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The Antioxidant Potential of Grains in Selected Cereals Grown in an Organic and Conventional System

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Abstract: The paper presents the effect of conventional (use of NPK mineral fertilizers and pesticides) and organic (no use of agrochemicals) farming systems on selected parameters of antioxidant properties of winter wheat, spring barley and oat grain. The research was carried out during the period 2017–2019 at the Czesławice Experimental Farm (central Lublin region, Poland) on loess soil (second quality class). The aim of the research was to evaluate the functional (antioxidant) properties of winter wheat, spring barley and oat grain in whole grain and its milling fractions (dehulled grain, flour and bran). The reduction potential ($Fe^{+3} \rightarrow Fe^{+2}$), the ability to eliminate the free DPPH• radical and the total antioxidant potential in the β-carotene/linoleic acid system were determined. Polyphenol content was also determined using Folin–Ciocalteau reagent. The organic system did not significantly increase the antioxidant properties of cereal grains compared to the conventional system. Under organic farming conditions, oat grain was characterised only by the most favourable antioxidant properties. A highly statistically significant correlation was found between total polyphenol content and DPPH• free radical quenching capacity, especially for oat and barley in the organic system. The closest correlations were for the fractions of bran and whole grain. Dehulling of grain, with the exception of oat grain, irrespective of the farming system, resulted in a significant deterioration of the antioxidant potential of grain extracts. In summary, the study showed that the bran obtained from oat grown under an organic system had the strongest antioxidant activity.

Keywords: wheat; barley; oat; polyphenols; antioxidant activity; DPPH•; organic farming; conventional farming

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1. Introduction

The antioxidant compounds found in cereal grains constitute a large group of antioxidants that protect cells against free radical damage. We can divide the biologically active compounds into hydrophilic compounds (polyphenols), which protect the aqueous environment of cells, and hydrophobic compounds (tocopherols, carotenoids), which protect cell membranes and lipoproteins [1–3]. The low-molecular-weight polyphenol compounds found in cereal grains, as well as tocopherols and sterols, exhibit strong antioxidant activity [4–6]. Free phenolic acids occur in small amounts in cereal grains and are mostly bound and occur as lignins and tannins. Phenolic compounds also occur in association with sugars, fatty acids and proteins. However, in acidic environments, hydrolysis of ester and glycosidic bonds can occur, causing an increase in free polyphenols [2,7,8].

The antioxidant properties of plant polyphenols are related to the presence of hydroxyl and methoxyl groups and involve the elimination of reactive oxygen species and chelation of metal ions. These compounds thus protect the human body from oxidative

stress and prevent the development of chronic non-communicable diseases [9–11]. Phenolic acid derivatives are the main antioxidants of cereal grains. The content of free and ester-linked phenolic acids in rye grains and oat is generally higher than in wheat and barley [12–18]. These compounds prevent the development of, among other things, vascular atherosclerosis and cancerous changes [9,19]. A unique group of cinnamic acid derivatives (p-coumaric, ferulic and caffeic acids) and anthranilic, 5-hydroxyanthranilic and 5-hydroxy-4-methoxyanthranilic acid, found only in oat, are aventramides [20]. This group includes at least 25 different compounds found in oat flakes and 20 in the husk. Their content can reach up to 300 mg kg^{-1} [5].

The total pool of phenolic acids in cereal grains consists of phenylcarboxylic acids (p-hydroxybenzoic, salicylic, protocatechuic, vanillic, gallic, ellagic) and phenylpropenoic acids (caffeic, p-coumaric, ferulic, sinapic), forming the so-called phenolic acids [20]. In cereal grains, the predominant phenolic acid is trans-ferulic acid. Cereal grains such as wheat, rye, barley, oats and buckwheat are rich in phenolic acids [16,21]. Bran and whole grains contain the most of these compounds [22].

