Analysis of Volatiles Formed during Oxidation of Extruded Oats

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Moistened oat flour was extruded using various processing parameters into two products, which were then stored for 18 weeks at 32 °C and regularly analyzed by headspace gas chromatography. The formation of 27 volatile compounds was followed using gas chromatography/mass spectrometry. The major volatiles were hexanal, decane, 2-pentylfuran, and nonanal. The relative amounts of major volatiles, especially hexanal, increased during storage, which was enhanced by higher extrusion temperature.

INTRODUCTION

Oat grains are oxidation resistant, and the flavor of the seed keeps well. Oat products are used worldwide as components in breakfast cereals, breads, cookies, and ready-to-eat-meals and as a meat extender (Heydanek and McGorrin, 1981; Webster, 1986). Extrusion technology is increasingly used in the processing of oats, mainly for direct expansion and forming of solid shapes. The enhanced oxidation of lipids may limit the use of some products. Heat treatment generates reactions of metal ions with lipids and increases oxidation regardless of inactivation of the oxidative enzymes. The process also induces complex formations between lipids and gelatinized starch, and some breakdown of the lipids by heat may occur (Williams et al., 1977; Maga and Sizer, 1978). Typically, a high-temperature, short-time extrusion process is applied, the extended shelf life being based mainly on low water content (Miller, 1990) with separate processes applied for cooking.

Extrusion has many advantages such as versatility, reduced costs, production rate, and lack of process effluents. However, nutritional and chemical changes can take place between the carbohydrates and proteins in extruded foods (Cheftel, 1986). Loss of vitamins occurs depending on the process conditions and food material (Björk and Asp, 1983). Extrusion may affect the sensory characteristics of the product by promoting flavor development, though the technology may sometimes cause up to 90% loss of free volatile compounds during processing (Sadafian and Crouzet, 1988).

Analysis of the headspace volatiles has been proposed in many papers as a measure of rancidity (Fritsch and Gale, 1977; Frankel et al., 1989; Löliger, 1990; Kinderlerer and Johnson, 1992). Aldehydes and ketones are typical products of oxidation of unsaturated lipids. Carbonyl compounds of lipid origin are important as they may often be the cause of off-flavor during storage. Determination of the content of hexanal has been reported to indicate oxidation in low-fat foods and samples containing $n-6$ polyunsaturated fatty acids (Fritsch and Gale, 1977; Frankel et al., 1989).

This study was designed to measure volatile oxidation products in oats extruded under high- and low-moisture conditions, followed by drying to equivalent moisture levels. Preliminary sensory evaluation was also carried out in addition to headspace analysis.

MATERIALS AND METHODS

Materials. A mixture of various oat cultivars, commonly grown in Finland for rolled oats production, was milled by Melia Ltd. (Raisio, Finland). The moistened flour was processed by a Pilot-Extruder ZE 25 × 33 D (Germany). The parameters were as follows: (LT) oat flour, 13 g/min; water, 116 g/min; speed, 200 rpm; pressure, 1.8 MPa; temperature of zones 1–7, 40, 40, 40, 70, 150, 150, and 140 °C, respectively; temperature of the expanding mass, 130 °C; (HT) oat flour, 13 g/min; water, 130 g/min; speed, 250 rpm; pressure, 2.8 MPa; temperature of zones 1–7, 40, 40, 70, 90, 180, 180, and 180 °C, respectively; temperature of the expanding mass, 157 °C. The diameter of the outlets in the nozzle was 2.8 mm. The moisture contents of the LT and HT were 10.2% and 8.5%, respectively. Products were immediately dried to a moisture content of 7–8% by heating in an oven at 120 °C for approximately 10 min.

Each product was divided into six paper bags, one duplicate sample consisting of two bags. The bags were stored at 32 °C, and samples of 6 g were taken after 4, 6, 8, 10, 12, 16, and 18 weeks of storage for headspace analysis. Thus, both products were analyzed 3 × 7 times, and each analysis was made using a pooled sample from two bags, the bags being carefully closed after sampling. The pooled 200-g samples for preliminary sensory evaluation were weighed into glass bottles after 4, 8, 12, and 18 weeks of storage. The 500-mL glass bottles were carefully closed with Teflon washers and stored at −20 °C until analysis.

