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Influence of the Addition of Raspberry Seed Extract on Changes in the Volatile Pattern of Stored Model Breakfast Cereal

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Laboratory-prepared muesli-type breakfast cereal (mixture of oat flakes, wheat flakes, corn flakes, hazelnuts, raisins, sunflower seeds, and flax seeds) was subjected to accelerated storage test at 60 °C with or without the addition of red raspberry seed extract. The oxidative changes in muesli resulting in the formation of secondary oxidation products were evaluated using solid phase microextraction (HS-SPME) and solvent-assisted flavor evaporation (SAFE) to isolate volatiles and GC-MS and chromatography−olfactometry to quantify them and determine the key odorants. During 14 days of storage the total amount of volatile compounds changed from 1.0 mg/kg, in freshly prepared muesli, to 32 mg/kg after storage. The predominant compound was hexanal; its content during storage increased 20-fold, reaching 17 mg/kg. Red raspberry seed extract addition limited the rate of lipid oxidation, and the total amount of volatiles was estimated at 11 mg/kg and that of hexanal at almost 5 mg/kg. An elevated temperature of the storage test also influenced the crucial flavor compounds determined using aroma extract dilution analysis (AEDA). The flavor dilution factor (FD) values for volatile lipid oxidation products were lower in samples with red raspberry seed extract added.

KEYWORDS: Muesli; natural antioxidants; lipid oxidation; SPME; SAFE

INTRODUCTION

Breakfast cereals and muesli-type products are considered to have health-promoting properties, especially because of their favorable nutrient composition. All of the main ingredients of these products are perceived as important elements of a healthy diet. Oat flakes, which comprise the basic fraction of muesli and are the source of water-soluble fiber, have been shown to help lower high blood cholesterol concentration and thereby reduce the risk of arteriosclerosis (*1, 2*), whereas fruits have been shown to significantly reduce the risk of cancer and other age-related diseases (*3*−*5*). Also, products such as nuts are rich in omega-3 fatty acids, which are associated with many health benefits, including the development of the nervous system (*6*). However, the higher lipid content in muesli and the composition of fatty acids make these products very susceptible to lipid oxidation (*7*). Lipid autoxidation leads to the formation of hydroperoxides, which decompose to secondary oxidation products, such as aldehydes, ketones, alcohols, and furans. These compounds are associated with changes in the odor and flavor (*8*). The unsaturated aldehydes, which have very low odor thresholds, are usually considered as a primary source of oxidized off-flavors (*9*). *E*-2-Nonenal was considered to be responsible for cardboard-like off-flavor in porcine liver (*10*), whereas in wines aged in green oak it has been identified as the cause of a sawdust-like off-odor (*11*). Furthermore, such compounds as hexanal, 2,4-heptadienals, and 2,4-decadienals contribute to painty flavors of oxidized fish oils (*12*).

There is a consumer demand for the use of "natural" antioxidants, especially in products such as muesli that are perceived by many as "healthy food". The increasing attention on natural antioxidants is caused by the concern over the safety of synthetic ones (*13*). Natural antioxidants have been shown to function as singlet and triplet oxygen quenchers, free radical scavengers, peroxide decomposers, enzyme inhibitors, and synergists (*14*). Additionally, many of the natural antioxidants, especially flavonoids, exhibit a wide range of biological effects, including antibacterial, antiviral, anti-inflammatory, antiallergic, antithrombotic, and vasodilatory actions (*15*). The phytochemicals in plant tissues responsible for the antioxidant capacity can largely be attributed to the phenolics, anthocyanins, and other flavonoid compounds (*16*). The antioxidant properties of red raspberry are associated with the high content of anthocyanins, flavonoids, ellagic acid, and vitamin C (*17*). Pachołek and Małecka (*18*) noticed the high antioxidant activity of ethanolic extracts from defatted black currant and red raspberry seeds. Compounds responsible for antioxidant activity of raspberries were recognized as ellagitannins, and those compounds, as opposed to berry proanthocyanidins and anthocyanins, for which the antioxidant effect was dose-dependent, appeared to be equally active at all analyzed concentration. The stabilizing effect of ethanolic extracts of red raspberry seeds depends on

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concentration, and its protective effectiveness is only slightly less than that of BHA (*19*).