Many scientific studies confirm that an organic farming system improves the quality of plant raw materials, including their antioxidant properties, compared to the conventional system [23–28]. Some studies show, however, that the differences in the antioxidant properties of grain between the compared farming systems may be small [23], or there may be no significant differences [25,29]. The positive influence of the organic system on the antioxidant properties of grain may be more evident in a stress situation caused by a nutrient deficiency in the soil [25]. Moreover, individual species and types of plants within a species react differently to organic cultivation, and thus may show more favourable antioxidant parameters under the conditions of conventional cultivation [26]. Kesarwani et al. [30] showed that, in rice and millet seeds, any change in agronomic practices from conventional farming to organic farming can result in minimal or no change in antioxidant activity, and that secondary metabolites in organic farming can be used as an available source of natural antioxidants in a regular diet. However, there is a paucity of studies on the effect of organic and conventional farming systems on the antioxidant activity of cereal grain fractions (whole grain, dehulled grain, flour, bran) in association with specific cereal species. In the present study, it was hypothesised that an organic farming system would improve the antioxidant properties of cereal grains compared with the conventional system, especially those cereals (oat) that best tolerate the abandonment of crops chemization.

The aim of the study was to evaluate the polyphenol content and in vitro antioxidant activity of whole grains of winter wheat, spring barley, oat and their milling fractions (dehulled grain, flour and bran) on the basis of the reduction potential ($Fe^{+3} \rightarrow Fe^{+2}$), the ability to eliminate the free $DPPH^{\bullet}$ radical (α,α-diphenyl-β-picrylhydrazyl) and the total antioxidant potential in the β-carotene/linoleic acid system. The study was conducted with grains from organic and conventional cultivation.

2. Materials and Methods

2.1. Experiment Design and Field Management

A field experiment with winter wheat (cv. 'Bockris'), spring barley (cv. 'Argento') and oat (cv. 'Kasztelan') was conducted during the period 2017–2019 at the Czesławice Experimental Farm (central Lublin region, Poland; 51°18′23″ N, 22°16′02″ W). The experiment was established using the split-plot method in 3 replications, on plots of 40 m^2. The mentioned cereal species were cultivated on a loess loam soil (pH at 1 mol KCl = 6.4) classified in the good wheat complex (II bonitation class) [31]. Before the establishment of the experiment, the soil was characterised by an average content of bioavailable macronutrients (N = 0.08%, P = 80.2; K = 86.6; Mg = 31.3 mg kg^{-1}). The humus content averaged 1.41%.

Two cereal farming systems were included in the experiment:

1. Conventional—recommended NPK mineral fertilization* rates, seed dressing, fungicide and herbicide application and mechanical weed control (harrowing before emergence and at 3–4 leaf stage).

2. Organic—fertilization with Humac Agro ** organic mineral fertilizer and mechanical weed control (harrowing before emergence and at 3–4 leaf stage).

* Mineral NPK fertilizers were applied in the following forms: ammonium nitrate (34% N), enriched superphosphate (40% P_2O_5), potassium chloride (60% K_2O). ** The chemical composition of the fertilizer Humac Agro is as follows: humic acid content—62% on a dry weight basis; macro- and micronutrient content on a dry weight basis: N = 10.3 g kg^{-1}, P = 1.05 g kg^{-1}, K = 1.18 g kg^{-1}; Ca = 16.80 g kg^{-1}; Na = 12.80 g kg^{-1}, Fe = 14.50 g kg^{-1}; Zn = 64 mg kg^{-1}; Br = 77 mg kg^{-1}; Cu = 19 mg kg^{-1}; Se = 6 mg kg^{-1}; and moisture content—20%.

Fertilization was adjusted to the nutritional requirements of individual cereal species and to the specificity of a given farming system (organic crops—Humac Agro fertilization; in conventional cultivation, mineral fertilization with NPK) as well as the initial abundance of available nitrogen, phosphorus and potassium compounds.

