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Variations in tocopherol, tocotrienol, avenanthramide and saponin content in oats and the influence of milling and baking processes

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ABSTRACT

Oats, as whole-grain cereal, are a good source of nutrients, including compounds located in the outer layers of groats, such as fibre and bioactive compounds. The aim was to study variations in selected bioactive compounds of oats and evaluate possible losses due to oats' milling into flour and the baking process. The levels of tocopherols and tocotrienols (i.e. tocols), avenanthramides and saponins of 30 Finnish-grown oat batches representing different cultivars were measured. The analysed sample materials were laboratory hulled non-heated groats, flours from a commercial mill and breads. The oat batches showed marked variation, and the greatest variation among the batches was observed in avenanthramide content, with a 10-fold difference. Meanwhile, the variation in tocols and saponins was approximately twofold. As a result of the change from groats to flours, the content of tocols, avenanthramides and saponins decreased by 1–40%, usually 1–33% and 1–57% in the oat batches, respectively. Losses in avenanthramides and saponins were also observed after baking. Avenanthramides seemed to tolerate the studied processing steps the best. This study showed that the oat batches' losses in the studied bioactive compounds differed due to multiple factors such as physical separation and chemical reactions.

1. Introduction

Oats (*Avena sativa*) are a valuable source of many nutrients for humans and animals (Holopainen-Mantila et al., 2023). Oats contain soluble dietary fibre (β-glucan), proteins with a balanced amino acid composition, unsaturated fatty acids, vitamins and minerals. The lipid content in oats is higher (4–9%) than that of other cereals. Unlike other cereals, oats are mostly used as a whole grain – that is, the bran is included in products. Health promoting components such as β-glucan and a wide range of biologically active compounds are enriched in the bran fraction (Grundy et al., 2018; Holopainen-Mantila et al., 2023; Piironen et al., 2023).

In oats, the most known antioxidants are tocols (tocopherols and tocotrienols), avenanthramides (AVNs) and other phenolic compounds (Piironen et al., 2023). In addition to these compounds, many other phytochemicals – such as sterols and saponins – are also present in oats. Consuming oats is beneficial to health due to these bioactive compounds.

The structure of oat grains is well organised and stable when the grains are intact. Milling of the oat grains starts with dehulling and as part of processing, hydrothermal treatment (i.e. kilning) is necessary to deactivate lipase enzyme and stabilise the groats (Holopainen-Mantila et al., 2023). Kilning followed by drying can cause the pre-gelatinisation of starch and increase its water absorption capacity (Grundy et al., 2018). Thermal treatment positively influences flavour via Maillard browning. On the other hand, heating induces the formation of oxidation products and the degradation of vitamins.

Tocols are lipid-soluble antioxidants in cereals. Tocopherols (α, β, γ, and δ) differ in their methyl substitution on the chromanol ring that is linked to a saturated isoprenoid-derived hydrocarbon chain (Piironen et al., 2023). The corresponding tocotrienols have three double bonds in the side chain. Currently, only α-tocopherol is considered to have the biological activity of vitamin E. In oats, α-tocotrienol is the main tocol, followed by α-tocopherol and the β-forms of tocopherol and tocotrienol.

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α-Tocotrienol is not regarded as a vitamin E compound but may have health benefits due to its antioxidant and anticancer activity (Holopainen-Mantila et al., 2023).

AVNs are nitrogen-containing phenolic compounds unique to oats. AVNs are esters of 5-hydroxyanthranilic acid and hydroxycinnamoyl acids, namely p-coumaric, caffeic and ferulic acid, or their corresponding avenalumoyl acids. Their anthranilic acid part can be hydroxylated or methoxylated, causing further diversity in the AVN structures (Wise, 2014; Yu et al., 2022). The most common AVNs in non-germinated oats are esters of 5-hydroxyanthranilic acid with p-coumaric, caffeic or ferulic acid (named as AVNs 2p, 2c and 2f, respectively). In the current work, AVNs with an avenalumoyl structure will be referred as type II AVNs, as in our previous study (Multari et al., 2018). AVNs have been shown to have antioxidative and anti-inflammatory properties (Holopainen-Mantila et al., 2023). They are related to cholesterol metabolism, preventing the oxidation of low-density lipoprotein cholesterol (Grundy et al., 2018). Additionally, AVNs play a role in plants' defence systems against pathogens, and they may also affect abiotic stress factors (Capouchová et al., 2020; Piironen et al., 2023).

In contrast to other cereals, oats contain saponins that are surface-active plant metabolites and participate in plant defence mechanisms (Önning and Asp 1993; Grundy et al., 2018). The main saponins in oat groats are avenacosides A and B, which are steroidal saponins (Pecio et al., 2013; Yang et al., 2016). They comprise nuatigenin-type aglycone that is glycosylated at C-3 and at C-26. Avenacosides are decomposed into desglucoavenacosides when the β-glucosidic bond at C-26 is hydrolysed. Hydrolysis increases their bioactivity because desglucoavenacosides are related to plant defence mechanisms as antimicrobial and antifungal compounds (Grundy et al., 2018). In the context of oats' cholesterol-lowering potential, saponins may enhance the excretion of cholesterol via complex formation (Grundy et al., 2018). Additionally, avenacosides have been reported to contribute to sensations of bitterness and astringency when consuming oat flour (Gunther Jordanland et al., 2020).

The contents of bioactive compounds in oats depend on both genetic and environmental factors (Shewry et al., 2008; Redaelli et al., 2016). Studies on different cultivars under various growing conditions have shown variations in antioxidant activity (Capouchová et al., 2020) and the content of tocols (Shewry et al., 2008; Redaelli et al., 2016; Capouchová et al., 2020), AVNs (Mattila et al., 2005; Multari et al., 2018; Michels et al., 2020) and saponins (Önning et al., 1993). In oats, saponin contents have typically been higher (from 100 to almost 1000 μg/g) than those of avenanthramides and tocols (approximately 100 μg/g or less). Processing of oats is crucial since these grains must undergo dehulling and hydrothermal treatment (Holopainen-Mantila et al., 2023). Processing likely affects the content and composition of bioactive compounds both mechanically and chemically. Limited data are available on oat products' bioactive compound content, and processing-induced changes should be studied more thoroughly. Earlier studies have determined contents from oat products without ability to compare the contents to oats before their processing.

This study was part of a broad study aiming to investigate links between chemical and physical properties and processability of oats (Jokinen et al. 2021, 2022). The aim was to study variation in the levels of selected bioactive compounds, tocols, saponins and AVNs, in oats and the effects of oat processing on these contents. A controlled setup enabled the comparison of non-heat-treated oat groats of thirty oat grain batches to the corresponding flours from a commercial milling process. In addition, twenty oat flour batches were used to make breads to investigate the effects of baking on the AVN and saponin content. Based on the determined tocol, saponin and AVN levels differences among the sample types were evaluated.

