

# Sensory and Instrumental Analyses of Volatiles Generated during the Extrusion Cooking of Oat Flours

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Three batches of oats were extruded under four combinations of process temperature (150 or 180 °C) and process moisture (14.5 and 18%). Two of the extrudates were evaluated by a sensory panel, and three were analyzed by GC-MS. Maillard reaction products, such as pyrazines, pyrroles, furans, and sulfur-containing compounds, were found in the most severely processed extrudates (high-temperature, low-moisture). These extrudates were also described by the assessors as having toasted cereal attributes. Lipid degradation products, such as alkanals, 2-alkenals, and 2,4-alkadienals, were found at much higher levels in the extrudates of the oat flour that had been debranned. It contained lower protein and fiber levels than the others and showed increased lipase activity. Extrudates from these samples also had significantly lower levels of Maillard reaction products that correlated, in the sensory analysis, with terms such as stale oil and oatmeal. Linoleic acid was added to a fourth oat flour to simulate the result of increased lipase activity, and GC-MS analysis showed both an increase in lipid degradation products and a decrease in Maillard reaction products.

**Keywords:** Cereal; oats; extrusion processing; aroma; volatiles; Maillard reaction; lipid degradation

## INTRODUCTION

Extrusion cooking is applied widely in the manufacture of breakfast cereals and snack foods. The advantages of such a single processing unit over traditional multistep baking methods are both economic and practical in terms of a reduction in space, time, and energy. The major disadvantages, however, are the lack of flavor development and the loss of flavor volatiles as the extrudate leaves the die. There have been several reviews of extrusion cooking (Kokini et al., 1991; Mercier et al., 1989) and the formation of flavors in cereals (Riha and Ho, 1996; Maga, 1989), in particular in wheat (Hwang et al., 1994) and maize and taro (Maga and Liu, 1994). The importance of the cereal feedstock on flavor formation has also been demonstrated (Bredie et al., 1998b).

Initially, oat flour attracted less attention as a cereal for extrusion cooking because of its high lipid content, but increasing awareness of the health benefits associated with oats (Lockhart and Hurt, 1986) has stimulated renewed interest in the flavor of oat products (Heydanek and McGorin, 1986). Lipid degradation products, in particular (*E,E*)- and (*E,Z*)-3,5-octadien-2-one, have been reported among the volatiles of dried oat groats (Heydanek and McGorin, 1981). Rancid oat groats, which had a pronounced "old chicken fat" aroma, were also analyzed in this work, and 22 volatiles derived from either oleic, linoleic, linolenic, or arachidonic acids were found. These included the (*Z,E*)- and (*E,E*)-isomers of C<sub>7</sub>, C<sub>9</sub>, and C<sub>10</sub> 2,4-alkadienals, which were associated with the chicken fat aroma. Sensory and instrumental

analyses of oil obtained from crude and roasted oats have also been carried out (Fors and Schlich, 1989). Lipid degradation products, such as 2-pentyl- and 2-octylfuran, were found in both types of oil, but Maillard products, such as pyrazines, were found in the oils from the roasted oats. Higher concentrations of the former were found to be correlated with the samples that were described by the panel with terms such as cooking oil and deep-frying fat. The samples that contained more pyrazines, however, were described using roasted, popcorn terms and were judged as only slightly rancid. Rancid off-flavors were also identified, by aroma extract dilution analysis (AEDA) (Guth and Grosch, 1993, 1994), in oat extrudates stored for up to one year at room temperature. These were attributed to hexanal, (*E*)-2,3-epoxyoctanal, pentanal, and (*E,E*)-2,4-nonadienal. Recently, in a study of extruded oats (Sjövall et al., 1997), an increase in oxidation products (hexanal, nonanal, and 2-pentylfuran) during postextrusion storage was observed, which was more pronounced when extrusion had occurred at a higher temperature.

In cooked foods, in which both lipid degradation products and Maillard reaction products are present, there can be an interaction between the two (Farmer and Mottram, 1990; Mottram and Whitfield, 1995). Pentyl- and hexylthiophenes, pentylthiopyrans, and pentylpyridines were found in meat model systems comprising cysteine, ribose, and phospholipid. Further evidence of Maillard–lipid interactions was found in a model oat system containing hexanal (Heydanek and McGorin, 1986). After 13 h of heating to 130 °C, a series of trisubstituted pyrazines with one hexyl chain were found. Fors and Schlich (1989) also reported pentylpyridine in roasted oat oil. These interaction products are a further possible source of off-notes.

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**Table 1. Chemical Analysis of Oat Flours**

oat flour code	lipid, %	protein, %	fiber, %	activity units, %	free fatty acids, %
OF1	9.9	13.4	10.2	0	0.2
OF2	9.8	15.5	8.8	0	0.2
OG1	9.3	14.9	10.4	0	0.1
OG2	7.6	9.6	2.4	3.9	1.7

Although feedstock is an important factor in flavor formation, extrusion conditions have also been shown to play a major role in the generation of volatiles. Moisture content and process temperature were found to be the most significant, whereas other parameters, such as screw speed, screw configuration, and residence time, were less important during the extrusion of wheat and maize flour (Bredie et al., 1998a,b). The desirable toasted cereal notes were produced as a result of the Maillard reaction and were usually favored by high-temperature and low-moisture conditions.

During the extrusion of oat flour, two major pathways are involved in the formation of volatiles. The first, the Maillard reaction, generates the desirable, toasted cereal notes, and the second, lipid degradation, is mainly responsible for the stale off-flavors. Both of these pathways will be influenced by the extrusion conditions. In this study, the effect of extrusion conditions on the generation of volatiles was examined using three different batches of oats and four sets of extrusion conditions (process temperatures of 150 and 180 °C, coupled with moisture contents of 14.5 and 18%). A fourth batch of oat flour was used as a model system in which the flour was dosed with linoleic acid, prior to extrusion, to simulate the presence of free fatty acids from residual lipase activity.

## EXPERIMENTAL PROCEDURES

**Materials.** Four batches of commercial oat flour of either French (OF1, OF2) or German (OG1, OG2) origin were obtained from Cereal Partners Ltd., Welwyn Garden City, U.K., and stored at -20 °C prior to extrusion. The flours were analyzed for their lipid, protein, fiber, and free fatty acid contents according to AACC methods 30.10, 46.16, 32.20, and 58.15, respectively (AACC, 1996), and for their lipase activity (Galliard, 1989). They all had similar analytical profiles except for OG2, which had been debranned, resulting in lower levels of protein and fiber (Table 1). OG2 also showed some lipase activity and a higher level of free fatty acids.

Linoleic acid was obtained from Sigma Chemical Co., Poole, U.K. It was 60% pure, and the remainder comprised oleic acid (29%), linolenic acid (6%), palmitic acid (2%), and unknowns (3%).

**Extrusion Processing.** The extrusion processing was carried out on an APV MPF 50D twin-screw extruder, as described previously (Bredie et al., 1997). The screw speed was 350 rpm, and the feed rate was 0.6 kg/min. Combinations of two moisture contents (14.5 and 18%) and two process temperatures (150 and 180 °C) were used, giving four processing conditions. The mean residence time was 35 s for all extrusions. The extrudates were ground in a Christy-Norris hammer mill (0.8 mm screen), sealed in bags with low oxygen permeability, and committed to cold storage (-20 °C) immediately.

