiles, but at 180 °C this result was reversed, the feedstock without SPI gave about 44% more volatiles. However, the analytical data showed that the principal variable in the quantities of volatiles obtained was the level of 3-methylbutanal in each extrudate. This compound was the major component in all extrudates (Table 2). Deletion of 3-methylbutanal gave a series of values that showed two trends; the extrudates obtained at 180 °C gave larger quantities of volatiles than did those obtained at 150 °C and the extrudates containing SPI gave slightly larger quantities of volatiles than did the extrudates without SPI. The major reason for these differences was the relative quantities of lipid-derived compounds in the four extrudates. The odour of the starch/glucose/aHVP extrudate obtained at 180 °C was described as "bakery" and "cheese cracker", and was of "moderate" to "strong" intensity (Solina et al., 2007). By comparison, the corresponding extrudate containing SPI was described as "savoury" and like "melted cheese on bread", and was of "moderate" intensity (Section 3.5). Analysis, by GCO, of the starch/glucose/aHVP extrudate obtained at 180 °C led to the detection of 54 odour points (Solina et al., 2007) compared with only 29 odour points in the corresponding extrudate containing SPI (Table 4). At least 10 of the odour points absent from the extrudate containing SPI had biscuit-like odours (Solina et al., 2007). The compounds responsible for these biscuit-like odours in the starch/glucose/aHVP extrudate are likely to be the major cause of the difference in odour of the two extrudates. Unfortunately, most of the compounds responsible for these biscuit-like odours have not been identified (Solina et al., 2007). Thus, the addition of SPI to the starch/glucose/aHVP feedstock produced a major reduction in both the number of volatile compounds and odour points detected in the extrudate obtained at 180 °C. Eight of the compounds not detected in the extrudate containing SPI were Maillard reaction-derived heterocyclic compounds. Furthermore, it is likely that most compounds responsible for the 11 "biscuit-like" odour points are also derived from the Maillard reaction (Solina et al., 2007). Compounds with "roasted" or "popcorn-like" odours can be formed by the reaction at pH 7 of proline, a component of aHVP (Solina et al., 2005), with glucose (Hofmann & Schieberle, 1998). However, as our extrudates have a pH of <6 such reaction products may be precluded. Based on this evidence, it would appear that SPI had the ability to modify the Maillard reaction so nitrogen heterocyclic compounds are either not formed or are formed in reduced quantities.

4. Conclusion

This study, in combination with earlier reported work (Solina et al., 2007), demonstrates the considerable effect that different combinations of ingredients, such as aHVP, SPI and glucose, at the 1% level, can have on the odour of starch based extrudates. These effects are achieved by modifying the variety and concentration of the volatile compounds generated, thereby altering the nature and complexity of the product's odour. They also show that using a range of ingredients in the feedstock increased the complexity of odour development during extrusion. The addition of aHVP and glucose to a starch-based feedstock gave, on extrusion, a product that contained over 67 volatile compounds and had a distinctive baked odour (Solina et al., 2007). By contrast, the addition of SPI to the above feedstock greatly reduced the number of compounds detected (44) and changed the odour of the extrudate to "savoury" and "melted cheese on bread" (Section 3.5). Such modifications could be due to the fortuitous binding of certain volatiles to the added protein in the extrudate containing SPI (Espinosa-Diaz, Seuvre, & Voilley, 1996; Franzen & Kinsella, 1974; Maga & Kim, 1992), or by the interaction of SPI with Maillard reaction precursors or their volatile products (Hwang, Chen, & Ho, 1996). However, it is of interest that such modifications to the volatile content can occur with such low concentrations (1%) of SPI. In addition, or alternatively, the SPI used in these studies had a lipid content of 3.5% and oxidation of free fatty acids derived from these lipids could yield carbonyl compounds that can interfere with some steps of the Maillard reaction (Whitfield, Mottram, Brock, Puckey, & Salter, 1988). Future investigations, involving the additions of SPI to suitable feedstocks, could demonstrate which of the above three processes have the dominant role in the modification of volatile content and odour of extruded products containing this ingredient. Furthermore, although the current studies have shown that certain combinations of ingredients greatly affect the odour of extruded products, many of the compounds responsible for these changes have not been identified. Further studies should be designed to identify such compounds.

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