2. Materials and methods

2.1. Materials

The sample material of this study comprised oat grain batches representing oat cultivars that are widely grown in Finland. Sampling was conducted to investigate extent of variation in chemical composition and physical properties of oats and their effects on processability (e.g., milling behaviour) (Jokinen et al. 2021, 2022). The composition and processing of the oat samples were described in detail by Jokinen et al. (2021). In total, 30 oat batches were obtained, and they represented 23 different oat cultivars from three cultivation years (2017–2019). According to Jokinen et al. (2021), the oat batches' protein content as non-heated groats varied from 11.4% to 20.5%, and their starch content varied from 46.6% to 75.3% per dry matter (DM). The average protein, starch, lipid, β-glucan and ash content was 15.6%, 60.6%, 7.7%, 5.2% and 2.2% per DM, respectively. The oat samples were obtained from the following providers: Boreal Plant Breeding Ltd., Jokioinen, Finland; Peltosiemen Ltd., Forssa, Finland; Vääksyn Mylly Ltd., Vääksy, Finland; Plantanova Ltd., Ruukki, Finland; Raisio plc, Raisio, Finland; and Lantmännen Agro Ltd., Vantaa, Finland.

Throughout the experimental setup, these 30 oat batches (named batches 1–30 as in Jokinen et al., 2021) were treated and processed separately to flours to enable a comparison of their properties. The produced sample types were non-heated groats (to study original levels of bioactive compounds), industrially produced flake flours (to study combined effects of industrial milling steps) and finally breads from the flours (to study effects of baking).

Native grains were dehulled at a laboratory scale to produce non-heated groats. Dehulling was performed using an oat dehuller (Rivakka, Nipere Ltd., Teuva Finland) and cleaning was conducted using a universal threshing machine (Baumann-Saatzuchtbedarf, Waldenburg, Germany). The obtained groats (50–100 g) were ground in an ultra-centrifugal mill (Retsch ZM 200, Haan, Germany) using a 0.5-mm sieve and a 15,000-rpm speed or with a KT-120 hammer mill (Koneteollisuus Ltd., Klaukkala, Finland) with a 0.5-mm sieve. The milled groats were stored at −20 °C.

Native grains were treated with an industrial-scale milling process at Vääksyn Mylly Ltd. (Asikkala, Finland). The size of the acquired oat batches was agreed according to the minimum requirement and capacity of the mill. The milling process – including drying, dehulling, kilning, flaking and milling – was performed as described by Jokinen et al. (2021). The obtained flake flours were stored at −20 °C prior to analysis. Twenty samples of flake flours (batches 11–30) from the growth year 2019 were used to bake whole-grain oat breads. The baking process was described by Sammalisto et al. (2021). Briefly, the breads were prepared by straight dough baking, and the other ingredients besides whole-grain oat flour and tap water were syrup (4%), baker's yeast (3%), salt (2%) and psyllium (2%) on a fresh weight (FW) basis. The bread samples were freeze-dried and stored at −20 °C prior to analysis. Before analysis, the bread samples were ground by a knife mill (Retsch GM 200, Haan, Germany).

2.2. Analyses of bioactive compounds

2.2.1. Tocol analysis

Tocols were extracted as presented by Moisio et al. (2015). The lipid extracts from the milled oat samples (1.0 g) were collected with acetone by accelerated solvent extraction (ASE, Dionex ASE-200, Dionex Corporation, Sunnyvale, CA, USA). The solvent was evaporated, the analytes were dissolved to heptane and transferred into 10-mL volumetric flasks. Prior to analyses by a normal-phase (NP) high-performance liquid chromatography (HPLC) method with fluorescence (FL) detection, the extracts were filtered (GHP, 0.45 μm, Acrodisc, Pall Corporation, USA). Three replicates were analysed from each sample.

Tocols were determined according to Moisio et al. (2015). Isocratic

separation was conducted with an Inertsil silica column (250 × 4.6 mm; 5 μm i.d.; 100 Å; Varian Chromapack, Middelburg, The Netherlands) equipped with a silica guard column (Guard-Pak Silica, Waters, Milford, MA, USA). The mobile phase consisted of 3% 1,4-dioxane in heptane at a flow rate of 2 mL/min at 30 °C. The FL detector was set to λ_{ex} 292 nm and λ_{em} 325 nm. The calibration curves of commercial α- and β-tocopherol standards from Tocopherol-Kit (Merck KGaA, Darmstadt, Germany) were used to quantitate both α- and β-tocopherols and the corresponding α- and β-tocotrienols. A commercial oat flour (Myllärin Gluteeniton Kaurajauho, Helsingin Mylly Ltd., Järvenpää, Finland) was used as an in-house reference for tocol analysis. The repeatability was good with a CV of 7–11% ($n = 22$).

2.2.2. Avenantramide analysis

AVNs were extracted according to Mattila et al. (2005). Briefly, milled oat samples (5.0 g) were extracted twice with 80% methanol (50 mL) for 30 min at room temperature using a magnetic stirrer. The samples were centrifuged (10 min; 600g; 18 °C), and the combined supernatants were evaporated to dryness under reduced pressure at 40 °C. The extracts were dissolved in 80% methanol (2 mL), filtered through 0.45 μm PTFE membrane filters (Pall Corporation, Port Washington, NY, USA), and analysed by a reversed phase (RP) HPLC method with ultraviolet (UV) detection. Oat samples were analysed as three replicates.

AVNs were identified and quantified as described by Multari et al. (2018). The system employed for this purpose was an Agilent 1100 HPLC equipped with a diode array detector (DAD; Agilent, Santa Clara, CA, USA). The HPLC pumps, autosampler, column oven and diode array system were operated by the ChemStation computer program. The analytical column was a Phenomenex Kinetex C18 (100 × 3.0 mm; 5 μm i.d.; 100 Å; Phenomenex, Torrance, CA, USA); the column oven was set to 35 °C. The mobile phase comprised a 0.05 M phosphate buffer (A) at pH 2.4 and methanol (B) with the following gradient: 5−60% B in 50 min and 60−90% B in 6 min. The flow was set to 0.6 mL/min.