Analysis of Volatiles. The volatiles were analyzed with a Varian Model 3700 gas chromatograph (Walnut Creek, CA) equipped with a flame ionization detector (250 °C) using a dual column system described earlier (Kallio, 1991). The 50-mL headspace vial containing a 2.5 ± 0.1 g sample was set in a water bath at a constant 25.5 ± 0.5 °C and allowed to stabilize for 5 min. The trapping column was a DB-1 (30 m × 0.25 mm i.d., film thickness 0.25 μm, J&W Scientific, Folsom, CA) and the analytical column a DB-1701 (30 m × 0.25 mm i.d., film thickness 0.25 μm). The volatiles in the headspace were transferred with 250 mL of helium over 0.5 h from the vial into the trapping column and flushed into a deactivated fused silica tubing immersed in liquid nitrogen. The temperature program of the flushing was 3 min isothermal hold at 28 °C followed by programming to 200 °C at a rate of 10 °C/min. The cold trap was removed and the analysis carried out after a 3 min isothermal period by a program from 28 to 200 °C at a rate of 3 °C/min.

Identification of the volatiles was carried out by a TSQ-700 mass spectrometer (EI-mode, positive ions, 70 eV, Finnigan

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Table 1. Volatile Compounds of Extruded Oat Products during Storage at 32 °C Analyzed with a DB-1701 Capillary Column

peak	mol wt	compound	I_K
1	86	pentanal	784
2	114	octane	800
3	92	toluene	817
4	100	hexanal	886
5	128	nonane	900
6	106	ethylbenzene	910
7	116	o/p-xylene	919
8	116	m-xylene	948
9	98	(E)-2-hexenal	965
10	114	2-heptanone	979
11	114	heptanal	984
12	102	1-hexanol	986
13	142	decane	1000
14	120	methylethylbenzene	1001
15	120	methylethylbenzene	1011
16	120	methylethylbenzene	1025
17	138	2-pentylfuran	1036
18	120	methylethylbenzene	1048
19	128	1-octen-3-ol	1084
20	128	octanal	1089
21	156	undecane	1100
22	126	3-octen-2-one	1154
23	126	(E)-2-octenal	1172
24	142	nonanal	1193
25	126	(E,E)-3,5-octen-2-ol	1197
26	170	dodecane	1200
27	142	(E)-2,3-epoxyoctanal	1220

Mat, San Jose, CA) with the same column and temperature program as used in the flame ionization detector analysis. Identification was based on the literature (Stenhagen et al., 1974) and the library of the mass spectrometry (NIST, National Technical Information Services, Springfield, VA).

Analysis of Fatty Acids. Extraction of oil was performed according to a modified Folch procedure (chloroform/methanol, 2:1 v/v) (Folch et al., 1957; Ways and Hanahan, 1964). Triacylglycerols were isolated from oil by Florisil column chromatography using hexane/diethyl ether (4:1 v/v) as eluent. Fatty acids of triacylglycerols were methylated by sodium methoxide catalyzed transesterification (Christie, 1982). The fatty acid methyl esters were analyzed by a Varian 3300 gas chromatograph with an NB-351 column (25 m × 0.32 mm i.d., film thickness 0.20 μm, HNU-Nordion, Helsinki, Finland). The injector temperature was 225 °C, and the temperature of the detector was 240 °C. The temperature program was 120 °C for 2 min, raised to 230 °C at 3 °C/min, and held at 230 °C for 10 min.