The four oat flours gave typical biscuit-like extrudates and had similar energy inputs for given extrusion conditions. Specific mechanical energy (SME) values showed the expected changes with extrusion conditions. Table 2 shows the values for OF1. Higher SMEs were obtained at lower temperatures and lower moisture content, when the melt was more viscous and more energy was generated through increased friction. These changes in viscosity were also reflected in the die

**Table 2. Typical Extrusion Parameters for Selected Extrudates**

oat flour code	process moisture, %	target process temp, °C	SME, <sup>a</sup> kJ/kg	temp, <sup>b</sup> °C	die temp, °C	die pressure, MPa
OF1	18	150	406	149	155	3.0
OF1	14.5	150	500	145	149	3.3
OF1	18	180	291	179	175	2.2
OF1	14.5	180	363	179	179	2.5
OG1	14.5	150	507	150	151	3.1
OG2	14.5	150	520	149	152	4.5
OF2	14.5	150	496	149	152	3.2
OF2-dos	14.5	150	395	149	150	1.9

<sup>a</sup> Specific mechanical energy. <sup>b</sup> Probe placed in last screw section before die in contact with the melt fluid.

pressure that increased under both low-moisture and low-temperature processing conditions.

**Addition of Linoleic Acid.** Linoleic acid was metered into the water that was added to the extruder during a second extrusion of flour OF2 to give ~2% linoleic acid in the raw flour. Addition of the linoleic acid (OF2-dos) caused a reduction in SME, but this was compensated by increased heat input from the barrel sections. This decrease in SME was probably due to the lubricating properties of the linoleic acid, which reduced both the viscosity and the friction of the extrudate, reducing the die pressure as well. During the high-temperature extrusions (target temperature = 180 °C), the SME was reduced to such an extent that it was not possible to reach the target temperature in the die, although it was attained in the shearing section. This precluded the use of high-temperature extrusion conditions in this experiment and restricted the comparison to the lower temperature extrudates (150 °C), in which target temperatures had been attained in both sections of the extruder. In the case of oats OG2, which contained higher levels of intrinsic free fatty acid as a result of poor processing (as opposed to direct addition), neither the SME nor the die pressure was similarly reduced during extrusion of the oat flour and, in fact, the SME was slightly raised. The required die temperature was attained, and, in this case, it is likely that the linoleic acid was contained within the starch particles and had less of a lubricating effect than in OF2-dos.

**Dynamic Headspace Collection.** Each extruded flour sample (10 g) was placed in a 250-mL conical flask fitted with a Drechsel head. Distilled water (30 mL) was added and the mixture shaken gently. Oxygen-free nitrogen was passed over the sample for 2 h at a rate of 40 mL/min. The volatiles were swept onto a preconditioned glass-lined stainless steel trap (105 mm × 3 mm i.d.) packed with 85 mg of Tenax GC (CHIS system, SGE Ltd., Milton Keynes, U.K.). Throughout the collection, the sample was maintained at 37 °C. At the end of the collection, 1 µL of 1,2-dichlorobenzene in ether (1.31 µg/µL) was injected onto the trap, as an internal standard, and the trap was then flushed with nitrogen for 5 min to remove moisture and solvent.

**Separation and Identification of Volatiles.** A Hewlett-Packard 5980/5972 GC-MS system, fitted with a 50 m × 0.32 mm i.d. fused-silica capillary column coated with BPX-5 at 0.5 µm film thickness (SGE Ltd.), was used to analyze the collected volatiles. The GC temperature program and details of the MS detection have been reported previously (Bredie et al., 1998a). Volatiles were identified by comparison of their mass spectra with spectra from authentic compounds analyzed at the University of Reading, from the NIST mass spectral database (NIST/EPA/MSDC, 1992), or published elsewhere. The linear retention index (LRI) was calculated for each component, using the retention times of a homologous series of C<sub>7</sub>-C<sub>22</sub> *n*-alkanes. Wherever possible, mass spectral identification was confirmed by comparing the LRI with those of authentic compounds analyzed under similar conditions.

**Quantitation.** The approximate quantity of each compound was estimated by comparing the peak area in the total ion chromatogram with that of the internal standard, using a

response factor of 1. The analyses were all carried out in triplicate on the complete sets of extrudates generated from oat flours OG1, OG2, and OF1. The mean coefficient of variance for quantities of individual components was 25% and, in 80% of cases, the coefficient of variance was <40%, the exceptions being, predominantly, the very early eluting compounds, which are difficult to quantify, and those which were present in small amounts.

**Sensory Evaluation.** The aroma profile of the extrudates from the two batches of oats was developed using a sensory panel, and the sensory attributes were estimated qualitatively. The sensory panel comprised 15 persons, 5 of whom had taken part in previous sensory studies of extruded cereals, who were recruited from within the Department of Food Science and Technology at the University of Reading and screened for motivation, health, and availability. General descriptive skills were developed using standard odorous chemicals. The assessors were then familiarized with the aromas of the extrudates by smelling all of the samples, one at a time, in 60 mL brown-glass wide-mouth bottles. For the assessment, 1 g of extrudate was moistened with 5 mL of water immediately prior to assessment and allowed to equilibrate for 60 s. This took place over two sessions, using one oat variety per session. The assessors were asked to provide as many descriptive terms as seemed appropriate. These terms were discussed, as a group, with the panel leader, and this led to the collection of a set of reference samples, which was used in the further development of the aroma profile. These included food items such as Weetabix, toasted sunflower seeds, oatmeal, and stale oil. Ninety-six terms were collected, and these were then presented to assessors, together with the samples, over two further sessions. The assessors were asked to indicate all terms that they found in the samples and to add any further relevant terms. A group meeting of all the assessors was held to obtain consensus for a set of terms to describe the samples. The assessors were provided with a list of 103 terms, and the discussion was supported by the reference samples for 65 terms from the list. Twenty-two terms were agreed upon to form a descriptive profile for the samples, with 16 of the terms supported by reference samples.

The qualitative sensory assessment took place in well-ventilated sensory booths, each equipped with a computer screen and a mouse. The interactive profiling option in the Taste software package (Reading Scientific Services Ltd., Reading, U.K.) was used to acquire the sensory data. The intensity of each attribute for each sample was recorded by the assessors on a line scale. Each extrudate was assessed three times over four sessions using a balanced block experimental design to select the samples for each session. The order of presentation was randomized. Fresh samples were prepared for each assessor and presented as described above. Reference samples for 16 of the 22 attributes were available at all panel sessions.

**Data Analysis.** The data were processed using two-way analysis of variance (ANOVA) and principal component analysis (PCA) from the Senpak software package (Reading Scientific Services Ltd.). Fisher's least significant difference (LSD) was calculated for those attributes that were significant at  $p < 0.05$  in the ANOVA.

## RESULTS AND DISCUSSION

**Aroma Compounds.** More than 120 volatile compounds were found in the extruded oat samples, including 11 alkanals, 7 alkenals, 8 alkadienals, 14 ketones, 6 alcohols, 12 furans, 16 pyrazines, 4 pyrroles, 26 sulfur-containing compounds, 3 terpenes, and a range of alkanes and alkylbenzenes. Nineteen of these volatiles were found exclusively in the most severely processed extrudates (14.5% moisture, 180 °C). Details are given in Table 3. It is appropriate to consider the volatiles in relation to their mode of formation either from the Maillard reaction or from lipid degradation.

The Maillard reaction comprises a complex network of reactions between sugars, amino acids, and their respective degradation products (Ledl and Schleicher, 1990; Mottram, 1994; Nursten, 1986). The volatile products of the reaction contribute to flavor in heated foods. Some of the most common volatile products of the Maillard reaction are Strecker aldehydes, formed by the decarboxylation and deamination of amino acids. Typical sugar dehydration products are furfural and furanones, whereas pyrroles and pyrazines are heterocyclic nitrogen compounds formed from the reaction of these sugar breakdown products with ammonia or amino acids. Small amounts of sulfur-containing heterocyclic compounds, such as thiophenes and thiazoles, are formed in the Maillard reaction, and, because many have very low odor threshold values, they may make an important contribution to the overall aroma, even at low concentrations.