AVNs were quantitated at a wavelength of 350 nm. For the identification, UV spectra were collected at 190–600 nm. The 2c, 2p and 2f AVNs were quantitated using commercial standards (ReseaChem GmbH, Burgdorf, Switzerland). The AVNs with the avenalumoyl structure (type II AVNs), were identified from their UV spectra with UV absorption maxima (356–362 nm) compared to the maxima of AVNs 2c, 2p and 2f (320–342 nm). Type II AVNs were quantitated as AVN 2c and reported as their sum. Also, other minor AVNs were quantitated as AVN 2c and included in the total AVN content. The LC-system's performance was followed by injecting a standard mixture in every sample sequence at the beginning and end of the sequence, as well as in the longer sample sequences after every six to eight sample injections.

2.2.3. Saponin analysis

Saponins were determined according to Önning and Asp (1993) with some modifications. The milled oat samples were first defatted in cellulose thimbles with petroleum benzine (boiling point: 40–60 °C) for 1 h at 100 °C in a Soxtec instrument (Soxtec Avanti, 2050; Foss Tecator, Denmark). The content of the extracted lipids was accounted for when the saponin content was calculated. Saponins were extracted from the defatted oat samples (1.0 g) twice with 80% methanol (10 mL), first overnight at room temperature and then for 20 min using an orbital shaker (Mini Shaker, Avantor, Radnor, PA, USA). The samples were centrifuged (5 min; 8000 g), and the combined supernatants were set to 20 or 25 mL. The final extracts were filtered through 0.45 μm syringe filters (Acrodisc GHP, Pall Corporation, USA) and analysed by RP-HPLC-UV. Three replicates were analysed from each oat sample.

The LC system comprised an Agilent 1200 HPLC equipped with a DAD (Agilent, Santa Clara, CA, USA). The analytes were separated with an Atlantis T3 C18 column (250 × 10 mm; 3 μm i.d.; 100 Å; Waters Corp., Milford, MA, USA) equipped with a guard column (20 × 4.6 mm; Waters Corp., Milford, MA, USA). The column oven was set to 30 °C. The mobile phase consisted of water (A) and acetonitrile (B) with the following gradient for a total of 35 min: 25% B for 3 min, 25–40% B for 10 min, 40% B for 5 min, 40–70% B for 8 min, and 70–25% B for 12 min. The flow was set to 0.8 mL/min. Avenacosides were quantitated at a wavelength of 210 nm.

The calibration curves of standard avenacoside A (Merck KGaA, Darmstadt, Germany) were used to quantify both avenacosides A and B. The identities of avenacosides A and B were confirmed by HPLC coupled with an electrospray ionisation tandem mass spectrometry (ESI-MS) in a negative ionisation mode. The in-house reference achieved good repeatability for avenacosides A and B with a CV of 5–7% ($n = 50$).

2.2.4. Data analysis

The content of tocols, AVNs and saponins were reported per dry matter (DM). In addition, either losses of these compounds (%) or remaining proportion (%) after each processing step are given.

Average values, standard deviations (SD), coefficients of variations (CV) and Pearson's correlation coefficients were calculated using the Excel spreadsheet software (Excel, 2016; Microsoft, Redmond, WA, USA). Statistical analysis was performed by one-way analysis of variance (ANOVA) followed by Tukey's test using SPSS version 22 (IBM SPSS Statistics, USA). A value of $p < 0.05$ was considered statistically significant.

3. Results

3.1. Tocol, avenanthramide and saponin content in oat groats

In this study, grains of 30 oat batches representing different cultivars were dehulled at laboratory-scale to obtain groats. The groats presented the original levels of bioactive compounds in oats, and these levels were used for calculating the losses and remaining portions of processing steps. Tocol, AVN and saponin content of each oat groat sample is presented in Supplementary Table A1.

The average total tocol content varied from 32 to 50 μg/g DM in groats (Table 1). The main tocol was α-tocotrienol, which comprised 58–69% of the total tocols. A strong positive correlation ($r > 0.80$) was observed between the α-tocotrienol and β-tocotrienol content and between the total tocotrienol content to the total tocol content (Table 2) indicating that tocotrienols had a more marked effect than tocopherols on the total tocol content. For α- and β-tocopherol, the variation between the lowest and the highest content was 7.3–12 and 0.8–2.4 μg/g DM in the groats, respectively. Meanwhile, for α- and β-tocotrienol, the corresponding content was 20–34 and 2.4–6.1 μg/g DM, respectively.

The sum of the three main AVNs – namely ANVs 2c, 2p and 2f – in the groats was 7.8–77 μg/g DM (Table 1). All these three AVN forms had a strong positive correlation ($r > 0.80$) with the AVN total content (Table 2) that was also seen in relatively equal proportions since ANV 2c contributed 33 ± 7% of the total, versus 31 ± 5% for ANV 2p and 36 ± 9 % for AVN 2f. The ANV 2c, 2p and 2f content of the groats was 3.4–30, 2.7–20 and 1.7–41 μg/g DM, respectively. The content of the type II AVNs was 2.4–48 μg/g DM. When all analysed AVNs were included, the total content of the AVNs varied from 14 to 143 μg/g DM.

The average total content of the main saponins (avenacosides A and B) was 0.35–0.82 mg/g DM in groats (Table 1). Both avenacoside A and B content had a strong positive correlation ($r > 0.80$) with the total saponin content (Table 2). The content of avenacosides A and B varied from 0.18 to 0.50 and 0.15–0.37 mg/g DM, respectively. The ratio of avenacosides A to B varied from 0.7 to 1.8 (proportion 41–65%).

The variation among the studied groats of the oat batches was approximately twofold for the total tocol and saponin content and 10-fold for the sum of the three main AVNs. The total tocol content did not correlate with the other studied compounds (Table 2); instead, the total saponin content had a weak positive correlation with the AVN sum ($r = 0.40$).

Table 1
Tocol, avenanthramide and saponin content in non-heated oat groats and oat flours from flakes.

	Non heated groats, n = 30				Flours from flakes, n = 30			
	Mean ± SD	CV%	Min	Max	Mean ± SD	CV%	Min	Max
Tocols μg/g DM								
α-tocopherol	9.1 ± 1.2	13	7.3	12	5.6 ± 1.2	21	3.4	8.0
α-tocotrienol	26 ± 3.8	14	20.0	34	24 ± 4.6	19	14	32
β-tocopherol	1.2 ± 0.3	28	0.8	2.4	0.8 ± 0.2	28	0.5	1.6
β-tocotrienol	3.9 ± 0.9	23	2.4	6.1	3.2 ± 0.7	22	2.2	5.2
Total tocols	41 ± 5.0	12	32.1	50	34 ± 5.8	17	21	43
Avenanthramides μg/g DM								
2c	12 ± 6.5	54	3.4	30	11 ± 5.3	49	3.3	24
2p	11 ± 5.3	48	2.7	20	9.6 ± 4.2	43	2.9	18
2f	14 ± 9.3	67	1.7	41	12 ± 8.0	67	1.8	37
Sum of 2c, 2p & 2f	37 ± 19	51	7.8	77	32 ± 16	49	8.5	69
Sum of type II AVNs	19 ± 12	61	2.4	48	18 ± 11	61	1.5	55
Total AVNs	64 ± 34	53	14	143	57 ± 30	52	14	129
Saponins mg/g DM								
Avenacoside A	0.30 ± 0.08	26	0.18	0.50	0.20 ± 0.07	33	0.12	0.34
Avenacoside B	0.25 ± 0.06	24	0.15	0.37	0.19 ± 0.05	26	0.087	0.27
Total saponins	0.54 ± 0.11	20	0.35	0.82	0.39 ± 0.10	25	0.20	0.59

Table 2
Pearson's correlation coefficients versus two measurement variables for tocols, avenanthramides and saponins in groat batches (n = 30).