RESULTS AND DISCUSSION

Table 1 lists the major volatile compounds of the headspace of extruded oats identified according to their mass spectra and Kovats indices (I_K). Compounds identified were mainly aldehydes, ketones, alcohols, and some aliphatic and aromatic hydrocarbons. The headspace of all samples contained hexanal, o/p-xylene, 2-pentylfuran, undecane, and nonanal in abundance, while other compounds were found occasionally or in minor proportions. All of the volatiles identified have previously been reported to appear in rancid oat groats or in extruded oat meal (Heydanek and McGorrin, 1981, 1986; Guth and Grosch, 1993). Guth and Grosch (1993) have previously analyzed odorants of extrusion products of oatmeal using solvent extraction, which led to a different profile of volatiles than did our investigation. Two main groups of volatile compounds formed in the extrusion cooking of cereals have been reported by Pfannhauser (1993). These are either products of germ lipids or pyrazines from reactions of proteins and starch.
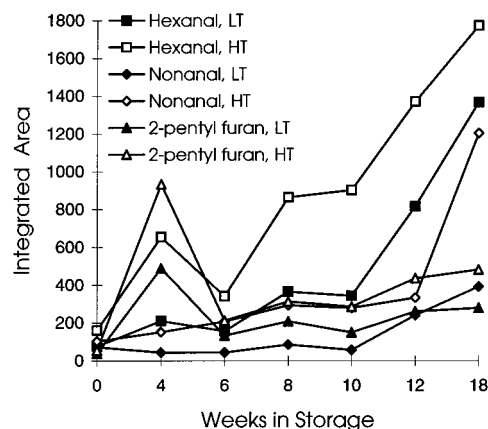

Figure 1. Averages of absolute integrated detector values of hexanal, 2-pentylfuran, and nonanal during storage in headspace of oats extruded at low (LT) and high temperature (HT). Temperatures of expanding masses were 130 and 157 °C, respectively.

Both extruded samples showed analogous chromatographic patterns. As expected, hexanal was the major volatile, its content increasing throughout the storage period as reported by Fritsch and Gale (1977). They further demonstrated that the rancid odor occurs in ready-to-eat oat cereals when the concentration of hexanal reaches the level 5–10 mg/kg. Linoleic, α-linolenic, and arachidonic acids as well as 2,4-decadienal are typical precursors of hexanal (Frankel, 1982; Ullrich and Grosch, 1987; Frankel et al., 1992). Hexanal, 2(Z)-octenal, and 2(E)-nonenal have been identified as the most potent flavor compounds in autoxidized linoleic acid by Ullrich and Grosch (1987). The further oxidation of hexanal yields hexanoic acid but no lower aldehydes or alcohols (Frankel et al., 1992).

The contents of hexanal, nonanal, and 2-pentylfuran gradually increased in both products during storage. The induction time of nonanal derived from oleic acid [18:1(n−9)] was longer than that of hexanal from the more unsaturated fatty acid species. Heat is commonly known to promote oxidation in extrusion (Fast, 1990). In accordance with this, the higher heating parameters resulted in a more rapid formation of hexanal, nonanal, and 2-pentylfuran in the headspace (Figure 1).

The sampling procedure may have affected the proportions of volatile compounds via dilution, although the sampling took place at regular intervals and in the same way each time. Extrusion products always have porous structures, thus accelerating oxidation by air (Cheftel, 1986). In our experiments, the expansion rates were low and highly porous structures were not developed, but there may, however, be differences between the two products in this respect. Trends of the curves (Figure 1) were based on standardized volumes of the headspace gas, and the detector response values indicated the relative rate of oxidation. The reason for the elevated emission of hexanal and 2-pentylfuran in the headspace after 4 weeks of storage is not clear.