Previous work carried out on wheat and maize flours (Bredie et al., 1998a) showed that the levels of such volatiles derived from the Maillard reaction generally increase as the extrusion conditions become more severe. These volatiles are often associated with desirable flavor characteristics, providing roasted, toasted cereal notes in many extruded products (Maga, 1992; Bredie et al., 1998b). In the present study, a similar effect of extrusion conditions was observed for each category of Maillard volatiles for the oat flours OF1, OG1, and OG2 (debranned). The pattern shown for total Maillard volatiles in Figure 1 is typical.

The group of Strecker aldehydes was dominated by 2- and 3-methylbutanal, the breakdown products of isoleucine and leucine, respectively. There were significantly higher levels of methylbutanals in the most severely processed extrudate (14.5% moisture and 180 °C) compared with the least severely processed extrudate (18% moisture and 150 °C). There was little difference between the two intermediate conditions (18%/180 °C and 14.5%/150 °C), the levels of methylbutanals lying between those found in the extremes. The differences between processing conditions were greater in the two non-debranned oat extrudates, OF1 and OG1, compared with OG2 (Table 3).

The type of oat clearly had a great effect on the volatiles produced. Overall, the Strecker aldehyde levels were much lower in the debranned oat flour, OG2, than in OF1 and OG1. Of the two non-debranned extrudates, OG1 consistently showed higher levels of Strecker aldehydes than OF1. Although the levels of free fatty acids were similar in the two oat flours, they differed slightly in their protein levels; OG1 and OF1 contained 14.9 and 13.4% protein, respectively. In general, the contribution to the Maillard reaction of protein-bound amino acids is considered to be small compared to that of free amino acids, but the increased protein levels may indirectly influence the rate of the Maillard reaction, either by hydrolysis or by deamidation of the bound amino acids (Izzo et al., 1993; Riha et al., 1996).

The trends observed for Strecker aldehyde levels were also found in the other Maillard-derived volatiles. Oxygenated furan derivatives are generally less important odor compounds, but they still followed the same trends with respect to oat type and extrusion conditions. The highest levels were found under the most severe conditions, in particular in OG1, whereas OG2 had consistently less than its non-debranned counterparts. The simple furans were present under all extrusion



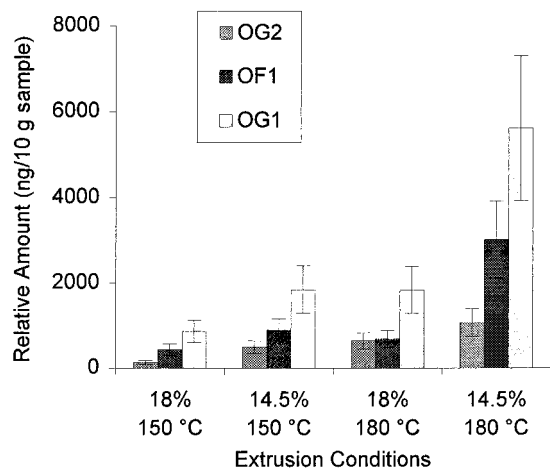
**Table 3. Volatile Compounds Identified in the Headspace of Extruded Oat Flours**