	α-T	α-T3	β-T	β-T3	Total tocols	AA	AB	Total saponins	2c	2p	2f	Sum of AVNs	Sum of type II AVNs	Total AVNs
α-T	1													
α-T3	–	1												
β-T	0.39	–	1											
β-T3	–	0.84	–	1										
Total tocols	0.41	0.96	–	0.84	1									
AA	–	–	−0.31	–	–	1								
AB	–	–	–	–	–	–	1							
Total saponins	–	–	–	–	–	0.85	0.73	1						
2c	–	–	–	–	–	–	0.38	0.34	1					
2p	–	–	–	–	–	–	0.36	0.38	0.88	1				
2f	–	−0.32	–	−0.34	–	–	0.38	0.36	0.58	0.76	1			
Sum of AVNs	–	–	–	–	–	–	0.41	0.40	0.87	0.95	0.90	1		
Sum of type II AVNs	–	−0.30	–	–	–	–	–	–	0.48	0.65	0.74	0.71	1	
Total AVNs	–	–	–	–	–	–	0.38	0.38	0.76	0.89	0.93	0.96	0.87	1

Abbreviations: α-T = α-tocopherol; α-T3 = α-tocotrienol; β-T = β-tocopherol; β-T3 = β-tocotrienol; AA = avenacoside A; AB = avenacoside B; AVNs = avenanthramides.

3.2. The effect of processing on the tocol, avenanthramide and saponin content

3.2.1. Losses due to the milling process

The grains of all the batches underwent the milling process (dehulling, kilning, flaking and milling) to obtain flake flour samples. Thus, a direct comparison of the content in groats vs in flours was enabled.

After the milling process, the total tocol content was 21–43 μg/g DM in flake flours (Table 1). The content of α-tocopherol, β-tocopherol, α-tocotrienol and β-tocotrienol varied from 3.4 to 8.0, 0.5 to 1.6, 14 to 32 and 2.2–5.3 μg/g DM, respectively. The sum of the three main AVNs was 8.5–69 μg/g DM and that of the type II AVNs 1.5–55 μg/g DM in flours (Table 1). The total sum of the AVNs varied from 14 to 129 μg/g DM. The total saponin content was 0.20–0.59 mg/g DM, and the content of avenacoside A and B varied from 0.12 to 0.34 and 0.087–0.27 mg/g DM, respectively. Detailed compositions are presented in Supplementary Table A2.

The tocol, AVN and saponin content was thus lower overall in flours than those of groats of the 30 oat batches. The losses in the total tocols were 7.7–41% in the flours compared to the groats. The losses in the tocotrienols were more moderate than those in the tocopherols. The losses in α- and β-tocopherol were 14–63% and 19–58%, while the corresponding percentages for α- and β-tocotrienol were 0.2–37% and 2.0–31%, respectively (Table 3). For AVNs as a total sum, a reduction of 0–33 % was observed in most cases. Losses in the three main forms – ANV 2c, 2p and 2f – varied from 0% to 65%, 0%–67% and 0%–68%, respectively (Table 3). The total saponin losses varied from 0.4% to 57% in the flours compared to the groats. The losses in avenacosides A and B

Table 3
Losses (%) in tocols, avenanthramides and saponins from groat batches to flours (n = 30).

	Percentual loss as a change from groats to flours				
	Mean ± SD	CV%	Median	Min	Max
Tocols					
α-tocopherol	38 ± 13	35	37	14	63
α-tocotrienol	9.3 ± 9.3	100	6.8	0.2	37
β-tocopherol	36 ± 11	30	34	19	58
β-tocotrienol	17 ± 8.4	49	17	2.0	31
Total tocols	17 ± 8.9	51	16	7.7	41
Avenanthramides					
2c	11 ± 14	129	9	0	65
2p	14 ± 15	107	9	0	67
2f	15 ± 14	93	14	0	68
Sum of 2c, 2p & 2f	13 ± 14	105	12	0	67
Sum of type II AVNs	13 ± 18	142	4	0	67
Total AVNs	13 ± 15	110	12	0	69
Saponins					
Avenacoside A	31 ± 17	56	33	0.8	71
Avenacoside B	24 ± 14	60	21	0	66
Total saponins	28 ± 15	53	29	0.4	57

reached 0.8–71% and 0–66%, respectively. Thus, among oat batches, losses in all studied compounds varied markedly.

3.2.2. Losses due to milling and bread baking

The 20 flake flours from the growth year 2019 were selected for a further study on AVNs and saponins and baked into breads. For the 20 oat batches the AVN content (2c, 2p & 2f) was 12–77 μg/g, 12–69 μg/g and 9.6–65 μg/g DM and the type II AVN content 2.4–45 μg/g, 1.5–43 μg/g and 1.2–32 μg/g DM in groats, flours and breads, respectively. The total saponin content was at the greatest in groats (0.41–0.82 mg/g DM) and decreased in flours (0.28–0.59 mg/g DM) and in breads (0.12–0.26 mg/g DM). These three sample types were compared in more detail by calculating the remaining proportion (%) of AVNs and saponins after the processing steps (Figs. 1 and 2). The content of AVNs and saponins in breads is presented in detail in Supplementary Table A3.

Fig. 1 shows proportion of AVNs (2c, 2p and 2f) remaining when treated from groats to flours, from flours to breads and from groats to breads. For the three main AVNs 33–100%, 83–100% and 30–100% were remaining from groats to flours, flours to breads and groats to breads. In most cases the proportion of remaining AVNs was higher than 60% after processing. However, differences were found among the oat batches. No clear trend showed whether the greatest losses occurred due to either the milling process (groats to flours) or the baking process (flours to breads) because 12 oat batches retained more AVNs after baking, while eight oat batches retained AVNs better after milling.