There are also other technological factors affecting the rate of oxidation of extruded oat products. Structural changes and chemical modifications of fats have been reported to take place in oats during processing, affecting the development of rancidity (Ekstrand et al., 1993). Furthermore, lipases and lipoxygenases contribute to changes in the lipid composition of oats, these being inactivated by heating in the milling processes. Extrusion also decreases enzyme activities as the processing

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Table 2. Fatty Acid Composition of Triacylglycerols of Extruded Oats

fatty acid	mol %[a] HT[b]	LT[c]
16:0	17.1	16.8
18:0	1.6	1.6
18:1(n−9)	40.6	41.1
18:1(n−7)	0.9	0.9
18:2(n−6)	36.4	36.1
18:3(n−3)	1.3	1.3
20:1(n−9)	0.8	0.9

[a] Average of six duplicates. [b] Oats extruded at high temperature. [c] Oats extruded at low temperature.

temperature increases (Fretzdorff and Seiler, 1987; Ekstrand et al., 1993). Enzyme activities were not tested in this study. Concentrations of the co-oxidants copper and iron were determined, but no elevated contents were observed in either extrusion product (LT, 55.7 mg of Fe/kg and 2.8 mg of Cu/kg; HT, 56.0 mg of Fe/kg and 3.5 mg of Cu/kg).

The fatty acid composition of triacylglycerols in the products is shown in Table 2. The major fatty acids known to be related to the development of rancidity were oleic (41 mol %), linoleic [18:2(n−6)] (36 mol %), and α-linolenic [18:3(n−3)] (1 mol %) acids. As expected, no distinct differences between the two products were observed; losses of the fatty acids were low when compared to the accuracy of the gas chromatographic analysis. A common problem in headspace analysis is the quantitative calibration of the sampling system (Macku et al., 1988). The aim of this study was not to analyze the contents of volatiles in the product matrix but to investigate their migration and evolution in surroundings at room temperature without any sample treatment. Thus, no internal standards were used. Headspace analysis would not be a proper choice at all, if the actual concentrations in the extruded products were to be measured.

One of the difficulties in the sensory evaluation of extruded products is that samples of this kind often have low intrinsic intensities of odor characteristics, which decrease during storage. The results of preliminary sensory evaluation showed progressively lower intensities of rancid odor for the samples stored for 4, 8, and 12 weeks than for the unstored sample. This may also be an indication as to the decrease in total intensity of odor. Volatile losses may have taken place through the porous paper bag. In this work, the rancid odor seemed to be detectable after 18 weeks of storage. A reliable odor assessment for this kind of product would necessitate a fairly large amount of the actual sample to be evaluated, e.g., a 200-g extruded sample weighed in a 500-mL bottle and evaluated after 4 h of stabilization. For the sensory panel of 15 assessors and 3 replications, this would require a minimum amount of 9 kg of sample for each storage time. The handling of such a large amount of samples was not possible in this work. Thus, quantitative sensory assessments of odor characteristics need to be carried out in further studies.

Loss of flavors due to cooking occurs by steam distillation at the point of expansion when the product is leaving the extruder, thus affecting the levels and balance of flavors (Fast, 1990). This study suggests that it is possible to obtain a relatively reliable estimation of the degree of oxidation by combining headspace gas chromatographic analysis with sensory evaluation.

LITERATURE CITED

Björck, I.; Asp, N.-G. The effects of extrusion cooking on nutritional value—A literature review. *J. Food Eng.* **1983**, *2*, 281−308.

Cheftel, J. C. Nutritional effects of extrusion-cooking. *Food Chem.* **1986**, *20*, 263−283.

Christie, W. W. A simple procedure for rapid transmethylation of glycerolipids and cholesteryl esters. *J. Lipid Res.* **1982**, *23*, 1072−1075.

Ekstrand, B.; Gangby I.; Åkesson, G.; Stöllman, U.; Lingnert, H.; Dahl, S. Lipase activity and development of rancidity in oats and oat products related to heat treatment during processing. *J. Cereal Sci.* **1993**, *17*, 247−254.

Fast, R. B. Manufacturing technology of ready-to-eat cereals. In *Breakfast Cereals and How They are Made*; Fast, R. B., Caldwell, E. F., Eds.; American Association of Cereal Chemists: St. Paul, MN, 1990.

Folch, J.; Lees, M.; Stanley, G. H. S. A simple lipid method for isolation and purification of total lipids from animal tissues. *J. Biol. Chem.* **1957**, *226*, 497−509.