compound	LRI <sup>a</sup>	identi- fication <sup>b</sup>	approximate quantity, ng from 10 g of sample <sup>c</sup>											
			8%/150 °C <sup>d</sup>			14.5%/150 °C			18%/180 °C			14.5%/180 °C		
			OG2 <sup>e</sup>	OF1	OG1	OG2	OF1	OG1	OG2	OF1	OG1	OG2	OF1	OG1
2-methylpropanal	<700	lri + ms	4	16	16	14	31	51	42	20	36	46	85	131
3-methylbutanal	<700	LRI + MS	40	168	368	185	300	626	254	252	550	374	787	1197
2-methylbutanal	<700	LRI + MS	37	127	289	131	228	495	179	180	442	272	646	1038
benzeneacetaldehyde	1069	LRI + MS	2	10	15	8	19	39	14	11	43	13	27	92
<b>total Strecker aldehydes</b>			<b>83</b>	<b>321</b>	<b>688</b>	<b>338</b>	<b>578</b>	<b>1211</b>	<b>489</b>	<b>463</b>	<b>1071</b>	<b>705</b>	<b>1545</b>	<b>2458</b>
dihydro-2-methyl-3(2 <i>H</i> )-furanone	821	LRI + MS	—	—	—	—	—	6	—	—	—	—	8	25
2-furfural	848	LRI + MS	3	16	47	16	22	88	22	19	89	38	60	153
2-furanmethanol	864	LRI + MS	—	—	—	—	—	—	—	—	—	—	8	41
1-(2-furanyl)-2-propanone	952	lri + ms	16	—	—	17	—	—	1	—	—	16	—	—
5-methyl-2-furfural	978	LRI + MS	—	—	—	—	t	—	—	—	—	11	+	17
<b>total sugar-derived furans</b>			<b>19</b>	<b>16</b>	<b>47</b>	<b>33</b>	<b>22</b>	<b>94</b>	<b>23</b>	<b>19</b>	<b>89</b>	<b>65</b>	<b>76</b>	<b>236</b>
2,3-butanedione	<700	lri + ms	27	30	—	—	—	—	24	—	—	—	82	—
2,3-pentanedione	709	LRI + MS	—	—	—	—	43	110	—	—	140	—	167	375
2,4-pentanedione	799	lri + ms	—	—	—	—	6	7	—	—	7	—	28	84
<b>total sugar-derived ketones</b>			<b>27</b>	<b>30</b>	<b>0</b>	<b>0</b>	<b>49</b>	<b>117</b>	<b>0</b>	<b>24</b>	<b>147</b>	<b>0</b>	<b>277</b>	<b>459</b>
pyrazine	745	lri + ms	—	7	13	14	32	40	19	19	54	42	124	281
methylpyrazine	838	LRI + MS	—	8	17	20	41	92	20	25	79	59	237	499
2,6(5)-dimethylpyrazine	927	LRI + MS	—	14	25	21	54	107	22	25	92	43	201	393
ethylpyrazine	930	LRI + MS	—	—	3	5	—	17	5	5	15	11	39	87
2,3-dimethylpyrazine	932	LRI + MS	—	—	t	—	7	13	—	2	11	—	20	46
vinylpyrazine	947	lri + ms	—	—	—	—	—	—	—	—	—	—	3	9
2-ethyl-6-methylpyrazine	1008	LRI + MS	—	—	—	6	7	5	—	15	5	17	26	40
trimethylpyrazine	1011	lri + ms	—	—	—	5	14	—	4	—	15	6	—	71
2-ethyl-5-methylpyrazine	1012	LRI + MS	—	—	—	—	—	35	—	6	—	—	68	77
a methylvinylpyrazine	1040	lri + ms	—	—	—	—	—	—	—	—	—	—	2	—
2,3-dimethyl-3-ethylpyrazine	1088	LRI + MS	—	—	—	—	11	15	2	8	16	7	33	52
2,6-diethylpyrazine	1093	LRI + MS	—	—	—	—	—	—	—	—	—	—	—	7
3,5-dimethyl-2-ethylpyrazine	1098	LRI + MS	—	—	—	—	—	—	—	—	—	—	7	18
2,3-dimethyl-5-ethylpyrazine	1105	LRI + MS	—	—	—	—	—	—	—	—	—	—	3	5
2,3-diethyl-5-methylpyrazine	1162	LRI + MS	—	—	—	—	—	—	—	—	—	—	—	8
3,5-diethyl-2-methylpyrazine	1166	lri + ms	—	—	—	—	—	—	—	—	—	—	—	3
<b>total pyrazines</b>			<b>—</b>	<b>29</b>	<b>58</b>	<b>71</b>	<b>166</b>	<b>324</b>	<b>73</b>	<b>104</b>	<b>287</b>	<b>185</b>	<b>763</b>	<b>1596</b>
1 <i>H</i> -pyrrole	765	LRI + MS	—	3	6	—	3	20	8	5	22	10	30	90
pyridine	757	LRI + MS	—	7	12	—	7	27	—	3	24	—	16	30
2-methyl-1 <i>H</i> -pyrrole	856	lri + ms	—	—	—	—	—	8	—	—	10	—	—	36
3-methyl-1 <i>H</i> -pyrrole	862	ms	—	—	—	—	—	—	—	—	—	—	—	22
1-(2-furanmethyl)-1 <i>H</i> -pyrrole	1182	LRI + MS	—	—	—	—	—	—	—	—	—	—	6	14
<b>total pyridines and pyrroles</b>			<b>—</b>	<b>10</b>	<b>18</b>	<b>—</b>	<b>10</b>	<b>55</b>	<b>8</b>	<b>8</b>	<b>56</b>	<b>10</b>	<b>52</b>	<b>192</b>
thiophene	636	LRI + MS	—	3	—	4	3	—	5	6	—	—	25	+
2-methylthiophene	788	LRI + MS	—	10	20	38	17	38	23	16	46	42	71	145
3-methylthiophene	794	LRI + MS	—	—	2	—	1	3	t	t	3	2	3	12
4,5-dihydro-3(2 <i>H</i> )-thiophenone	976	LRI + MS	—	—	—	—	—	—	—	—	2	—	10	25
4,5-dihydro-2(5)-methyl-3(2 <i>H</i> )-thiophenone	1011	LRI + MS	—	—	—	—	—	—	—	—	—	—	—	49
3-thiophenecarboxaldehyde	1018	LRI + MS	—	—	—	—	—	—	—	—	4	—	t	8
2-thiophenecarboxaldehyde	1026	LRI + MS	—	—	—	—	8	15	—	11	28	—	32	58
5-methyl-2-thiophenecarboxaldehyde	1117	LRI + MS	—	—	—	—	t	—	—	—	—	—	20	32
<b>total thiophenes</b>			<b>—</b>	<b>13</b>	<b>22</b>	<b>42</b>	<b>29</b>	<b>56</b>	<b>28</b>	<b>33</b>	<b>83</b>	<b>44</b>	<b>161</b>	<b>329</b>
dimethyl disulfide	751	LRI + MS	9	4	4	10	—	5	11	5	8	24	6	—
3-methylthiane	1008	ms	—	—	—	—	4	—	3	4	11	17	19	47
3-methyl-1,2-dithiolan-4-one	1103	LRI + MS	—	4	3	—	10	14	5	9	17	12	41	72
3,5-dimethyl-1,2-dithiolan-4-one ( <i>E</i> or <i>Z</i> )	1124	lri + ms <sup>f</sup>	—	—	—	—	—	—	—	—	—	—	—	10
3,5-dimethyl-1,2-dithiolan-4-one ( <i>E</i> or <i>Z</i> )	1134	lri + ms <sup>f</sup>	—	—	—	—	—	—	—	—	—	—	—	13
1,2-dithian-4-one	1209	ms <sup>h</sup>	—	—	—	—	1	—	—	—	—	—	12	13
4-methyl-1,2-dithiepane	1245	lri + ms <sup>i</sup>	—	—	—	—	—	—	—	—	—	—	6	14
<b>total miscellaneous S compounds</b>			<b>9</b>	<b>8</b>	<b>7</b>	<b>10</b>	<b>15</b>	<b>19</b>	<b>19</b>	<b>18</b>	<b>36</b>	<b>53</b>	<b>84</b>	<b>169</b>
thiazole	735	LRI + MS	—	12	13	—	—	17	—	6	53	—	7	56
2-methylthiazole	819	LRI + MS	—	—	—	—	—	—	—	—	—	—	1	6
4-methylthiazole	836	LRI + MS	—	—	—	—	2	—	—	2	—	3	14	29
5-methylisothiazole	862	lri + ms	—	—	—	—	—	—	—	—	—	—	6	12
5-methylthiazole	869	lri + ms	—	—	—	—	—	—	—	—	—	—	1	8
4,5-dimethylthiazole	945	LRI + MS	—	—	—	—	—	—	—	—	—	—	4	7
4,5-dihydro-2-methylthiazole	956	ms	—	—	—	—	—	—	—	—	—	—	4	13
5-ethylthiazole	959	lri + ms	—	—	—	—	—	—	—	—	—	—	1	—
2-acetylthiazole	1040	LRI + MS	—	+	13	—	25	14	5	8	18	7	16	38
<b>total thiazoles</b>			<b>—</b>	<b>12</b>	<b>26</b>	<b>—</b>	<b>27</b>	<b>31</b>	<b>5</b>	<b>15</b>	<b>71</b>	<b>10</b>	<b>54</b>	<b>169</b>
1-pentanethiol	826	lri + ms	—	—	—	4	t	—	3	—	—	7	11	23
2-pentylthiophene	1170	LRI + MS	—	—	—	—	—	—	—	—	—	—	—	2
2-butyl-2 <i>H</i> -thiapyran	1223	LRI + MS	—	—	—	—	—	—	—	—	—	—	—	2
2-pentyl-2 <i>H</i> -thiapyran	1344	LRI + MS	—	—	—	—	—	—	—	—	3	—	—	19
<b>total lipid-derived S compounds</b>			<b>—</b>	<b>—</b>	<b>—</b>	<b>4</b>	<b>—</b>	<b>—</b>	<b>3</b>	<b>—</b>	<b>3</b>	<b>7</b>	<b>11</b>	<b>46</b>
pentanal	710	LRI + MS	514	139	275	728	85	110	312	—	143	769	94	—
hexanal	812	LRI + MS	3279	526	655	4595	450	549	1560	484	614	4185	506	602
heptanal	912	LRI + MS	52	39	83	68	39	83	66	38	90	65	36	90
octanal	1014	LRI + MS	18	39	31	24	21	21	45	40	33	25	22	—
nonanal	1114	LRI + MS	28	44	73	27	33	61	57	45	80	32	40	65
decanal	1216	LRI + MS	13	14	7	t	11	t	9	26	21	5	5	6
<b>total alkanals</b>			<b>3904</b>	<b>801</b>	<b>1124</b>	<b>5442</b>	<b>639</b>	<b>824</b>	<b>2050</b>	<b>633</b>	<b>981</b>	<b>5081</b>	<b>703</b>	<b>763</b>