In Fig. 2, corresponding comparison is shown for saponins. When treated from groats to flours, from flours to breads and from groats to breads, 56–90%, 32–58% and 20–48% of saponins were remaining, respectively. Saponins thus showed great losses after the milling and baking processes. After milling (groats to flours), usually, more than 60% of the saponins were retained, but only less than 50% of the saponins in groats were determined in breads.

4. Discussion

4.1. Variation among oat groats

In this study, the 30 oat batches comprised 23 different cultivars that had been grown in different locations. The selected oat cultivars covered the most used cultivars grown in Finland, and some were included over two growing years. The study's comprehensive number of oat samples enabled a good content comparison.

The variation in the total tocol content (32–50 μg/g DM) among the groats aligned with that in most of the previous studies (Shewry et al., 2008; Piironen et al., 2023). The reported tocol content was higher than 50 μg/g DM in some recent studies (Redaelli et al., 2016; Capouchová et al., 2020). The differences may partly depend on the extraction conditions and analysis methods used. The proportion of the α-tocotrienol content of the total tocol content (58–69%) was similar as reported previously (Shewry et al., 2008; Redaelli et al., 2016). Interestingly, the correlation between the total tocotrienol content and the total tocol content indicated that tocotrienols influenced the variation in the oat batches more significantly than tocopherols. Both genetic and environmental factors may have affected the variation in the tocol content of the studied oat batches (Redaelli et al., 2016; Capouchová et al., 2020). Soil type and cropping methods did not show in an earlier study relationship with tocol content (Capouchová et al., 2020).

Among the studied compounds, the AVN content varied the most in groats. However, the sums of AVN 2c, 2p and 2f content (7.8–77 μg/g DM) aligned with the content previously analysed in oat seeds (Shewry et al., 2008; Multari et al., 2018; Jágr et al., 2023) and groats (Michels et al., 2020). The average content of the three main AVNs was fairly equal (proportions of 33%, 31% and 36% for AVN 2c, 2p and 2f, respectively). As in earlier studies (Multari et al., 2018; Michels et al., 2020), there was thus no predominant form across the oat batches. The variation in the content (2.4–48 μg/g DM) and composition of type II AVNs aligned with that of eight oat samples studied by Multari et al. (2018). In a study by Jágr et al. (2023), the sum of the three main type II AVS was in 12 non-germinated oat cultivars 0.39–25.99 μg/g DM and in the study by Hu et al. (2019) in one non-germinated commercial oat sample 16.76 μg/g FW. The AVN content has been reported as cultivar-dependent (Michels et al., 2020), and environmental conditions also markedly affected the AVN content and composition (Redaelli et al., 2016). The high variation deriving from both genetic and environmental factors across the oat batches indicated that the AVN content of oat raw materials may be difficult to predict.

To our knowledge, saponin contents of oat groats grown in Finland were presented for the first time in this study. The total saponin content

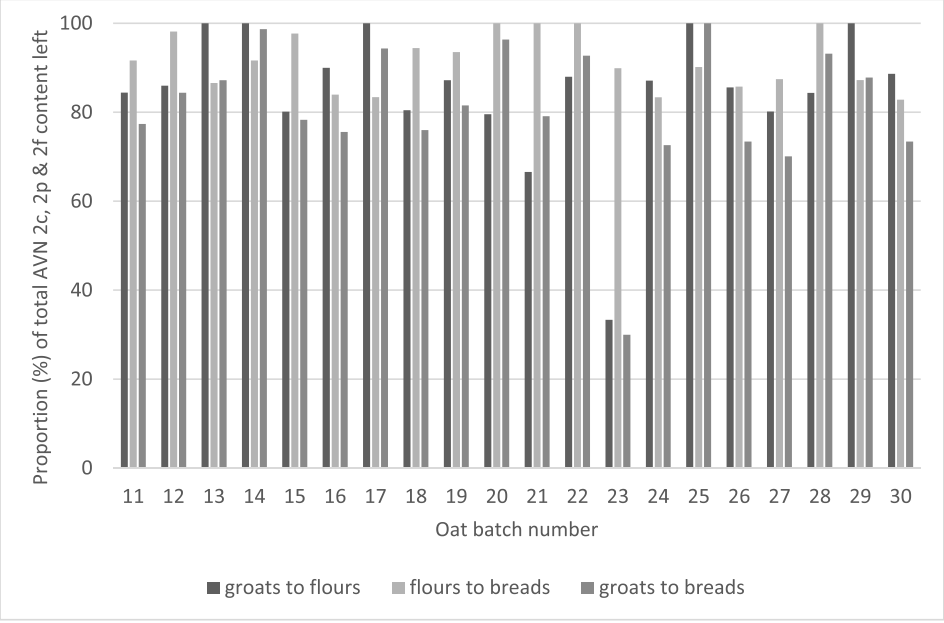

Fig. 1. Remaining AVNs as the average proportion (%) of the sum of AVN 2c, 2p and 2f left from groats to flours, from flours to breads and from groats to breads in 20 oat samples (11–30).

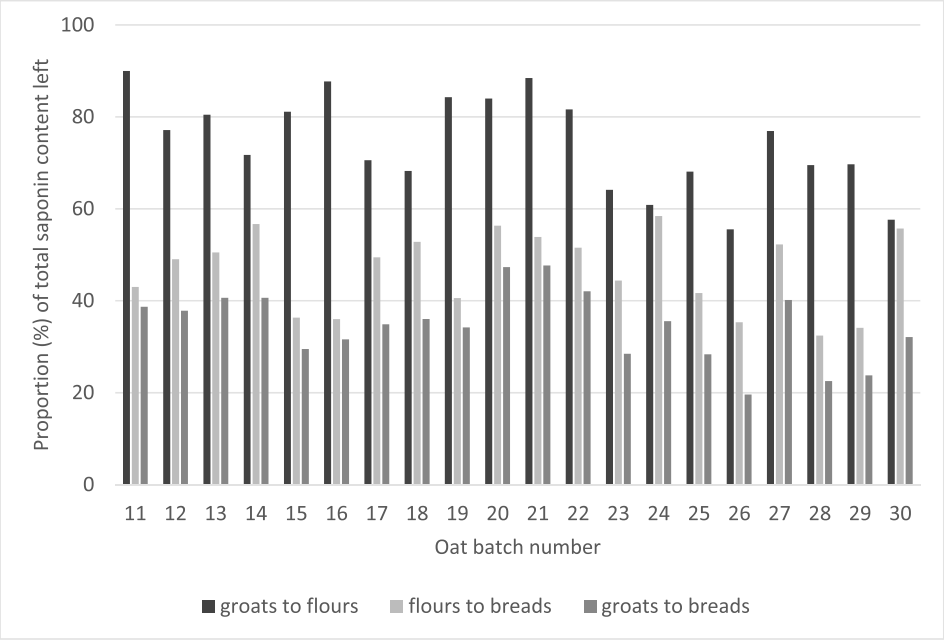

Fig. 2. Remaining saponins as the average proportion (%) of the sum of avenacosides A and B left from groats to flours, flours to breads and groats to breads in 20 oat samples (11–30).

