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ANALYSIS OF VOLATILE ALDEHYDES IN OAT FLAKES BY SPME-GC/MS

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A headspace solid-phase microextraction (HS-SPME) procedure followed by gas chromatography coupled with mass spectrometry (GC/MS) has been developed for the determination of volatiles formed during oxidation of polyunsaturated fatty acids in oat samples. Several SPME coatings were tested and DVB/CAR/PDMS (divinylbenzene/ carboxen/ polydimetylosiloxane) was chosen as the most appropriate for the analysis of these analytes. Experimental SPME parameters such as selection of coating, extraction temperature and time, addition of water and grinding were studied. The elaborated method enabled the qualitative and quantitative analyses of volatile aldehydes in fresh and aged samples. The concentration of total aldehydes, excluding hexanal, which was the predominant volatile carbonyl compound, ranged from 67±3 to 133±5 μg/kg in fresh and from 137±4 to 398±12 μg/kg in aged samples.

Hexanal content in fresh samples was up to 158 μg/kg, whereas in all aged samples exceeded 1 mg/kg.

INTRODUCTION

Low-molecular weight aldehydes, which have unpleasant odor, are usually present at low concentrations in various food products. In fat-containing foods, these compounds can be formed by enzymatic or nonenzymatic reactions, especially by oxidation of unsaturated fatty acids. Rancidity caused by lipid peroxidation has been recognized as a huge problem in storage of fats and fat-rich foods. Aldehydes formed during lipid peroxidation have been shown highly cytotoxic and genotoxic; some of them are able to generate stable products with various biomolecules including DNA, which can contribute to the pathogenesis of vascular diseases [Uchida, 2000]. Moreover, they can react with a number of compounds, such as proteins, nucleic acids, glutathione, cysteine, lysine and coenzyme A. These interactions influence the nutritive value as well as functionality of protein compounds; they can also lead to changes in colour and to the production of unpleasant odours and tastes [Kataoka *et al.*, 1995; Frankel, 1996; Pokorny & Davidek, 1979]. In view of those dangerous properties of aldehydes, the measurement of their presence and concentration in foods is very important.

Oats, which are perceived as a tasty cereal with a positive health image, represent a very complicated matrix where apart from protein, sugars and fats, there are volatile compounds present [Heinio, 2001, 2002]. Volatiles isolated by vacuum steam distillation were found to be a mixture of 3-methyl-1-butanol, 1-pentanol, 1-hexanol, hexanal, 1-octen-3-ol, 3,5-octadienone and nonanal. In addition, other volatile components were detected in raw oats, and the most notable from a flavor standpoint included 3-methylbutanal, 2,4-decadienal and benzaldehyde which engender weed-hay and grass-like flavour [Haydanek & McGorrin, 1986]. Oat flavour is mainly formed during processing: volatiles appear after the rolling and flaking stages, and are a complex mixture of precursor- and heat-dependent compounds [Sides *et al.*, 2001; Heinio *et al.*, 2001]. However, oat flakes aroma differs from that of raw oat flavour, and miscellaneous volatile compounds combined give them a typical nutty scent. Among dominant flavours identified in oat flakes there were floral, grassy, boiled oats (oatmeal), roasted nuts, camphor and dried fruits flavour [Kamiński *et al.*, 1973].

The fat content of oats is the highest of all cereals and the fatty acid composition is considered to be favorable and therefore has health promoting properties. However, the use of oats is limited due to a tendency to go rancid and the formation of bitter off-flavours [Heinio *et al.*, 2001]. The development of rancidity, which is considered to be the most important off--flavour of oats, is generally considered to be a consequence of the deteriorative reactions of lipids and caused either by volatile compounds such as aldehydes, ketones and alcohols or by high amounts of free fatty acids or phenolic compounds [Heinio *et al.*, 2001; Moltenberg *et al.*, 1996; Sjovall *et al.*, 1997; Zhou *et al.*, 1999]. One of the reactions which take place during storage of oats is the deterioration of polyunsaturated fatty acids which are converted to hydroperoxide and further to secondary oxidation products [Heinio *et al.*, 2001]. Hexanal is one of the most abundant volatile compounds in oats; it is continuously formed from degradation of oleic and linoleic acid. Moreover, hexanal accumulates only partly in the product because it may evaporate or be converted into nonvolatile compounds [Heinio *et al.*, 2002].