The aim of this research was to investigate the influence of natural antioxidants from red raspberry seeds on volatile compounds characteristic for lipid oxidation process undergoing during muesli-type breakfast cereal storage at elevated temperature. Solid phase microextraction (SPME) was applied for a rapid evaluation of the main volatile compounds formed during oxidative changes, whereas solvent-assisted flavor evaporation (SAFE) followed by gas chromatography−olfactometry (GC-O) was used to monitor the influence of raspberry extract addition on the key odorants in stored model muesli.

MATERIALS AND METHODS

Chemicals. The following compounds were used as standards for GC-MS and GC-O analyses: butanal, pentanal, 1-pentanol, hexanal, *E*-2-hexenal, *E*-2-decenal, 1-hexanol, 2-heptanone, heptanal, *E*-2-heptenal, benzaldehyde, 1-heptanol, 1-octen-3-ol, 2-pentyl furan, octanal, 1-octanol, nonanal, *E*-2-nonenal, 2,4-nonadienal, decanal, 2-methyl-3-furanthiol, dimethyl trisulfide, 2-ethyl-3,5-dimethylpyrazine, phenylacetaldehyde, and methional were obtained from Sigma-Aldrich-Fluka (Poznań, Poland). Labeled pyrazine-d_4 (Fluka) was used as an internal standard for quantitative purposes. Red raspberry seed extract was obtained from Prof. M. Małecka (Poznan University of Economics). The defatted raspberry seeds were extracted three times using 80% ethyl alcohol at a temperature of 80 °C. Solvent was evaporated under reduced pressure at a temperature of 45 °C, and the dry mass was disolved in 96% ethyl alcohol (*20*). Phenolic compound content using caffeic acid as a calibration standard was estimated at the level of 2370 mg/100 g of dry matter. 2-Acetyl-1-pyrroline was obtained as a kind gift from Prof. Dr. P. Schieberle.

Muesli Samples. Muesli-type breakfast cereal containing oat flakes (30% w/w), wheat flakes (30% w/w), corn flakes (10% w/w), hazelnuts (10% w/w), raisins (10% w/w), sunflower seeds (5% w/w), and flax seeds (5% w/w) was prepared in the laboratory. Prepared muesli was a mixture of given compounds without any technological treatment. Analyzed samples included (I) freshly prepared muesli (control sample), (II) muesli subjected to accelerated oxidation test (sample stored for 14 days at 60 °C in a glass vessel in darkness), and (III) muesli with the addition of 0.3% red raspberry seed extract subjected to accelerated oxidation test as sample in II.