Table 3. (Continued)

compound	LRI <sup>a</sup>	identi- fication <sup>b</sup>	approximate quantity (ng from 10 g of sample) <sup>c</sup>											
			8%/150 °C <sup>d</sup>			14.5%/150 °C			18%/180 °C			14.5%/180 °C		
			OG2 <sup>e</sup>	OF1	OG1	OG2	OF1	OG1	OG2	OF1	OG1	OG2	OF1	OG1
1-penten-3-ol	<700	LRI + MS	27	3	13	23	4	—	12	4	49	28	6	—
1-pentanol	775	LRI + MS	325	36	56	167	16	—	101	21	83	212	17	—
1-hexanol	876	LRI + MS	12	17	17	16	13	7	18	13	9	19	11	—
1-heptanol	978	LRI + MS	12	—	—	—	—	—	—	—	—	—	—	—
1-octen-3-ol	987	LRI + MS	196	—	—	195	7	t	38	—	—	156	—	—
2-ethyl-1-hexanol	1040	LRI + MS	—	—	—	—	—	17	—	—	—	—	—	20
<b>total alcohols</b>			<b>573</b>	<b>56</b>	<b>86</b>	<b>401</b>	<b>40</b>	<b>24</b>	<b>170</b>	<b>38</b>	<b>141</b>	<b>415</b>	<b>34</b>	<b>20</b>
2-methyl-2-butenal	749	LRI + MS	t	4	8	t	t	17	t	6	16	t	16	53
2-pentenal	768	LRI + MS	13	t	t	18	—	—	t	—	—	20	—	—
2-hexenal	865	LRI + MS	69	7	16	121	6	11	39	4	12	122	—	—
2-heptenal	970	LRI + MS	318	19	37	338	13	28	94	10	30	299	19	—
2-octenal	1071	LRI + MS	180	13	19	218	—	14	38	13	17	176	15	14
2-nonenal	1171	LRI + MS	12	7	11	10	4	12	t	8	14	13	4	6
2-decenal	1278	LRI + MS	12	—	—	11	—	—	5	—	—	13	—	—
<b>total 2-alkenals</b>			<b>604</b>	<b>50</b>	<b>91</b>	<b>716</b>	<b>23</b>	<b>82</b>	<b>175</b>	<b>40</b>	<b>89</b>	<b>643</b>	<b>54</b>	<b>73</b>
( <i>E,E</i> )-2,4-hexadienal	925	LRI + MS	5	—	—	—	—	—	—	—	—	—	—	—
( <i>Z,Z</i> )-2,4-heptadienal	1013	LRI + MS	21	—	—	25	—	—	—	—	—	27	—	—
( <i>E,E</i> )-2,4-heptadienal	1029	LRI + MS	42	—	4	39	—	—	21	—	—	43	—	—
2,4-octadienal	1125	lri + ms	4	—	—	—	—	—	—	—	—	3	—	—
( <i>Z,Z</i> )-2,4-nonadienal	1212	LRI + MS	6	—	—	5	—	—	—	—	—	8	—	—
( <i>E,E</i> )-2,4-nonadienal	1235	LRI + MS	38	—	—	34	—	—	3	—	—	34	—	—
( <i>Z,Z</i> )-2,4-decadienal	1312	LRI + MS	27	—	—	13	—	—	1	—	—	21	—	—
( <i>E,E</i> )-2,4-decadienal	1338	LRI + MS	32	5	3	12	—	—	1	—	1	22	—	t
<b>total 2,4-alkadienals</b>			<b>174</b>	<b>5</b>	<b>7</b>	<b>128</b>	—	—	<b>26</b>	—	<b>1</b>	<b>158</b>	—	—
2-methylfuran	<700	LRI + MS	—	—	—	t	—	—	t	t	—	t	8	t
2,5-dimethylfuran	<700	LRI + MS	—	+	—	—	—	—	+	6	7	—	20	+
2-ethylfuran	706	LRI + MS	10	20	45	—	10	33	+	14	47	—	33	74
2-ethyl-5-methylfuran	804	LRI + MS	—	2	7	—	1	7	t	3	9	—	3	9
2-pentylfuran	996	LRI + MS	49	35	68	66	26	36	78	32	54	63	23	37
<b>total lipid-derived furans</b>			<b>59</b>	<b>57</b>	<b>120</b>	<b>66</b>	<b>37</b>	<b>76</b>	<b>78</b>	<b>55</b>	<b>117</b>	<b>63</b>	<b>87</b>	<b>120</b>
2-butanone	<700	LRI + MS	14	22	78	34	48	177	109	40	154	—	143	430
3-pentanone	725	LRI + MS	14	13	27	22	10	46	9	126	—	—	26	103
2-hexanone	803	LRI + MS	—	—	—	—	—	5	—	—	5	—	7	15
cyclopentanone	808	LRI + MS	—	—	5	—	—	6	—	3	—	—	4	—
2-heptanone	898	LRI + MS	23	23	35	52	34	45	49	28	46	56	44	68
2,3-octanedione	993	lri + ms	32	2	13	40	7	16	41	8	18	33	8	—
6-methyl-5-hepten-2-one	995	LRI + MS	—	5	6	6	5	—	4	9	—	5	5	15
( <i>Z</i> )-3-octen-2-one	1055	lri + ms	87	10	—	110	6	—	24	9	—	115	—	—
( <i>E,Z</i> )-3,5-octadien-2-one	1083	lri + ms	24	—	—	25	2	—	4	3	—	26	—	—
( <i>E,E</i> )-3,5-octadien-2-one	1107	lri + ms	36	8	—	47	3	—	7	6	—	32	2	—
6,10-dimethyl-5,9-undecadien-2-one	1460	LRI + MS	—	—	—	—	2	—	—	—	—	0	2	—
<b>total ketones</b>			<b>228</b>	<b>83</b>	<b>164</b>	<b>336</b>	<b>117</b>	<b>295</b>	<b>246</b>	<b>231</b>	<b>223</b>	<b>267</b>	<b>241</b>	<b>631</b>
hexane	600	LRI + MS	10	25	—	30	14	76	18	13	61	29	14	114
heptane	700	LRI + MS	16	—	—	11	—	—	12	1	t	20	—	—
octane	800	LRI + MS	35	23	—	46	18	8	41	11	10	37	21	—
nonane	900	LRI + MS	—	—	15	—	—	—	—	17	—	—	—	—
decane	1000	LRI + MS	8	9	7	10	7	13	12	8	13	7	7	15
undecane	1100	LRI + MS	4	t	8	8	6	—	6	—	7	7	—	—
dodecane	1200	LRI + MS	6	5	3	4	4	7	3	4	8	6	5	—
tridecane	1300	LRI + MS	4	6	3	3	4	—	3	4	—	4	9	4
tetradecane	1400	LRI + MS	2	2	—	—	—	—	1	—	—	—	6	t
<b>total alkanes</b>			<b>85</b>	<b>70</b>	<b>36</b>	<b>112</b>	<b>53</b>	<b>104</b>	<b>96</b>	<b>58</b>	<b>99</b>	<b>110</b>	<b>62</b>	<b>133</b>
toluene	778	LRI + MS	30	60	124	33	58	121	80	62	84	29	56	131
benzaldehyde	983	LRI + MS	34	60	110	49	52	101	53	44	120	66	64	173
C <sub>8</sub> alkylbenzenes			30	94	264	37	75	325	71	98	242	38	90	284
C <sub>9</sub> alkylbenzenes			33	59	41	41	33	30	44	50	37	31	30	15
C <sub>10</sub> alkylbenzenes			9	12	13	3	8	5	13	33	10	8	3	5
<b>total aromatic hydrocarbons</b>			<b>135</b>	<b>285</b>	<b>552</b>	<b>163</b>	<b>225</b>	<b>582</b>	<b>260</b>	<b>286</b>	<b>493</b>	<b>172</b>	<b>243</b>	<b>608</b>
α-pinene	939	lri + ms	9	10	36	7	6	25	13	8	32	7	7	30
limonene	1038	LRI + MS	10	7	67	11	9	45	17	—	54	8	—	48
<b>total terpenes</b>			<b>25</b>	<b>30</b>	<b>134</b>	<b>24</b>	<b>15</b>	<b>70</b>	<b>40</b>	<b>24</b>	<b>119</b>	<b>15</b>	<b>19</b>	<b>78</b>

<sup>a</sup> Linear retention index on a BPX-5 column. <sup>b</sup> LRI + MS, mass spectrum and LRI agree with those of the authentic compounds run under similar GC-MS conditions; lri + ms, unless otherwise referenced, mass spectrum agrees with spectrum from NIST/EPA/MSDC mass spectral database and retention index agrees with that reported in Kondjoyan and Berdagué (1996); ms, compound tentatively identified by comparison with literature mass spectrum alone. <sup>c</sup> Estimated quantity (ng) in headspace from 10 g of sample, calculated by comparison with 1.31 mg of 1,2-dichlorobenzene used as an internal standard; average values of triplicate analyses are given; compounds identified in quantities below 0.5 ng are reported as trace (t), and those coeluting with another compound are reported as present (+). <sup>d</sup> Extrusion conditions: moisture content (%)/temperature (°C). <sup>e</sup> Oat batch. <sup>f</sup> Whitfield and Mottram (1999). <sup>g</sup> Farmer et al. (1989). <sup>h</sup> Yu et al. (1994).