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One of the most popular methods for flavour isolation from different foodstuff has been headspace sampling [Zhou *et al.*, 1999]. Static headspace has been used to recover volatiles from extruded flaked oatmeal by Guth & Grosch [1994] and lipid oxidation products from raw and heat-treated oat flours by Moltenberg *et al.* [1996]. Extruded oat samples were also analysed using dynamic headspace by Parker *et al.* [2000]. Recently, solid phase microextraction (SPME) has been an alternative for the dynamic headspace analysis. The SPME method has a wide range of applications in analysis of various components and contaminants in food samples which have been reviewed by Kataoka *et al.* [2000] and Wardencki *et al.* [2004]. Microextraction has also been used as a tool for the extraction of volatiles from different grains, such as rice [Grimm *et al.*, 2002; Wongpornchai *et al.*, 2004], soybean [Boue *et al.*, 2003], wheat [Jeleń *et al.*, 2003] and distilled grains [Biswas & Staff, 2001]. However, this technique has had a limited application to oat products. Zhou *et al.* [2000] employed a headspace SPME (HS-SPME) method with a polydimethylosiloxane non-bonded fiber for the determination of flavour volatiles from oatmeal. The application of SPME as extraction technique allowed determination of alkanes, alcohols, acids and aldehydes in oatmeal processed from groats. Sides *et al.* [2001] adopted the SPME technique with divinylbenzen/ carboxen/ polydimethylsiloxane fiber to isolate volatiles from oats during processing (raw oats, groats, kiln dried dehulled and rolled-flaked oats). These authors reported that volatile components identified in headspace of oats were mainly aldehydes and alcohols.

In the present work, investigations addressed the application of HS-SPME for sampling volatile aldehydes generated during the oxidation of polyunsaturated fatty acids in oat breakfast cereals.

MATERIALS AND METHODS

Chemicals. The following standards of carbonyl compounds were used for method development: butanal (99%, Aldrich), *E-2*-butenal (98%, Aldrich), pentanal (96%, Fluka), *E-2*-pentenal (95%, Fluka), hexanal (97%, Fluka), *E-2*-hexenal (97%, Fluka), heptanal (95%, Aldrich), *E-2*--heptenal (98%, Fluka), octanal (99%, Aldrich), *E-2*-octenal (94%, Aldrich), nonanal (95%, Fluka), *E-2*-nonenal (97%, Aldrich), decanal (95%, Fluka), *E-2*-decenal (97%, Fluka). A stock solution of standards was prepared in freshly refined rapeseed oil by weighing approximately 100 mg of analyte into 100 mL volumetric flask for further addition to oat samples.

Oat flakes samples. Four different types of oat flakes, purchased in a local store, were used for method evaluation. All samples used for the aldehyde analysis were stored at 60°C for 14 days. Control samples were kept refrigerated.

SPME fiber. For headspace SPME, 65 μm polydimethylosiloxane/ divinylbenzene (PDMS/DVB), 50 μm divinylbenzene/ carboxen/ polydimethylosiloxane (DVB-CAR-PDMS), 75 μm carboxen/ polydimethylosiloxane (CAR/PDMS), 65 μm carbowax/divinylbenzene (CW-DVB) fiber coatings were evaluated to determine aldehydes in oat flakes samples. The SPME fibers were purchased from Supelco (Bellefonte, PA). Before the analysis, all fibers were conditioned in order to remove contaminants and to stabilize the solid-phase.

GC conditions. Aldehydes were analysed using a Hewlett-Packard HP 5890II gas chromatograph coupled to a quadrupole mass detector HP 5971 (Hewlett Packard, Palo Alto, CA) and fitted with a DB-5 capillary column (25 m × 0.2 mm × 0.25 μm). Helium was the carrier gas at a flow rate of 0.6 mL/min. The front inlet temperature was 260°C and transfer line was set to 280°C. The oven temperature program used was 40°C for 1 min, followed by an increase of 4°C/min to 160°C and 10°C/min to 280°C. Injection port was set to a splitless mode.

RESULTS AND DISCUSSION

Optimization of extraction procedure

In order to develop a headspace-SPME-GC/MS method for the analysis of aldehydes in oat flakes, different experimental parameters were optimized such as SPME coating, extraction temperature and time, effect of granulation and addition of water to increase extraction efficiency. All analyses were repeated four times.