Muesli Volatile Compounds Analysis. *SPME Analysis.* Volatile compounds for quantitative purposes were isolated by HS-SPME and analyzed using Hewlett-Packard HP 5890 II coupled to a quadrupole mass detector HP 5971 MSD (Hewlett-Packard, Palo Alto, CA) fitted with a DB-5MS capillary column (25 m × 0.2 mm × 0.33 μm). Helium was used as carrier gas at a flow rate of 0.6 mL/min. The inlet temperature was 260 °C, and the transfer line was set to 280 °C. The oven temperature was 40 °C for 1 min, followed by an increase of 4 °C/min to 160 °C and an increase of 10 °C/min to 280 °C. The injection port was set to a splitless mode (1 min). Mass spectra were recorded in an electron impact mode (70 eV) in a scan range of 33−333. The quantification was done using selected ion for each compound: pyrazine-d_4, 84; butanal, 72; pentanal, 58; 1-pentanol, 55; hexanal, 82; 1-hexanol, 56; 2-heptanone, 58; heptanal, 70; *E*-2-heptenal, 83; benzaldehyde, 105; 1-heptanol, 70; 1-octen-3-ol, 77; 2-pentylfuran, 81; octanal, 84; *E*-2-octenal, 93; 1-octanol, 97; 2-nonanone, 58; nonanal, 98. The procedure for volatiles isolation was based on our previous experience (*21*). A three-phase fiber (DVB/CAR/PDMS) was used in all analyses. Muesli samples (5 g) were placed in glass vials (20 mL). The headspace sampling was performed for 30 min at 50 °C; water (10%) was added to the vial followed by vortexing the sample. All analyses were repeated at least three times. Due to unavailability of labeled standards for aldehydes and ketones, which were the most abundant volatiles in muesli samples, pyrazine-d_4 was used as an internal standard. All samples were spiked with pyrazine-d_4 methanolic solution providing a concentration of 2 μg/g of sample. The MS response factors were determined for all standards mentioned at two different concentrations (50 and 500 ppb) and averaged.

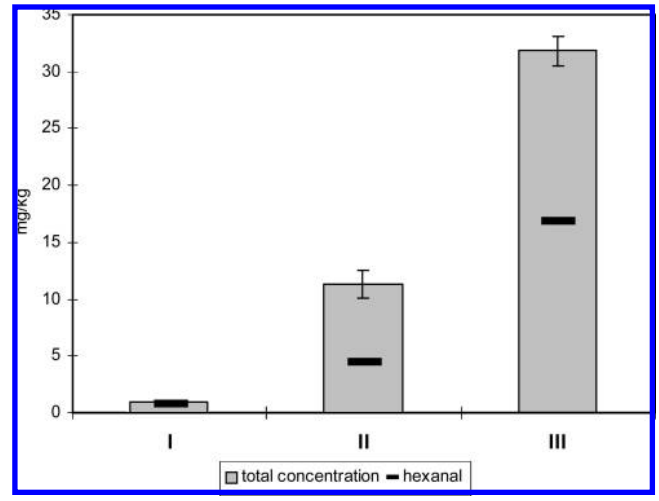

Figure 1. Total concentration of volatile compounds and hexanal contents detected in muesli stored at different conditions: (I) control sample; (II) stored sample + 0.3% red raspberry seeds extract; (III) stored sample without raspberry seeds extract addition.

Table 1. Compounds Detected in Muesli Samples by HS-SPME-GC/MS: (I) Control Sample; (II) Stored Sample + 0.3% Red Raspberry Seed Extract; (III) Stored Sample without Raspberry Seed Extract Addition

		concentration (μg/kg)		
compound	RI	I	II	III
butanal	<600	32 ± 3	−[a]	70 ± 5
pentanal	702	−	158 ± 25	794 ± 25
1-pentanol	774	55 ± 5	665 ± 35	1277 ± 24
hexanal	801	802 ± 82	4476 ± 479	16894 ± 362
1-hexanol	874	58 ± 6	2199 ± 283	2504 ± 232
2-heptanone	890	−	291 ± 32	688 ± 55
heptanal	898	−	605 ± 53	2106 ± 116
E-2-heptenal	959	−	−	60 ± 6
benzaldehyde	967	−	104 ± 8	145 ± 8
heptanol	973	−	688 ± 24	1486 ± 165
1-octen-3-ol	984	−	91 ± 11	170 ± 9
2-pentyl furan	987	33 ± 3	588 ± 90	1060 ± 132
octanal	999	−	774 ± 125	2730 ± 228
E-2-octenal	1068	−	40 ± 4	77 ± 6
1-octanol	1083	−	374 ± 48	983 ± 91
2-nonanone	1102	−	37 ± 3	160 ± 15
nonanal	1115	9 ± 0.2	190 ± 26	620 ± 66

[a] −, not detected in analyzed sample; identification of all compounds was done by comparing their mass spectrum and RI with those of standard compound.