(0.35–0.82 mg/g DM) aligned with the content in groats of 16 oat cultivars from Sweden and New Zealand (Önning et al., 1993), although their total content varied from 0.2 to 0.5 mg/g DM and was, thus, somewhat lower. In groats of 16 Polish cultivars, the total content at 0.55–0.91 mg/g FW was somewhat similar to the content observed in the current study (Pecio et al., 2013). The proportion of the avenacoside A content from the total saponin content (41–65%) aligned with the proportions of 42–61% and 63–79% in studies by Pecio et al. (2013) and Önning et al. (1993), respectively. Additionally, forms other than avenacosides A and B have been reported in oats, such as desglucoavenacosides and other minor avenacoside forms (Pecio et al., 2013; Yang et al., 2016; Gunther Jordanland et al., 2020). Deglucoavenacosides were not detected in this study, as they comprised only less than 5% of the total avenacoside content when detected using the HPLC-ESI-MS method (Pecio et al., 2013). Similarly, as for the other studied compounds, saponin contents are likely dependent on genetic and environmental factors.

The content of bioactive compounds as secondary metabolites in oats varies, depending on environmental factors such as nutrient uptake or stress (Capouchová et al., 2020). The oat batches used in this study were selected to represent varying genetic and environmental backgrounds with a focus on obtaining knowledge about the variation among oat batches, to evaluate usability of oats in different oat products. The marked variation in the AVN content indicated the dependency on varying factors. Despite the high variation in AVN content, observed weak positive correlation between saponin and AVN contents in the studied oat batches could indicate some similarities in these compounds' occurrence.

4.2. Physical separation during milling

In this study, the dataset of 30 oat batches showed a marked variation in the loss of tocols, AVNs and saponins when groats and flours were compared. Some batches tolerated the milling process well, while others showed notable losses (up to 41%, usually up to 33% and up to 57% for tocols, AVNs and saponins, respectively). This variation was likely partly related to physical separation due to differences in the batches' dehullability and groat breakage. The data on dehulling of these oat batches showed great variation among batches (Jokinen et al., 2021). The proportion of hulls from the grains was 14–67% in the dehulling treatment used at the laboratory scale. The high variation showed that the individual samples behaved differently in the dehulling process. In comparison, dehulling in a mill to obtain the flours resulted in a higher hull proportion of 24–76%. More groat breakage likely occurred during the milling process than during laboratory-scale dehulling, which may partly explain the losses in the studied compounds. Partial removal of outer layers of groat (the bran and the germ) is supported by the finding that proportion of hulls have been on average 25% in oats (Holopainen-Mantila et al., 2023). This partial removal of groat parts was also supported by the findings of Jokinen et al. (2021) that the ash and β-glucan content was lower in mill-processed oat flours than in groats that had been dehulled at a laboratory scale.

Location of bioactive compounds in groats may crucially influence their losses by physical separation. The main tocol in oats, α-tocotrienol, is mostly located in the endosperm, while α-tocopherol is mainly located in the germ (Peterson 1995). In addition to physical losses, tocols are likely to degrade due to oxidative reactions that should also be considered. AVNs are more concentrated in the outer aleurone and the subaleurone layers, although they were present in all parts of the groats (Dimberg et al., 1993). Only moderate losses in AVNs despite of differing proportion of hulls removed in this study indicate that AVNs are located both in the outer layers of groats and in the endosperm. Location of saponins in oat groat is poorly known. To our knowledge it has only been studied by Önning et al. (1993). In their study, groats of two oat cultivars were milled followed by separation to four fractions based on the particle size. The results indicated that oat saponins were situated mainly in the endosperm (Önning et al., 1993). However, comparison of commercial oat products showed that oat bran was richer in saponins than oat meal and that the content was at the lowest in processed oat products (Yang et al., 2016). In our study, outer layers of the groats were possibly partly lost inducing lower contents found in flours. Overall, greater losses in tocopherols and saponins could indicate separation of groat parts rich in these compounds. However, especially location of saponins requires further studies.

The dataset used in this study showed a marked variation in losses of the bioactive compounds among the studied oat batches. Differences in dehullability and groat breakage leading to differing physical separation likely affected this variation. Therefore, many factors, such as grain size

and other cultivar-dependent differences affecting milling should be taken into account.

4.3. Stability of tocols, avenanthramides and saponins during processing

The losses in the studied compounds were partly explained by physical separation. Simultaneously, however, chemical and enzymatic reactions (e.g. hydrolysis, oxidation and decomposition) are induced by moisture, heat and size reductions during the milling process.

The decrease in tocol content (8−41%) originating from the milling process was moderate, given that tocols are reacting as antioxidants (Piironen et al., 2023). Interestingly, in our study, the losses in tocopherols were greater than the losses in tocotrienols. In the earlier studies, the α forms of tocols were less stable than the β forms in processing and during the seven-month storage of both oat groats and products at room temperature (Peterson 1995), and respectively during six-month storage of 20 oat flours of this study at room temperature (Puganen et al., 2023). To conclude, the greater losses in tocopherols in our study may not only have resulted from oxidation but, rather, from differences in the oat samples' hullability and thus physical separation. The decrease in tocopherols may indicate the loss of the groats' germ, while the losses in tocotrienols were more likely related to a chemical reaction – that is, oxidation. Furthermore, in our study, kilning was performed at a high temperature and over a short time (155 °C and 40 s), while Bryngelsson et al. (2002) performed kilning at 100 °C for 1 h. Our study's relatively short steaming time may have led to better α-tocotrienol stability in milling process.

AVNs seem to withstand normal commercial milling processing steps well. The AVN content tended to be somewhat lower in the flours compared to groats, but the average reduction was only 13%. All three main AVN forms exhibited similar losses. Earlier studies have suggested patterns for the losses reporting that AVN 2p content decreased the most after flaking (Bryngelsson et al., 2002) and that AVN 2c was prone to decrease under neutral conditions, especially when heated (Dimberg et al., 2001). In our study, the average losses in AVN 2c, 2p and 2f were 18%, 20% and 17%, respectively; thus, no form stood out in terms of its decrease pattern. Overall, AVNs have been reported to be relatively heat-stable during processing (Dimberg et al., 2001; Bryngelsson et al., 2002).