SPME coating selection – extraction efficiency

The SPME process is based on the partitioning of analytes between the phase coating, the sample and headspace above it. The microextraction is complete when the analyte concentration reaches distribution equilibrium between these three phases. Therefore, the choice of the best coating is an essential part of the optimization process and depends on the chemical nature of the target analytes.

Four fused-silica fiber coatings were evaluated in the selection of the most appropriate coating for this method. Oat flakes samples were analysed four times with each fiber. The extraction time was 20 min at 50°C and desorption time was 5 min at 260°C. The extraction efficiency of the SPME fibers was evaluated by plotting the TIC areas obtained for the hexanal peak with the different fibers. Hexanal was chosen because it is the most abundant and easily detectable secondary lipid oxidation product, and it can also serve as a marker of lipid oxidation [Ekstrand *et al.*, 1993; Lehtinen,

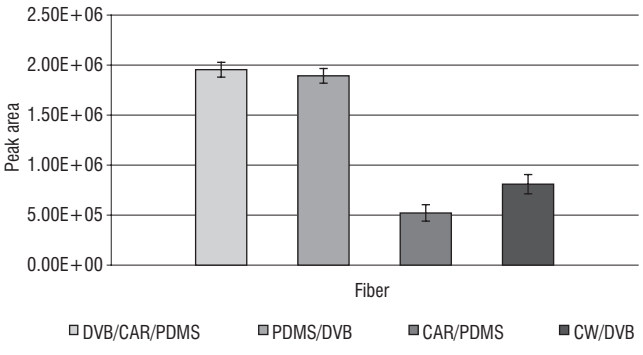

FIGURE 1. Plot of extraction efficiency (detector response area of hexanal) using different SPME fibers.

2003]. DVB/CAR/PDMS was selected among different coatings as the most appropriate and giving the best reproducibility (Figure 1). The difference between DVB/CAR/PDMS and DVB/PDMS was statistically insignificant ($p<0.05$). Extraction efficiency on other coatings, such as CAR/PDMS and CW/DVB, was significantly lower ($p<0.05$) than that observed on the selected coating. Peak areas of extracted hexanal using the CAR/PDMS and CW/DVB fibers were 3.7 and 2.4 times lower, respectively. Sides *et al.* [2001] determined volatile compounds in oats at different stages of processing using the SPME method with a three-phase mixed fiber because of its great absolute adsorption, length and thickness.

Effect of temperature

Temperature is a parameter which affects sensitivity as well as extraction kinetics. It is an important variable to optimize, especially because an increase in extraction temperature translates to increased diffusion coefficients leading to a faster equilibrium time. Generally, the highest possible temperature should be used in the method evaluated. In headspace-mode extraction, higher temperature leads to an increase in analyte concentration in the headspace; furthermore, it helps to facilitate faster extraction [Pawliszyn, 1997; Keszler & Herberger, 1999]. It must be remembered, however, that the character of the matrix is always a factor to be considered in the choice of extraction temperature.

The effect of 20, 30 and 50°C temperatures with a constant extraction time of 20 min on the extraction efficiency was investigated. Figure 2 shows that an increase in temperature improved the extraction efficiency (increase in peak area of extracted hexanal). The highest detector response area was observed when the temperature was increased to 50°C. On the basis of these results, subsequent analyses were conducted at this temperature.

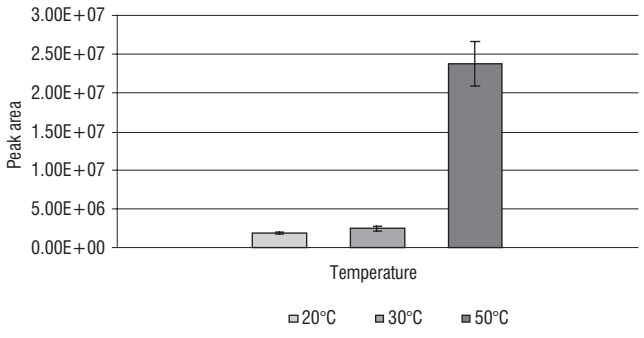

FIGURE 2. Effect of temperature on the extraction efficiency (detector response area of hexanal) DVB/CAR/PDMS fiber, 20 min.