Frankel, E. N. Volatile lipid oxidation products. *Prog. Lipid Res.* **1982**, *22*, 1−33.

Frankel, E. N.; Hu, M.-L.; Tappel, A. L. Rapid headspace gas chromatography of hexanal as a measure of lipid peroxidation in biological samples. *Lipids* **1989**, *24*, 976−981.

Frankel, E. N.; Selke, E.; Neff, W. E.; Miyashita, K. Autoxidation of polyunsaturated triacylglycerols. IV. Volatile decomposition products from triacylglycerols containing linoleate and linolenate. *Lipids* **1992**, *27*, 442−446.

Frezdorff, B.; Seiler, K. The effects of twin-screw extrusion cooking on cereal enzymes. *J. Cereal Sci.* **1987**, *5*, 73−82.

Fritsch, C. W.; Gale, J. A. Hexanal as a measure of rancidity in low fat foods. *J. Am. Oil Chem. Soc.* **1977**, *54*, 225−228.

Guth, H.; Grosch, W. Geruchsstoffe von extrudiertem Hafermehl, Veränderungen bei der Lagerung. *Z. Lebensm. Unters. Forsch.* **1993**, *196*, 22−28.

Heydanek, M. G.; McGorrin, R. J. Gas chromatography-mass spectrometry identification of volatiles from rancid oat groats. *J. Agric. Food Chem.* **1981**, *29*, 950−954.

Heydanek, M. G.; McGorrin, R. J. Oat flavor chemistry: principles and prospects. In *Oats: Chemistry and Technology*; Webster, F. W., Ed.; American Association of Cereal Chemists: St. Paul, MN, 1986.

Kallio, H. Method of sensitive analysis of wine headspace volatiles based on selective capillary column trapping. *J. Chromatogr. Sci.* **1991**, *29*, 438−443.

Kinderlerer, J. L.; Johnson, S. Rancidity in hazelnuts due to volatile aliphatic aldehydes. *J. Sci. Food Agric.* **1992**, *58*, 89−93.

Löliger, J. Headspace gas analysis of volatile hydrocarbons as a tool for the determination of the state of oxidation of foods stored in sealed containers. *J. Sci. Food Agric.* **1990**, *52*, 119−128.

Macku, C.; Kallio, H.; Takeoka, G.; Flath, R. Aspects on the use of headspace GC on-column injections in flavor research. *J. Chromatogr. Sci.* **1988**, *26*, 557−560.

Maga, J. A.; Sizer, C. E. Ascorbic acid and thiamin retention during extrusion of potato flakes. *Lebensm. Wiss. Technol.* **1978**, *11*, 192−194.

Miller, R. C. Extrusion and extruders. In *Breakfast Cereals and How They are Made;* Fast, R. B., Caldwell, E. F., Eds.; American Association of Cereal Chemists: St. Paul, MN, 1990.

Pfannhauser, W. Volatiles formed during extrusion cooking of cereals. *Flavour Fragrance J.* **1993**, *8*, 109−113.

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Sadafian, A.; Crouzet, J. Aroma compounds retention during extrusion-cooking. *Dev. Food Sci.* **1988**, *17*, 623−637.

Stenhagen, E.; Abrahamsson, S. A.; McLafferty, F. W. *Registry of Mass Spectra Data*; Wiley: New York, 1974.

Ullrich, F.; Grosch, W. Identification of the most volatile flavour compounds formed during autoxidation of linoleic acid. *Z. Lebensm. Unters. Forsch.* **1987**, *184*, 277−282.

Ways, P.; Hanahan, D. J. Characterization and quantification of red cell lipids in normal man. *J. Lipid Res.* **1964**, *5*, 318−328.

Webster, F. H. Oat utilization: past, present, and future. In *Oats: Chemistry and Technology*; Webster, F. W., Ed.; American Association of Cereal Chemists: St. Paul, MN, 1986.

Williams, M. A.; Horn, R. E.; Rugala, R. P. Extrusion. An indepth look at a versatile process. *Food Eng.* **1977**, *11*, 57−62.