GC-O. Muesli portions of 20 g were ground to a powder and mixed with 150 mL of water. Volatile components were isolated by high-vacuum distillation using the SAFE technique (*22, 23*). Volatiles were distilled at 40 °C under reduced pressure obtained using an Edwards RV5 rotary vane pump. The volatile fraction was collected in a liquid nitrogen cooled flask and then extracted five times with 10 mL of pentane/ether (1:1 v/v) mixture. The organic fraction was pooled and concentrated to 250 μL under a delicate stream of nitrogen. The obtained extracts were analyzed on an HP 5890 chromatograph with an SPB-5 (30 m × 0.53 mm × 1.5 μm) column, and confirmatory analyses were run on a Supelcowax-10 (30 m × 0.25 mm × 0.25 μm) column. The effluent was split, using a Y-type splitter, evenly between a sniffing port and a flame ionization detector (FID). Retention indices were calculated by linear interpolation from the retention times of C_6−C_{16} *n*-alkanes.

Aroma Extract Dilution Analysis (AEDA). To determine the dilution factor (FD) of each of the odorants, AEDA was applied (*24*). The flavor extract (2 μL) was injected into a GC column, and odor-active regions were detected by sniffing the GC effluent (GC-O). Three panelists determined the description of the volatiles. Extracts were diluted stepwise with pentane/ether (1:1 v/v), and each dilution was analyzed

Table 2. Key Odorants Identified in Muesli Samples after Isolation Using SAFE: (I) Control Sample; (II) Stored Sample + 0.3% Red Raspberry Seed Extract; (III) Stored Sample without Raspberry Seed Extract Addition

compound	odor description[a]	RI[b]		FD[c]		
		SPB-5	Supelcowax-10	I	II	III
2,3-butanedione[e]	buttery	594		8	16	4
3-methylbutanal[f]	malty	658		16	64	64
hexanal[d]	grassy/green	796	1092	16	64	256
unknown	garlic	820			8	32
2-methyl-3-furanthiol[e]	cooked oatmeal/roast	868	1289	32	1024	1024
unknown	paint	888	1217			32
2-heptanone[d]	musty	892	1208	2	64	128
heptanal[d]	rancid	895	1211	16	128	128
methional[d]	cooked potatoes	901	1409	8	32	128
2-acetyl-1-pyroline[e]	popcorn	920	1291	4		
dimethyl trisulfide[d]	cabbage	966	1319	4	16	64
1-octen-3-ol[d]	mushroom	975	1365	8	32	256
octanal[e]	citrus	994	1251	8	128	512
phenylacetaldehyde[d]	flowery	1055	1584	4	4	4
2-ethyl-3,5-dimethylpyrazine[d]	earthy	1111	1385	16	256	1024
2-methyl-3,5-diethylpyrazine[f]	parsley root	1159	1466	8	32	128
E-2-nonenal[e]	cardboard	1171	1493	2	16	128
2,4-nonadienal[e]	fried oil	1227	1660		32	64

[a] Odor description at sniffing port. [b] Retention index. [c] Flavor dilution factor determined on DB-5 type column (SPB-5). [d] Compound identified by comparing its mass spectrum, RI, and odor descriptors with a standard compound. [e] Compound identified by comparing its RI and odor description with a standard compound. [f] Compound identified by comparing its RI and odor notes with data in the literature: tentative identification.

until no odor was perceivable at the sniffing port. Analyses were repeated in three independent sessions.

Fatty Acid Composition. The analysis of fatty acid methyl esters (FAMEs) was done by gas chromatography according to the method described by Wąsowicz (*25*). Identification of separated FAMEs was performed by comparison of the retention data of analyzed samples with those obtained for standard solution. FAMEs were analyzed using a Hewlett-Packard HP 5890 gas chromatograph equipped with an FID and fitted with a Supelcowax-10 column (30 m × 0.25 mm × 0.25 μm). The relative amounts of fatty acids were determined on the basis of an internal normalization method as a percentage of total peak area.