All crops tested were grown in two crop rotations (organic and conventional): sugar beet—spring barley—red clover—winter wheat—oat. Each year, the same mineral fertilization was applied to each cereal. In the variant with conventional cultivation, the mineral fertilization was (kg ha^{-1}):

- Winter wheat: N—100 kg ha^{-1} (40 kg pre-sowing, 40 kg dose in spring just after the start of vegetation (BBCH 21–24), 20 kg at the turn of the shooting and earing stages (BBCH 32–36), P—80 kg ha^{-1} (pre-sowing), K—120 kg ha^{-1} (pre-sowing).
- Spring barley: N—60 kg ha^{-1} (20 kg pre-sowing, 40 kg in spring at the stalk shooting stage (BBCH 32–34), P—40 kg ha^{-1} (pre-sowing), K—80 kg ha^{-1} (pre-sowing);
- Oat: N—40 kg ha^{-1}, P—30 kg ha^{-1}, K—50 kg ha^{-1} (all fertilizers pre-sowing).

In the case of organic farming, Humac Agro mineral fertilizer was applied at (kg ha^{-1}):

- Winter wheat: 400 kg (pre-sowing),
- Spring barley: 350 kg (pre-sowing),
- Oat: 300 kg (pre-sowing).

Cereal grains (winter wheat, spring barley, oat) grown in the conventional system were treated with Raxil 060 FS (tebuconazole) at a dose of 50 mL 100 kg^{-1} seeds. Sowing of seeds (grain) of individual cereal species was carried out in the following quantities and times: spring barley (180 kg ha^{-1}) in the 2nd decade of April, winter wheat (220 kg ha^{-1}) in the 3rd decade of September, oat (200 kg ha^{-1}) in the 1st decade of April.

The following plant protection products were used in conventional care:

- Winter wheat, spring barley and oat: herbicide Sekator 6.25 WG (amidosulfuron + iodosulfuron methyl sodium + mefenpyr diethyl)—0.25 kg ha^{-1} at the tillering stage BBCH 27–28; fungicide—Alert 375 SC (flusilasol + carbendazim)—1.0 L ha^{-1} (at the stalk shooting stage BBCH 31–32).

2.2. Plant Sampling and Measurement

The test material was the grain of winter wheat, spring barley (hulled form) and oat (hulled form). The husk from the grain was removed in a laboratory hulling machine and then the grain was separated in a laboratory mill (TYPE QG 109, sieve −0.4 mm) into two fractions: endosperm and bran. After milling, the proportions of endosperm and bran were, respectively, winter wheat −30 and 70%, spring barley −28 and 72%, and oat −24 and 76%. Samples for analysis were ground in a laboratory mill and sieved through a sieve with a mesh diameter of 0.4 mm.

The following cereal grain analyses were carried out:

- Total polyphenols were determined by the method of Naczk et al. [32] using Folin–Ciocalteau reagent (Sigma-Aldrich). In a first step, polyphenols from the material were extracted with 80% methanol and, after centrifugation, with 70% acetone. The absorbance of the supernatant was read at 725 nm. Polyphenol concentration was expressed in catechin equivalents (±) (mg g^{-1} DM).

Total polyphenol content was defined as the total level of free and esterified phenolic acids and insoluble, bound polyphenols [32].

- The antioxidant activity of the extracts analysed was assessed by:

1. Total reduction potential ($Fe^{+3} \rightarrow Fe^{+2}$, FRAP method), determined by the ability of the extracts to reduce ferric ions to ferrous ions [33]. The extracts obtained were mixed with phosphate buffer and potassium ferrocyanide; after incubation of the mixture, trichloroacetic acid was added, and the absorbance of the sample was read at 700 nm. Increasing absorbance indicated increasing reducing power of the mixture. The results of the FRAP method are expressed in the magnitude of the absorbance of the sample.

2. Free radical quenching capacity using the stable artificial free radical DPPH$^{\bullet}$ (α,α-diphenyl-β-picrylhydrazyl) [34]. The antiradical properties of phenolic compounds, expressed as % RSA (Free Radical Scavenging Activity), were assessed by measuring the decrease in absorbance of an alcoholic solution of DPPH$^{\bullet}$ over time, which resulted from the quenching of this radical by the phenolic compounds present in the extracts.