Effect of time

The objective of SPME is to reach distribution equilibrium in the system. Equilibrium time is reached when the quantities of extracted analytes are constant. The time of exposure strongly influences the extraction efficiency and may affect detection limits.

The optimal extraction time was also tested. The DVB/CAR/PDMS fiber was held in samples for 1, 5, 10, 30, 60 and 90 min (Figure 3). Each determination was repeated four times. The rate of extraction was the highest during the first 60 min of this process, after which it decreased. The chromatographic analysis took just over 40 min. To reduce analysis time and to minimize lipid oxidation at elevated temperatures, an extraction time of 30 min was chosen for the quantitative analysis.

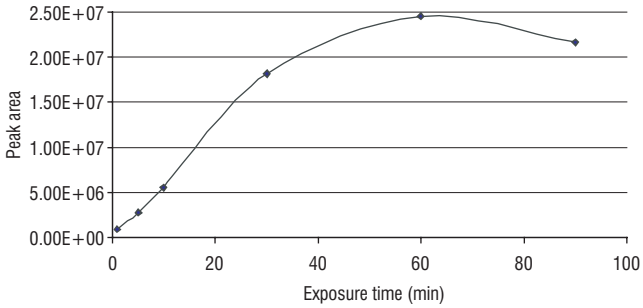

FIGURE 3. Adsorption profile (DVB/CAR/PDMS fiber) for hexanal by HS-SPME.

Effect of grinding and addition of water

Oat flakes samples were analysed both as whole flakes and as a milled powder product. They differed to a great extent. Better extraction efficiency of volatile lipid oxidation products was observed when whole flake samples were analysed. Lipid oxidation takes place mostly on the surface of the product. After milling, volatile components are probably bound up with the flour and extraction becomes more difficult.

With the addition of water to oat samples prior to the microextraction process, an increase in peak area of extracted compounds was obtained. As a consequence, the diffusion of carbonyl compounds into the headspace was favoured. The addition of 10, 20, 30, 40, 50 and 60% water was investigated. The biggest improvement in SPME efficiency was observed when 10% water was added to the sample. There was no statistically significant difference ($p<0.05$) between the addition of 10, 20 and 30% water. For subsequent analyses, the lower addition level was chosen. The addition from 40 to 60% reduced the extraction efficiency to a remarkable extent.

Calibration

For calibration purposes, detector response areas were used for calculation. Five-point calibration curves for five saturated and five unsaturated aldehydes were measured. The calibration range was 1–100 ppb. The correlation coefficient (R^2) values calculated for carbonyls varied from 0.960 for decanal to 0.995 for *E-2*-heptenal, which indicated the possibility of using this method in a wide range of concentrations. The values of coefficient of variation (CV) calculated below 15% show an acceptable repeatability of the elaborated method to identify volatile secondary oxidation product using SPME.

Oat flakes analysis

Volatile compounds extracted from oat flakes samples by means of HS-SMPE were identified with gas chromatog-

raphy coupled with mass spectrometry. Volatile compounds found in oat flakes are listed in Table 1 and chromatograms of fresh and stored sample are shown in Figure 4. Using SPME to analyse volatiles from commercial sample of oat

TABLE 1. Compounds tentatively identified in oat flakes samples. Extraction was performed for 30 min at 50°C with DVB/CAR/PDMS fiber.