**Figure 1.** Effect of processing conditions and oat batch on total Maillard-derived volatiles.

conditions, and 2-furfural was the predominant species in this group, accounting for over half of the furans present. However, 2-furanmethanol, 5-methylfurfural, dihydro-2-methyl-3(2*H*)-furanone, and 1-(2-furanmethyl)-1*H*-pyrrole were present only in the samples processed under the most severe extrusion conditions. 2-Pentylfuran is lipid derived and is discussed below.

The pyrazines followed the same pattern, but the difference between the most severely processed extrudates and the others was much greater. At 14.5% moisture, for the non-debranned extrudates, the pyrazine levels were ~5 times greater at 180 °C than at 150 °C, whereas the Strecker aldehydes only doubled. There was an overall increase in both the quantity and the range of pyrazines as the conditions became more extreme. In the mild OG1 extrudate, only pyrazine and its methyl, ethyl, and dimethyl derivatives were formed, whereas in the extreme sample, the range of alkyl-substituted pyrazines extended to more complex trisubstituted pyrazines, such as diethylmethylpyrazines. These trisubstituted pyrazines have much lower odor thresholds than the mono- or disubstituted ones (Maga, 1992), and they may contribute to the roasted toasted cereal notes that were present in the most severely processed extrudates. Pyrazine levels in OG2 were much lower than in the non-debranned counterparts.

Four pyrroles were identified in these extrudates, and overall they tended to follow the same pattern as the other Maillard-derived volatiles. 1*H*-Pyrrole was the most abundant species, whereas 2-methyl-1*H*-pyrrole was formed only in the OG1 extrudates and 1-(2-furanmethyl)-1*H*-pyrrole was found only in the extreme extrudates of OF1 and OG1.

All of these results reflect the higher temperatures and lower moisture content required to generate the desirable Maillard reaction products. They also highlight differences in the levels of important volatile compounds between batches of oat flour. In particular, they show that oat flour OG2, which had been debranned and possessed raised levels of lipase activity and free fatty acids before extrusion processing, gave rise to significantly reduced levels of these Maillard-derived volatiles. Two explanations can be offered. About one-third of the protein was lost during debranning, so the overall nitrogen content in OG2 would have been reduced, resulting in less nitrogen being available for the Maillard reaction. Alternatively, the available nitrogen may have been reduced as a result of the

increase in aldehydes from lipid degradation. These provide a further source of carbonyls, which compete for the free amino groups, thus reducing their availability for the formation of nitrogen-containing compounds, such as pyrazines and pyrroles (see below).

Sulfur-containing compounds are extremely important in the overall aroma profile, because many are potent odorants with low odor threshold values. Under mild extrusion conditions, the sulfur-containing species were mainly restricted to trace amounts of early-eluting compounds, such as 2-methylthiophene, dimethyl disulfide, and thiazole, whereas, under severe conditions, 28 different sulfur-containing compounds were identified in one or the other of the two non-debranned oat types (OF1 and OG1). The debranned oat flour extrudates (OG2) contained fewer sulfur compounds at lower levels than the non-debranned counterparts.

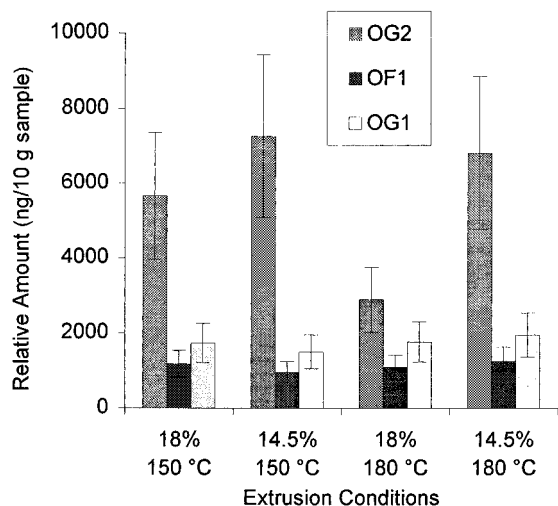
Thiophenes were present in all but the mildly extruded debranned oat flour. Extreme conditions, however, were required to generate 4,5-dihydro-3(2*H*)-thiophenone, 4,5-dihydro-2(5)-methyl-3(2*H*)-thiophenones, and 5-methyl-2-thiophenecarboxaldehyde. The latter could be derived from 5-methyl-2-furfural, which was also present only in the extremely processed extrudates. Of the thiazoles found, low levels of 2-acetylthiazole were present in most of the samples, and thiazole itself was present in most of the non-debranned samples, but other thiazoles were present only in the two non-debranned flours processed under the most extreme conditions. 3-Methyl-1,2-dithiolan-4-one was found in most samples. Disulfides are known to be formed during the Maillard reaction, and some have particularly low odor thresholds. Dimethyl disulfide was present in most samples. Additional disulfides were sought by examining key mass spectral ions in the chromatogram. Thus, trace amounts of 2-methyl-3-(methylthio)furan and 2-[(methylthio)methyl]furan were found in the most severely processed samples for all three oat types. The former is described as having typical meaty flavor notes, with some characteristics resembling cheese, egg, yeast, leek, and onion, and an odor threshold of 10–80 ng/kg (Werkhoff et al., 1993), whereas the latter has been reported to possess golden bread-crust aromas with an odor threshold value in water of 40 ng/kg (Mulders et al., 1976).

The sulfur-containing volatiles were formed to a significant extent only under the most severe processing conditions, and the effects of variety and extrusion conditions were similar to those for other Maillard volatiles. In general, those that involve incorporation of sugar fragments require more extreme conditions.

The volatiles derived from lipid autoxidation are well-documented (Grosch, 1982; MacLeod and Ames, 1988; Forss, 1972) and are mainly aliphatic aldehydes, alcohols, and ketones containing 5–10 carbon atoms derived from unsaturated fatty acids. The products are dependent on the original fatty acid profile. In oats, the main fatty acids are oleic and linoleic, each comprising ~40% of the total, palmitic (14%), and low levels of stearic and  $\alpha$ -linolenic acids.

The overall trends for lipid degradation products were completely different from those found for the Maillard-derived volatiles. The typical pattern can be seen in Figure 2 for total lipid-derived volatiles. The most notable feature is the much higher level of lipid degradation products found in the debranned oats (OG2) independent of extrusion conditions (see also Table 3).