RESULTS AND DISCUSSION

Muesli Volatiles Analysis by HS-SPME-GC-MS. The analysis of volatiles profile and volatiles concentration of muesli-type product revealed considerable changes as a result of adverse storage conditions. The total concentration of volatile compounds isolated using SPME in muesli is shown in **Figure 1**. The lowest concentration of volatile compounds, 989 ± 89 μg/kg, was observed in the control sample, after 14 days of storage at an elevated temperature of 60 °C, the total concentration having risen over 32 times from 32 ± 1 mg/kg. The gross increase in volatile compounds was due mainly to the formation of volatiles from fatty acid precursors. The most abundant fatty acids in analyzed muesli samples were oleic and linoleic acids (57 and 26%, respectively). In addition, a small amount of linolenic acid (2.5%) contributed to the autoxidation process. Red raspberry seed extract addition used in the experiment retarded the autoxidation process in analyzed samples. Although the concentration of secondary oxidation product was relatively high (11 ± 1 mg/kg), it was significantly lower ($p < 0.05$) than in samples stored without raspberry seed extract addition. It can be concluded that red raspberry seed extract hinders the autoxidation processes of fatty acids in muesli. Its positive effect on the degradation of β-carotene was shown before by Pachołek and Małecka (*18*).

The predominant aldehyde identified in stored as well as control samples was hexanal, a product of oleic acid autoxidation. The hexanal content has already proven to be a good indicator of lipid oxidation in muesli, especially when storage conditions included high oxygen availability combined with light exposure (*7*). The amount of hexanal detected increased significantly, from 802 ± 82 μg/kg in the control sample to 16.9 ± 0.4 mg/kg in the sample after storage, comprising 81 and 53% of the total volatile concentration, respectively. Hexanal content in samples stored with raspberry antioxidant addition was almost 4 times lower than in samples stored without antioxidants (4.5 mg/kg). Viljanen et al. (*19*) showed that, in general, most berry phenolics inhibited the formation of hexanal efficiently; however, only raspberry phenolics did not exhibit a pro-oxidant activity.

Table 1 shows the concentration of volatile compounds detected in the headspace of muesli prepared for these experiments. The detected compounds were mainly aldehydes and alcohols; however, some ketones and one furan were identified. The concentration of 2-pentylfuran was estimated at levels of 33 μg/kg in the control sample and >1 mg/kg in the stored sample. 2-Pentylfuran is also commonly detected in oat products (*26, 27*). Additionally, 2-heptanone and 2-nonanone were detected; they were not present in the control sample, but elevated temperature caused their formation. Furthermore, elevated temperature also provoked the formation of unsaturated aldehydes such as *E*-2-heptenal, detected in the stored sample at the level of 60 μg/kg, and *E*-2-octenal, detected at 77 μg/kg. Red raspberry seed extract added to muesli samples before storage partly limited the autoxidation process, and the concentration of volatile compounds derived from the decomposition of fatty acids was much lower. The effectiveness of red raspberry extract can be related to ellagitannins, which were found to be among the most efficient antioxidants, especially toward the formation of carbonyl compounds and conjugated diene hydroperoxides (*18*).