In contrast to AVNs, the saponin content markedly decreased from groats to flours (up to 57%). To separate physical separation and reactions leading to losses, more knowledge of location of saponins in oat groats is needed. As discussed in 4.1, knowledge of location of saponins is scarce.

This study presented the full data for 30 oat batches from which 20 oat batches from the growth year 2019 were utilised further for baking experiments. Comparison of groats, flours and breads from these 20 batches showed that both main three and type II AVNs had good stability and retention in comparison of flours and breads (on average 81–91% of main three AVNS and 69–87% type II AVNs remaining). Only oat batch 23 differed unexpectedly from other batches and showed more marked losses. The average AVN content of the flours (8.5–69 μg/g DM) and breads (12–69 μg/g DM) aligned with AVN contents of 28–50 μg/g FW in commercial rolled oats, flaked oats and oat bran that were purchased from shops (Soycan et al., 2019). Commercial products were in line with our results also in the study of Mattila et al. (2005) that reported 25–26 μg/g FW for oat flakes and 13 μg/g FW for oat bran in FW. The greatest challenge in comparing AVN content between oat products is the high variability in raw materials and lack of processing details.

Saponin content decreased markedly from flours to breads (32–58% remaining) and from groats to breads (20–48% remaining). The losses during milling may have resulted from both physical separation and reactions, but in baking, only reactions and interaction with other compounds could have affected. Stability of steroidal saponins as those in oats, is not well-known. To our knowledge, no studies on their stability in milling or baking are available. When avenacosides were heated in buffer solution they were stable at 100 °C and pH 4–7 for 3 h (Önning et al., 1994). Addition of iron ions and stainless-steel particle accelerated their degradation. Avenacoside A and B could also have hydrolysed to desglucoavenacosides by endogenous or, in baking, also by yeast β-glucosidase enzymes. In fermentation with *Saccharomyces cerevisiae* 69% of triterpene saponins of quinoa were degraded (Arjmand et al., 2023). Fermentation with *S. cerevisiae* together with lactic acid bacteria also decreased saponin content. However, formation of desglucoavenacosides was not seen with the method used in the current study. Avenacosides may also interact with other compounds due to their surface-active nature (Önning and Asp 1993). More knowledge of stability and interaction of saponins in milling and baking-related conditions is needed to explain the losses in detail.

Also, for saponins only data on commercial products is available. Our results for flours (0.20–0.59 mg/g DM) and breads (0.12–0.26 mg/g DM) aligned with those of earlier studies on the total avenacoside content in oat products. This content stood at 0.37–0.41 mg/g FW for oat flour (Gunther Jordanland et al., 2020; Bljahhina et al., 2023), 0.10–0.29 mg/g FW for flakes (Yang et al., 2016) and 0.30–0.44 mg/g FW for brans (Yang et al., 2016), which were similar to our results for flours, whereas the saponin content of an oat protein concentrate, 0.76 mg/g FW, was somewhat higher (Bljahhina et al. (2023). Breakfast cereals contained relatively low saponin content, 0.050–0.091 mg/g FW, in the study by Yang et al. (2016), which was comparable to our results for breads.

Chemical reactions could thus have caused losses especially in tocols and saponins. For saponins, also enzymatic degradation was possible. Some losses could have already occurred during dehulling as part of the milling process, and further losses could have occurred during the later processing steps. Importantly, therefore, the early steps of processing could cause notable losses in bioactive compounds.

5. Conclusions

The comprehensive dataset of this study enabled a full comparison of the content of bioactive compounds in non-heated groats, oat flours and breads as final products. The 30 examined oat batches showed especially high variation in AVN contents thus indicating varying antioxidant capacity in oats. A tenfold variation in AVN content was observed, versus a twofold variation in tocols that are also important antioxidants in oats. Saponins, which might play a versatile role in oats, exhibited a twofold variation across the studied oat groats.

Despite the effect of milling process, the studied flake flours still contained notable amounts of tocols, AVNs and saponins. Tocols were moderately decreased in the milling process, and some variation in these losses was observed among the oat batches. AVNs were mostly retained after milling and baking; thus, they were not notably affected by the possible physical separation of outer layers of groats or the processes. A greater decrease in saponin content indicated losses due to either physical separation during processing or chemical and enzymatic reactions and interactions. Both location of saponins in oat groats and their stability in oat products should be studied further.

To predict stability of the end-products' properties, the factors that affect oats' quality and properties must be identified. This study has provided background information on the variation in tocols, AVNs and saponins among oat batches and knowledge of their levels after processing.

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CRediT authorship contribution statement

Marjo Pöysä: Visualization, Validation, Methodology, Investigation,

Formal analysis, Writing – original draft, Writing – review & editing. **Juha-Matti Pihlava:** Investigation, Formal analysis, Methodology, Writing – review & editing. **Anna Fedotov:** Formal analysis, Investigation. **Anna-Maija Lampi:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Veli Hietaniemi:** Writing – review & editing, Funding acquisition, Conceptualization. **Vieno Piironen:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

Arjmand, S., Mollakhalili-Meybodi, N., Akrami Mohajeri, F., Madadizadeh, F., Khalili Sadrabad, E., 2023. Quinoa dough fermentation by Saccharomyces cerevisiae and lactic acid bacteria: changes in saponin, phytic acid content, and antioxidant capacity. Food Sci. Nutr. 00, 1–11.

Bljahhina, A., Pismennõi, D., Krišèiunaite, T., Kuhtinskaja, M., Kobrin, E.G., 2023. Quantitative analysis of oat (avena sativa L.) and pea (pisum sativum L.) saponins in plant-based food products by hydrophilic interaction liquid chromatography coupled with mass spectrometry. Foods 12 (5), 991.

Bryngelsson, S., Dimberg, L.H., Kamal-Eldin, A., 2002. Effects of commercial processing on levels of antioxidants in oats (Avena sativa L.). J. Agric. Food Chem. 50 (7), 1890–1896.

Capouchová, I., Burešová, B., Paznocht, L., Eliášová, M., Pazderů, K., Konvalina, P., Satranský, M., Dvořáček, V., 2020. Antioxidant activity and content of selected antioxidant compounds in grain of different oat cultivars. Plant Soil Environ. 66 (7), 327–333.

Dimberg, L.H., Theander, O.L.O.F., Lingnert, H.A.N.S., 1993. Avenanthramides-a group of phenolic antioxidants in oats. Cereal Chem. 70, 637, 637.

Dimberg, L.H., Sunnerheim, K., Sundberg, B., Walsh, K., 2001. Stability of oat avenanthramides. Cereal Chem. 78, 278–281.