**Figure 2.** Effect of processing conditions and oat batch on total lipid-derived volatiles.

This indicates that significantly more lipid oxidation had occurred in the debranned sample. Hexanal and pentanal were the dominant volatile alkanals contributing to this increase, and both of these have been identified by Guth and Grosch (1993) as key odor impact compounds in rancid extruded oats. Hexanal is one of the main breakdown products of linoleic acid, the most abundant fatty acid found in oat lipids. Alcohol levels were also higher in the OG2 extrudates, being dominated by high levels of 1-pentanol and 1-octen-3-ol (again derived from linoleic acid). The levels of 2-alkenals showed a trend similar to that of the alkanals and were influenced mainly by high levels of 2-heptenal and, to a lesser extent, 2-hexenal and 2-octenal. These can be derived from linoleic or linolenic acid and, in the case of 2-octenal, from the retro-aldol reaction of 2,4-decadienal (Josephson and Glinka, 1989). The 2,4-alkadienals, particularly *E,E*-2,4-nonadienal and *E,E*-2,4-decadienal, impart fried and fatty notes to oat extrudates (Guth and Grosch, 1993). They are formed from the autoxidation of linoleic and linolenic acids and were found almost exclusively in the debranned oats OG2. These showed much higher levels of free fatty acids prior to extrusion than the non-debranned flours (OF1 and OG1) with a correspondingly higher lipase activity. Free fatty acids undergo autoxidation much more readily than fatty acids bound in acylglycerols or phospholipids, and the large quantities of aldehydes, alcohols, and other lipid oxidation products in OG2 are explained by the higher levels of free fatty acids.

Volatiles derived from the interaction between Maillard-derived volatiles and lipid-derived volatiles have been reported in the literature, especially in model meat systems (Farmer and Mottram, 1990; Mottram and Whitfield, 1994). These include alkylpyridines, alkylthiophenes, and their isomeric alkylthiapyrans, which are formed by the addition of hydrogen sulfide to 2,4-dienals followed by cyclization. Significant levels of 2-pentyl-2*H*-thiapyran were found in the high-temperature treatment of the OG1 extrudate, together with smaller quantities of 2-pentylthiophene and its isomeric 2-butyl-2*H*-thiapyran. Pentanethiol is another compound resulting from a Maillard-lipid interaction, which could be formed by the interaction of pentanol with hydrogen sulfide, and was present in low levels in the OG2 extrudates. However, it was formed to a greater extent in OF1 and under extreme conditions. The

**Table 4.** Comparison of Classes of Volatile Compounds Found in Oat Flour OF2 and OF2 Dosed with 2% Linoleic Acid

class of volatile	approximate quantity, ng/4.8 L of headspace from 10 g of sample			
	14.5%/150 °C <sup>a</sup>		18%/150 °C	
	OF2	OF2-dos <sup>b</sup>	OF2	OF2-dos
<b>lipid-derived</b>				
alkanal	1172	1960	1001	1419
2-alkenals	129	387	56	225
2,4-alkadienals		188	5	56
alcohols	135	375	109	217
lipid furans	27	45	26	33
pentanethiol		6		3
<b>Maillard-derived</b>				
Strecker aldehydes	1401	868	886	279
furans	140	113	62	51
pyrazines	654	139	103	11
pyrroles	46		42	
thiophenes	101		24	
thiazoles	75	70	59	15
thiolans	37	5	4	

<sup>a</sup> Extrusion conditions: moisture content (%) / temperature (°C).

<sup>b</sup> OF2 dosed with 2% linoleic acid.

formation of these interaction products appears to depend on both extrusion conditions and lipid content.

**Addition of Linoleic Acid to Oat Flour.** Comparison of the volatiles generated from extrudates of OF1, OG1, and OG2 showed a major difference between the non-debranned oat flours (OF1 and OG1) and the debranned oat flour (OG2) that had raised levels of free fatty acids (1.7 versus 0.2%). To determine the effect of increased levels of free fatty acids on the extrudates, a second batch of French oat flour (OF2) was dosed with 2% linoleic acid immediately prior to extrusion (OF2-dos) at 150 °C and 14.5 or 18% moisture. Control samples (OF2) were also extruded under these conditions.

Under both sets of extrusion conditions, similar trends in lipid degradation products were observed. In both cases, the addition of linoleic acid resulted in a 50% increase in alkanals and larger increases in 2-alkenals, 2,4-alkadienals, and alcohols (Table 4). It also resulted in the formation of pentanethiol, which was undetected in the control. A similar effect had been observed with oat flour OG2 that contained considerably more free fatty acids than the comparable flour OG1.

A decrease in the quantity of Maillard-derived volatiles was observed in the flour with added linoleic acid. This was true for all classes of Maillard volatiles but most noticeably for pyrazines, which were reduced to less than one-fourth that of the control, and pyrroles, which were absent from the dosed extrudates. Likewise, the sulfur-containing compounds were all reduced, particularly the thiophenes, which were absent from the dosed extrudates. Thus, the addition of linoleic acid suppressed production of these important flavor volatiles formed via the Maillard reaction, and it is reasonable to suggest that the reduction in Maillard volatiles in OG2 compared to OG1 was also due (at least in part) to the increased levels of linoleic acid in the oat flour OG2. Because the greatest reduction was in the volatiles incorporating sulfur and nitrogen into the molecule, it is suggested that aldehydes, generated by lipid degradation of free fatty acids such as linoleic acid, act as scavengers of nitrogen and sulfur, thus reducing their total availability for the formation of heterocyclic Maillard volatiles. These observations demonstrate that