Peak no	RT	Compounds	Control sample				Aged Sample			
			I	II	III	IV	I	II	III	IV
1	4.13	pentanal[b]					+	+	+	+
2	5.79	1-pentanol[b]			+				+	
3	6.75	hexanal[ab]	+	+	+	+	+	+	+	+
4	7.81	2-furancarboxaldehyde (furfural)					+	+	+	+
5	8.55	*E-2*-hexenal							+	
6	8.82	ethylbenzene	+	+	+	+				
7	9.06	1-hexanol[b]	+	+	+	+	+	+	+	+
8	9.81	2-heptanone[b]	+	+	+	+	+	+	+	+
9	10.29	heptanal[b]	+	+	+	+	+	+	+	+
10	11.55	α-pinene[b]	+	+	+	+				
11	12.30	benzeneacetaldehyde	+							
12	12.41	*E-2*-heptenal[b]					+	+	+	+
13	12.58	1-ethyl-3-methyl benzene	+	+	+	+				
14	12.67	benzaldehyde[a]	+	+	+	+	+	+	+	+
15	12.88	1-heptanol[b]					+	+		
16	13.49	2,3-octanedione[b]		+			+	+	+	+
17	13.71	2-pentyl furan[a]	+	+	+	+	+	+	+	+
18	14.23	octanal[ab]	+	+	+	+	+	+	+	+
19	14.50	3-carene	+	+	+	+				
20	15.11	1-methyl-3-(1methylethyl)benzene[a]	+	+	+	+				
21	15.31	D-limonene[b]	+	+	+	+		+		+
22	15.55	3-octen-2-one					+		+	
23	16.36	*E-2*-octenal[b]						+		
24	16.79	1-octanol					+	+	+	
25	17.59	2-nonanone						+		+
26	17.73	(*E,E*)-3,5-octadien-2-one[b]				+	+	+	+	+
27	17.99	Linalool	+	+	+	+	+	+	+	+
28	18.17	nonanal[b]	+	+	+	+	+	+	+	+
29	20.23	*E-2*-nonenal[b]							+	+
30	21.96	decanal[ab]			+	+		+	+	

[a] – compounds identified earlier in oat flakes using SPME by Sides *et al*. [2001]; [b] – compounds identified earlier in extruded oat flour using dynamic headspace by Parker *et al*. [2000]; + the presence of volatile compound in the headspace of oat flakes

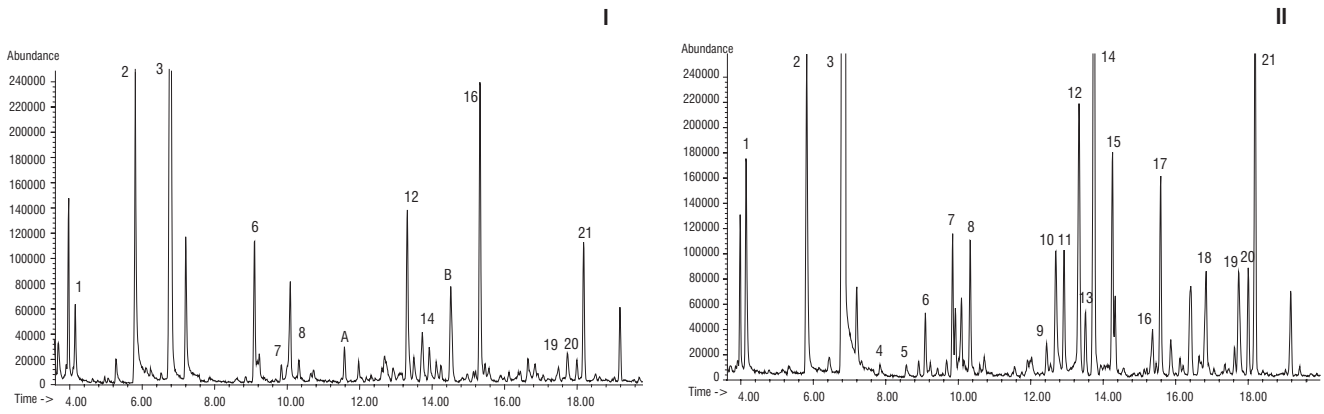

FIGURE 4. Total ion chromatograms corresponding to the headspace fraction of fresh (**I**) and stored at 60°C for 14 days (**II**) samples: (1) pentanal, (2) 1-pentanol, (3) hexanal, (4) furfural, (5) *E-2*-hexenal, (6) 1-hexanol, (7) 2-heptanone, (8) heptanal, (9) *E-2*-heptenal, (10) benzaldehyde, (11) 1-heptanol, (12) 1-octen-3-ol, (13) 2,3-octanedione, (14) 2-pentyl furan, (15) octanal, (16) D-limonen, (17) 3-octen-2-one, (18) 1-octanol, (19) E,E-3,5-octadien-2-one, (20) linalol, (21) nonanal, (A) α-pinen, (B) 3-carene.