Grundy, M.M., Fardet, A., Tosh, S.M., Rich, G.T., Wilde, P.J., 2018. Processing of oat: the impact on oat's cholesterol lowering effect. Food Funct. 9, 1328–1343.

Gunther Jordanland, K., Dawid, C., Hofmann, T., 2020. Quantitation and taste contribution of sensory active molecules in oat (Avena sativa L.). J. Agric. Food Chem. 68 (37), 10097–10108.

Holopainen-Mantila, U., Linderborg, K.M., Piironen, V., Sontag-Strohm, T., Nordlund, E., 2023. Oats. In: Shewry, P.R., Koksel, H., Taylor, J.R. (Eds.), ICC Handbook of 21st Century Cereal Science and Technology. Academic Press, pp. 173–180.

Hu, C., Tang, Y., Zhao, Y., Sang, S., 2019. Quantitative analysis and anti-inflammatory activity evaluation of the A-type avenanthramides in commercial sprouted oat products. J. Agric. Food Chem. 68 (46), 13068–13075.

Jágr, M., Hofinger-Horvath, A., Ergang, P., Čepková, P.H., Schönlechner, R., Pichler, E. C., D Amico, S., Grausgruber, H., Vagnerová, K., Dvořáček, V., 2023. Comprehensive study of the effect of oat grain germination on the content of avenanthramides. Food Chem. 437, 137807.

Jokinen, I., Pihlava, J.-M., Puganen, A., Sontag-Strohm, T., Linderborg, K.M., Holopainen-Mantila, U., Hietaniemi, V., Nordlund, E., 2021. Predicting the properties of industrially produced oat flours by the characteristics of native oat grains or non-heat-treated groats. Foods 10, 1552.

Jokinen, I., Sammalisto, S., Silventoinen-Veijalainen, P., Sontag-Strohm, T., Nordlund, E., Holopainen-Mantila, U., 2022. Variation in the physical properties of oat groats, flakes and oat flake flour–Processability of thirty pure cultivar oat batches from Finland. Lebensm. Wiss. Technol. 163, 113595.

Mattila, P., Pihlava, J.-M., Hellstrom, J., 2005. Contents of phenolic acids, alkyl- and alkenylresorcinols, and avenanthramides in commercial grain products. J. Agric. Food Chem. 53 (21), 8290–8295.

Michels, D.K., Chatham, L.A., Butts-Wilmsmeyer, C.J., Juvik, J.A., Kolb, F.L., 2020. Variation in avenanthramide content in spring oat over multiple environments. J. Cereal. Sci. 91, 102886.

Moisio, T., Damerau, A., Lampi, A.M., Partanen, R., Forssell, P., Piironen, V., 2015. Effect of extrusion processing on lipid stability of rye bran. Eur. Food Res. Technol. 241, 49–60.

Multari, S., Pihlava, J.M., Ollennu-Chuasam, P., Hietaniemi, V., Yang, B., Suomela, J.P., 2018. Identification and quantification of avenanthramides and free and bound phenolic acids in eight cultivars of husked oat (Avena sativa L) from Finland. J. Agric. Food Chem. 66 (11), 2900–2908.

Önning, G., Asp, N.-G., 1993. Analysis of saponins in oat kernels. Food Chem. 48 (3), 301–305.

Önning, G., Asp, N.-G., Sivik, B., 1993. Saponin content in different oat varieties and in different fractions of oat grain. Food Chem. 48, 251–254.

Önning, G., Juillerat, M.A., Fay, L., Asp, N.-G., 1994. Degradation of oat saponins during heat processing - effect of pH, stainless steel, and iron at different temperatures. J. Agric. Food Chem. 42, 2578–2582.

Pecio, Ł., Wawrzyniak-Szołkowska, A., Oleszek, W., Stochmal, A., 2013. Rapid analysis of avenacosides in grain and husks of oats by UPLC–TQ–MS. Food Chem. 141 (3), 2300–2304.

Peterson, D.M., 1995. Oat tocols: concentration and stability in oat products and distribution within the kernel. Cereal Chem. 72, 21–24.

Piironen, V., Lampi, A.M., Siitonen, A.I.I., Kariluoto, S., 2023. Vitamins and phytochemicals in cereal grains. In: Shewry, P.R., Koksel, H., Taylor, J.R. (Eds.), ICC Handbook of 21st Century Cereal Science and Technology. Academic Press, pp. 87–95.

Puganen, A., Damerau, A., Pöysä, M., Lampi, A.-M., Piironen, V., Baoru, Y., Linderborg, K.M., 2023. Lipid and Volatile Profiles of Finnish Oat Batches of Pure Cultivars: Effect of Storage on the Volatile Formation. Submitted to Food Chem. Unpublished results.

Redaelli, R., Dimberg, L., Germeier, C.U., Berardo, N., Locatelli, S., Guerrini, L., 2016. Variability of tocopherols, tocotrienols and avenanthramides contents in European oat germplasm. Euphytica 207, 273–292.

Sammalisto, S., Laitinen, M., Sontag-Strohm, T., 2021. Baking quality assessment of twenty whole grain oat cultivar samples. Foods 10 (10), 2461.

Shewry, P.R., Piironen, V., Lampi, A.-M., Nyström, L., Li, L., Rakszegi, M., Fraś, A., Boros, D., Gebruers, K., Courtin, C.M., Delcour, J.A., Andersson, A.A., Dimberg, L., Bedo, Z., Ward, J.L., 2008. Phytochemical and fiber components in oat varieties in the HEALTHGRAIN Diversity Screen. J. Agric. Food Chem. 12 (56), 9777–9784, 21.

Soycan, G., Schär, M.Y., Kristek, A., Boberska, J., Alsharif, S.N., Corona, G., Shewry, P.R., Spencer, J.P., 2019. Composition and content of phenolic acids and avenanthramides in commercial oat products: are oats an important polyphenol source for consumers? Food Chem. X 3, 100047.

Wise, M.L., 2014. Avenanthramides: chemistry and biosynthesis. In: Chu, Y. (Ed.), Oats Nutrition and Technology. John Wiley& Sons. Ltd., pp. 195–226

Yang, J., Wang, P., Wu, W., Zhao, Y., Idehen, E., Sang, S., 2016. Steroidal saponins in oat bran. J. Agric. Food Chem. 64 (7), 1549–1556.

Yu, Y., Zhou, L., Li, X., Liu, J., Li, H., Gong, L., Zhang, J., Wang, J., Sun, B., 2022. The progress of nomenclature, structure, metabolism, and bioactivities of oat novel phytochemical: avenanthramides. J. Agric. Food Chem. 70 (2), 446–457.