**Table 5. Mean Panel Scores<sup>a</sup> for Aroma Attributes of Extruded Oat Flours**

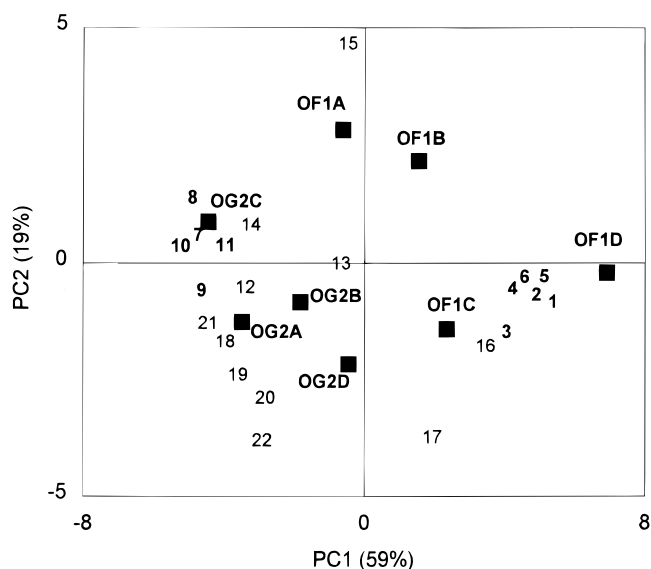
code	attribute	OF1				OG2				LSD <sup>b</sup>
		18%/150 °C <sup>c</sup>	14.5%/150 °C	18%/180 °C	14.5%/180 °C	18%/150 °C	14.5%/150 °C	18%/180 °C	14.5%/180 °C	
1	puffed wheat	31 <sup>bc</sup>	51 <sup>c</sup>	44 <sup>def</sup>	72 <sup>g</sup>	25 <sup>ab</sup>	17 <sup>a</sup>	36 <sup>bcd</sup>	39 <sup>cde</sup>	12
2	Weetaflakes	15 <sup>ab</sup>	18 <sup>bc</sup>	17 <sup>b</sup>	24 <sup>c</sup>	14 <sup>ab</sup>	10 <sup>a</sup>	14 <sup>ab</sup>	15 <sup>ab</sup>	6.4
3	toasted wheat/ maize	12 <sup>ab</sup>	20 <sup>ab</sup>	18 <sup>ab</sup>	37 <sup>c</sup>	15 <sup>ab</sup>	15 <sup>ab</sup>	17 <sup>ab</sup>	21 <sup>b</sup>	8.2
4	digestive biscuit	8 <sup>abc</sup>	13 <sup>c</sup>	10 <sup>bc</sup>	12 <sup>c</sup>	7 <sup>ab</sup>	4 <sup>a</sup>	8 <sup>abc</sup>	8 <sup>abc</sup>	5.6
5	toasted sunflower seed	12 <sup>ab</sup>	20 <sup>bc</sup>	19 <sup>bc</sup>	24 <sup>c</sup>	13 <sup>ab</sup>	10	13 <sup>ab</sup>	14 <sup>ab</sup>	7.3
6	burnt	9 <sup>a</sup>	18 <sup>b</sup>	15 <sup>ab</sup>	30 <sup>c</sup>	7 <sup>a</sup>	8 <sup>a</sup>	13 <sup>ab</sup>	11 <sup>ab</sup>	8.1
7	oatmeal	18 <sup>cde</sup>	8 <sup>a</sup>	15 <sup>abc</sup>	10 <sup>ab</sup>	24 <sup>e</sup>	22 <sup>de</sup>	22 <sup>de</sup>	15 <sup>bcd</sup>	7.2
8	oatcakes/ cardboardy	19 <sup>abc</sup>	12 <sup>a</sup>	16 <sup>ab</sup>	12 <sup>a</sup>	23 <sup>bc</sup>	25 <sup>c</sup>	17 <sup>ab</sup>	16 <sup>ab</sup>	8.5
9	dried vegetables	5 <sup>ab</sup>	3 <sup>a</sup>	2 <sup>a</sup>	3 <sup>a</sup>	10 <sup>bc</sup>	11 <sup>c</sup>	5 <sup>ab</sup>	6 <sup>abc</sup>	5.6
10	wet washing	3 <sup>ab</sup>	1 <sup>a</sup>	4 <sup>abc</sup>	<1 <sup>a</sup>	7 <sup>c</sup>	6 <sup>bc</sup>	6 <sup>bc</sup>	2 <sup>ab</sup>	3.7
11	stale oil	4 <sup>ab</sup>	4 <sup>ab</sup>	5 <sup>ab</sup>	2 <sup>a</sup>	9 <sup>b</sup>	17 <sup>c</sup>	6 <sup>ab</sup>	6 <sup>ab</sup>	5.5
12	stale	4	4	2	2	3	6	4	5	ns
13	Shredded Wheat	14	14	13	15	16	14	14	13	ns
14	cooked rice	17	13	12	6	12	14	17	15	ns
15	wholemeal flour	15	8	12	12	9	13	10	8	ns
16	malty	10	10	9	18	10	8	11	13	ns
17	sweet	20	29	18	32	24	23	24	30	ns
18	apple puree	3	4	6	3	12	7	9	7	ns
19	acidic	5	9	7	5	12	11	11	8	ns
20	boiled milk	10	11	6	6	12	8	12	13	ns
21	chicken bones/ broth	5	5	4	3	8	7	6	5	ns
22	musty	4	5	4	4	6	6	6	7	ns

<sup>a</sup> Sample means with the same superscript letters in an attribute row are not significantly different at  $p < 0.05$ . <sup>b</sup> Fisher's least significant difference; ns, not significant at  $p < 0.05$ . <sup>c</sup> Extrusion conditions: moisture content (%) / temperature (°C).

inefficient processing of the oats, leaving residual lipase activity and increased levels of free fatty acid, can be detrimental to the final extruded product, not only because of off-flavors from lipid degradation but also because the quantity of desirable Maillard-derived flavors is reduced.

**Sensory Analysis.** A trained panel was used to generate an aroma profile of the set of extrudates of OF1 and OG2 (debranned). At the end of the profile development, 22 terms were agreed on by the panel for the quantitative assessment of the aroma of the extrudates. Table 5 gives the mean panel scores for these attributes and significant differences as determined by ANOVA.

Principal component analysis (PCA) was carried out on the correlation matrix of all samples and all attributes (Figure 3). The first principal component (PC1) contained 59% of the variance in the data, and the second principal component (PC2) contained 15%. The difference in oat type was the predominant distinguishing factor in the sensory analysis, with PC1 separating the OF1 extrudates from OG2. Also, all of the significant attributes (coded 1–11) were clustered together at one or the other end of this axis. Desirable toasted cereal terms, puffed wheat (1), Weetaflakes (2), toasted maize (3), digestive biscuit (4), toasted sunflower seeds (5), and burnt (6), lay at the one extreme associated with OF1, whereas the other extreme was associated with OG2 and terms such as oatmeal (7), oatcakes (8), and the less desirable terms such as dried vegetable (9), wet washing (10), and stale oil (11). Under the most severe extrusion conditions, OF1 produced the highest component along PC1, and the highest scores for the toasted cereal notes, but this was greatly reduced for the two intermediate samples and was less still for the most mildly treated extrudate. In general, the OG2 samples were closer to the oatmeal (7) and wet washing (10) terms, in particular extrudate 14.5%/150 °C that had the highest mean panel score for stale (12), stale oil (11), oatcakes, and cardboard (8) terms. PC2 accounted for only 15% of the variation, and the distinctions were much less clear. PC2 did not separate the cluster of toasted cereal terms but, for OF1 extrudates, it separated the low-moisture from the high-moisture.



**Figure 3.** Principal component plot (PC1 versus PC2) for sensory profile of eight oat extrudates showing correlations with attributes. Attribute codes are shown in Table 5, oat batch codes are as in the text, and process codes are A = 150 °C/18% (least severe), B = 180 °C/18%, C = 150 °C/14.5%, and D = 180 °C/14.5% (most severe).

The sensory analysis linked well with the instrumental data. The two samples most closely correlated with the generally desirable toasted cereal terms were the two low-moisture OF1 extrudates, with the high-temperature extrudate having the highest sensory scores for these attributes. These terms are generally associated with pyrazines and, indeed, this OF1 sample contained both the largest range and the greatest quantity of pyrazines (760 ng/10 g of sample). Thereafter, OF1/14.5%/150 °C and OG2/14.5%/180 °C contained the next highest levels of pyrazines (166 and 185 ng/10 g of sample, respectively) and had very similar distributions of other Maillard-derived compounds. Generally, OG2 extrudates were closely associated with oatcakes, oatmeal, wet washing, and stale oil. These



terms, especially the last, suggest lipid degradation products, which were, indeed, very much higher in all the OG2.

**Conclusion.** Both sensory analysis and instrumental analysis of volatiles have identified significant differences between the oat samples that can be attributed to either extrusion processing conditions or oat batch. The more severe extrusion conditions were required to generate the products of the Maillard reaction, such as pyrazines and sulfur-containing alicyclic compounds, and those containing high levels of Maillard products were generally described by the assessors as having desirable toasted cereal aromas. The differences found between oat batches were dominated by the high levels of lipid degradation products found in the debranned oats. These samples were identified by assessors who gave high scores for the stale oil attributes and lower scores for the toasted cereal attributes. This was supported by the instrumental analysis, which found substantially higher levels of lipid degradation products in the debranned oat extrudates and substantially lower levels of Maillard-derived volatiles. This reduction in Maillard-derived volatiles, particularly the nitrogen- and sulfur-containing volatiles, suggests that less nitrogen and sulfur was available to participate in the Maillard reaction. This may be the result of an interaction between the lipid-derived aldehydes and the nitrogen- and sulfur-containing precursors of these compounds.

Extrusion of a non-debranned oat flour, dosed with linoleic acid to model the raised levels of free fatty acids in OG2, showed, as anticipated, raised levels of lipid degradation products. More importantly, it also showed decreased levels of Maillard-derived products. This suggests that if, during the preparation of the flour, the destruction of the lipase activity is not effective, then the free fatty acids generated by the residual lipase activity will not only produce unpleasant lipid degradation products but also inhibit the formation of the more pleasant Maillard-derived flavors.

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