flakes, 30 volatile compounds were detected. These compounds belonged to alkanals, 2-alkenals, alkanes, alcohols, ketones, terpenes, lipid-derived furans and one aromatic hydrocarbon. In the samples analysed, the presence of hexanal, heptanal, octanal, nonanal and decanal was observed. These carbonyl compounds are known to result from the oxidation of polyunsaturated fatty acids, which takes place in foods rich in fat. Sides *et al.* [2001] reported that hexanal, octanal, nonanal and decanal were identified in oat samples at four stages of processing using the HS-SPME method. In addition, Sjovall *et al.* [1997] described the headspace analysis of extruded oat products containing saturated aldehydes with 6 to 9 carbons. Zhou *et al.* [2000] used the PDMS fiber for SPME analysis of volatiles from cooked oatmeal. Of all the volatiles adsorbed to the fiber, hexanal, octanal, nonanal and decanal were detected. The SPME method was also used by Boue *et al.* [2003] to recover 49 volatile compounds in soybean, including carbonyl compounds such as aldehydes.

Among carbonyl compounds found in the headspace, 2-heptanone was identified, which is formed from octanoic acid. It should be pointed out, that 2-heptanone is partially responsible for typical flavour of some mould-ripened cheese. Moreover, this compound along with short chain fatty acids and lactones are important flavour constituents of butter aroma [Kochhar, 1993]. In addition, one of the aromatic aldehydes – benzaldehyde – was observed in both control and aged samples.

Besides carbonyl compounds, α-pinene, limonene and 2-pentyl furan were identified, but only one of these can results from lipid deterioration. 2-Pentyl furan has been detected in soybean oil and found to contribute to its flavour reversion [Min & Boff, 2003]. Lehtinen [2003] described the mechanism of 2-pentyl furan formation in oats from linoleic acid during photo-oxidation; which also represents a major product from the cleavage of 9-hydroperoxide linoleic acid. An HS analysis of extruded oat products and oats at different stages of processing as well by HS-SPME as HS-GC indicated the presence of 2-pentyl furan. Moltenberg *et al.* [1996] reported that besides hexanal the major volatile component found in stored flours was 2-pentyl furan, whose concentration varied during storage. In addition, Sides *et al.* [2001] identified limonen in raw and kiln-dried dehulled oats.

Oat groats have the highest lipid concentration of the common cereal grains; their composition is similar to other cereals, being highly unsaturated and containing considerable amounts of linoleic acid [Becker, 1992]. Haydanek and McGorrin [1981a,b] studied the inherent flavour constituents in oats before processing and those of oxidatively rancid oat groats. These authors used vacuum distillation methods and Tenax headspace trapping for extraction; they identified 45 compounds including 24 aldehydes in rancid groats, and reported the presence of pentanal, hexanal, furfural, heptanal, benzaldehyde and nonanal in the total volatile fraction of oat groats. However, according to Sides *et al.* [2001], the concentration of volatiles in oats during processing can change and lower concentrations can be recognized in the final product.

The results of quantification of dominant aldehydes in oat flakes are shown in Table 2. Four different kinds of oat flakes were analysed using HS-SPME method and there were four replicates performed on each sample. The aim of these analyses was to determine secondary oxidation products. In all analysed samples, the most abundant carbonyl compound was hexanal, its concentration varied from 64±6 μg/kg to 158±15 μg/kg in control samples while in the aged ones it exceeded the range of the calibration curve (Table 2). Hexanal was also described as the predominant volatile in raw oats and its content increased to the highest extent during heating or storage of flours [Moltenberg *et al.*, 1996]. Haydanek & McGorrin [1981a,b] reported that even though hexanal was present in oat samples, the product exhibited an acceptable flavour character for consumers. However, Shin *et al.* [1986] evaluated the off-flavors of stored brown rice and reported that the amount of hexanal was linearly proportional to oxidized linoleic acid, which proves that hexanal arises from oxidative degradation of linoleic acid. The contents of other carbonyls determined in control samples were under the level of 25 μg/kg except for nonanal, whose content was estimated to range from 35±3 μg/kg to 48±7 μg/kg. During the storage of oat flakes at the elevated temperature for 14 days, additional compounds originating from polyunsaturated fatty acids appeared in the headspace. There were mainly unsaturated aldehydes and one unsaturated ketone – 2-nonanone. The quantity of the other carbonyls increased in samples stored at 60°C against the control. The amount of saturated aldehydes rose over 28±1 μg/kg for octanal and 185±14 μg/kg for nonanal. The content of unsaturated aldehydes varied from 3.2±0.2 μg/kg for *E-2*-heptenal and 13±1 μg/kg for *E-2*-nonenal. The total content of all volatile aldehydes was estimated at

TABLE 2. Concentration of secondary volatile oxidation products (aldehydes) in control and aged samples (μg/kg).