GC-O. To evaluate the influence of particular compounds on the flavor of, especially, stored oxidized muesli, GC-O analysis was performed. In the analyzed extract from the control sample 15 odor-active compounds were identified showing dilution factor FD in the range of 2−32. In extracts from samples stored at 60 °C during 14 days with the addition of natural antioxidants 16 odor-active compounds were identified, whereas in extracts from stored sample 17 odor-active compounds were identified. Odor-active compounds of muesli

samples are listed in **Table 2**. The compound with the highest FD factor (32 in the control sample and 1024 in both stored samples) had a cooked oatmeal/roast flavor. On the basis of its retention index and odor description compared with a standard it was identified as 2-methyl-3-furanthiol. This polyfunctional thiol has an extremely low odor threshold and therefore can be a key aroma compound even at extremely low concentration (*28*). 2-Methyl-3-furanthiol originates from a thermal degradation of thiamin (*29*), which is one of the main vitamins in cereal products. Therefore, it is highly probable that the high temperature involved in the processing of muesli components, especially oat flakes and corn flakes, and an elevated temperature during storage influence the formation of this thiol in muesli samples. Oat flakes and hazelnuts, compared to other muesli components, are rich sources of thiamin, and its concentration could rise to almost 500 and 300 μg/100 g, respectively (*30*).

The positive effect of red raspberry seed extract was also recognized during GC-O analyses, because FD factors were significantly lower for all secondary oxidation products. Among odor-active compounds, products of fatty acid oxidation prevailed in stored samples. Octanal with its oxidized and slightly citrus flavor was characterized by the highest FD value (512). However, hexanal (FD 256), 1-octen-3-ol (FD 256), 2-heptanone (FD 128), and *E*-2-nonenal (FD 128) were also recognized as responsible for the characteristic aroma of stored muesli. In isolates obtained from sample stored at elevated temperature an unknown compound (FD 32) with paint flavor was detected. Such an intense paint flavor was detected earlier by Moltenberg et al. (*27*) in heat-treated oat flours after 42 weeks of storage.

Besides the secondary oxidation product, among the odor-active fraction were also such compounds as 3-methylbutanal with a malty flavor, methional with a cooked potato flavor, dimethyl trisulfide with a cabbage flavor, 2-ethyl-3,5-dimethylpyrazine with an earthy flavor, and 2-methyl-3,5-diethylpyrazine with a parsley root flavor. Dilution factors of those compounds were generally higher for isolates of stored sample than for samples stored with red raspberry seed extract addition. The decrease of FD factors of Maillard-type aroma compounds could be the effect of phytochemical addition. Totlani and Peterson (*31*) reported that the addition of epicatechin significantly reduced the quantity of aroma compounds generated in Maillard reactions; their results imply that epicatechin quenched 3-deoxy-2-hexosulose and therefore inhibited Maillard product formation.

By comparison of the identified compounds listed in **Tables 1** and **2** it becomes evident that for the characterization of flavor compounds in a product one isolation method can provide incomplete results. Only five compounds (hexanal, heptanal, octanal, 1-octen-3-ol, and 2-heptanone) were detected using both methods. Solid matrix is especially challenging for SPME extraction, and although some compounds can migrate easily into headspace, others, bound to the matrix, cannot be released. It is especially important for odoriferous compounds present in trace amounts. SPME, which is a nonexhaustive extraction, although giving accurate results in the quantitation of calibrated compounds, provides incomplete information on the real profile of volatile compounds. Vacuum distillation (SAFE) allows the isolation of compounds often bound to the matrix, and a low temperature during the distillation process (40 °C) minimizes artifact formation. SAFE was an especially efficient method for the extraction of sulfur compounds from analyzed muesli and a necessity for AEDA. Combining results from both volatile extraction methods provides more information on the volatile compounds in muesli: on the most abundant ones, most easily released from the matrix, which can be rapidly quantitated by SPME for a quality control purposes, and on those influencing the flavor of muesli to the highest degree and isolated using the SAFE technique. To obtain sufficient data for the characterization of muesli flavor and facilitate both quantitative analysis and aroma characterization by GC-O, these two methods should be used as complementary techniques.

In our study red raspberry seed extract inhibited lipid oxidation in analyzed muesli samples as could be observed in the differences in content of volatile lipid oxidation products measured using SPME and also by the comparison of FD values determined using GC-O. Raspberry seed extract can be a suitable antioxidant added to muesli and probably other cereal products.

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