Volatile aldehyde	Concentration (μg/kg)								Odor thresholds in oil μgkg^{-1}
	I		II		III		IV		
	control	aged	control	aged	control	aged	control	aged	
Hexanal	101±7	1533.42a±120.88	64±6	1173.62a±121.68	158±15	3356.28a±235.31	86±2	1190.86±65.69	240
E-2-hexenal	nd	nd	nd	nd	nd	10.9±0.1	nd	nd	10000
Heptanal	16±1	51±3	16±2	39±4	24±1	66±1	14±2	41±2	3200
E-2-heptenal	nd	4.9±0.4	nd	3.2±0.2	nd	9±1	nd	3.3±0.1	14000
Octanal	17±1	56±5	15±1	31 ±2	18±1	93±6	17 ±1	28±1	320
E-2-octenal	nd	nd	nd	10±1	nd	nd	nd	nd	7000
Nonanal	35±3	79±6	42±4	58 ±4	78 ±5	185±14	48±7	56±1	13500
E-2-nonenal	nd	nd	nd	nd	nd	13±1	nd	9±1	900
Decanal	nd	nd	nd	nd	nd	nd	3.7±0.4	nd	6700

nd – not detected; a – above the calibration range

the level of 67±3 to 133±5 μg/kg and 137±4 to 398±12 μg/kg (excluding hexanal) in control and aged samples, respectively. Parker *et al.* [2000] used dynamic headspace to identify 120 volatile compounds in the headspace of extruded oat samples, including 6 saturated and 15 unsaturated aldehydes. The contents of all carbonyl compounds were estimated at the ng level from 10 g of sample. The total content of saturated volatiles in the headspace from 10 g of samples varied from 633 to 5442 ng, and that of the unsaturated ones from 23 to 844 ng (depending on the extraction conditions).

CONCLUSIONS

The research demonstrated that the determination of secondary oxidation products, such as aldehydes, by HS-SPME provided good precision and sensitivity with simple and fast procedures. Of the 30 compounds observed, several specific secondary oxidation products could be identified, mainly aldehydes, ketones and lipid-derived compounds such as 2-pentyl furan. The content of secondary oxidation products increased remarkably during storage at elevated temperature. Hexanal, which was the most abundant volatile in the samples analysed, is commonly used as an indicator of lipid oxidation in cereals [Ekstrand *et al.*, 1993; Piggott *et al.*, 1991, Shin *et al.*, 1986]. The reported results indicate that hexanal as well as other volatile aldehydes can be useful in predicting oxidation changes during the storage of oat flakes.

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OZNACZANIE LOTNYCH ALDEHYDÓW W PŁATKACH OWSIANYCH METODĄ SPME-GC/MS

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W pracy podjęto próbę opracowania parametrów metody do oznaczania związków lotnych powstających w czasie utleniania wielonienasyconych kwasów tłuszczowych. Do izolacji związków lotnych zastosowano technikę mikroekstrakcji do fazy stacjonarnej (HS-SPME). Identyfikacji lotnych związków dokonano metodami chromatografii gazowej połączonej ze spektrometrią masową. Zbadano przydatność dostępnych włókien SPME, spośród których do badań wybrano włókno pokryte fazą DVB/CAR/PDMS. Opracowanie optymalnych parametrów SPME poza doborem włókna obejmowało także temperaturę i czas ekstrakcji, dodatek wody i rozdrobnienie produktu. Opracowana metoda umożliwiła jakościową i ilościową analizę lotnych aldehydów w świeżych jak i przechowywanych płatkach. Całkowita zawartość aldehydów, wyłączając heksanal, który był dominujacym związkiem karbonylowym, wahała się od 67±3 do 133±5 μg/kg w próbach świeżych oraz od 137±4 do 398±12 μg/kg w próbach przechowywanych (tab. 2).

Zawartość heksanalu w próbkach świeżych wynosiła do 158 μg/kg, natomiast w próbkach przechowywanych przekraczała dla wszystkich próbek 1 mg/kg.