3. Total antioxidant potential in the β-carotene-linoleic acid conjugate system [4,35]. β-Carotene (95%, Sigma-Aldrich) was dissolved in chloroform, and the resulting solution was mixed with linoleic acid (95%, Sigma-Aldrich) and Tween 40 (sorbiton-palmitate polyoxyethylene) as an emulsifier. The resulting β-carotene/linoleic acid emulsion was added to the methanol–acetone extracts and incubated at 50 °C. The degree of β-carotene oxidation was determined by measuring the absorbance at 470 nm, against the emulsion prepared without added β-carotene. Antioxidant activity (AA) was expressed as a percentage of β-carotene oxidation inhibition relative to the control.

Polyphenol content and antioxidant activity in the grains of the cereals analysed were performed in triplicate.

2.3. Statistical Analyses

A three-factor analysis of variance (ANOVA) was used to statistically analyse the results by employing Statistica PL 13.3, while Tukey's test was applied to determine honest significant difference (HSD) values at $p < 0.05$. The mean for the study period is given in the results tables because the year-to-year differences between the characteristics analysed were statistically insignificant. The standard deviation (SD) value is also given for all results. Pearson's correlation coefficients (r) between total phenolic content (TPC) and DPPH$^{\bullet}$ scavenging activity were also calculated (taking into account the cereal species studied, grain fractions and cultivation system).

3. Results

The content of phenolic compounds in the analysed extracts of winter wheat, spring barley and oat grain fractions is shown in Table 1. The level of polyphenols in cereal grain, irrespective of grain fraction and cultivation system, was significantly modified by cereal species. In oat, it was 2.21 mg g^{-1} DM of catechin and was significantly higher (by 7.7%) than that found in barley and by 13.2% than that found in winter wheat. Dehulling cereal grain reduced the polyphenol content by an average of approximately 11%, relative to whole grain. An even greater loss of polyphenol content in relation to whole grain was caused by the flour fraction (reduction in content by about 13% on average). The highest polyphenol content was found in the bran fraction, with an average of 2.26 mg g^{-1} d.m. of catechin. This value was significantly higher, by 5.1%, 17.7% and 20.2%, respectively, than the whole grain, dehulled grain and flour fractions. The loss of polyphenol content due to dehulled grain was significantly correlated with the cereal species. Namely, in the case of oat, the reduction in polyphenol content due to grain dehulling was only 3.9% (a statistically insignificant value). In contrast, dehulling winter wheat grain resulted in a loss of polyphenols in relation to the whole grain by 9.7%, and in the case of spring barley by as much as 13.2%. The farming system did not significantly differentiate the content of polyphenols in cereal grain. There was only a trend towards higher polyphenol content in grain from the organic system in the case of spring barley and oat, as well as a trend

towards higher polyphenol content in conventionally grown winter wheat grain. However, a significant interaction was found (highest polyphenol content of 2.47 mg g^{-1} DM of catechin): bran fraction of organically grown oats (Table 1).

The reduction potential of winter wheat, spring barley and oat grain extracts, determined by the ability of the extracts to reduce ferric ions to ferrous ions, is presented in Table 2. Statistically significant differences were found between the cereal species. Oat grain showed a significantly higher reduction potential (by 9.9% and 6.5%, respectively) compared to winter wheat and spring barley. In all winter wheat, spring barley and oat grain, the reduction potential, regardless of management, was, respectively, 0.219, 0.220 and 0.233 (significantly highest). Dehulling oat grain did not significantly ($p > 0.05$) reduce the iron ion reducing capacity of the extract obtained (reduction was only 1.3%). On the other hand, dehulling winter wheat and spring barley grain had a significant reduction in the reduction potential of the extracts, by 9.6% and 5.5%. The iron-reducing capacity from Fe^{+3} to Fe^{+2}, found in the extract obtained from the endosperm of dehulled grain (flour), was significantly lower for all the cereals analysed than in the whole grain. However, in the case of oat endosperm, this loss was the smallest. Bran extracts of all analysed cereals were characterised by the highest reduction potential within the grain fractions studied. Compared to the fractions of flour, dehulled grain and whole grain, the reduction potential of bran was higher by 14.5%, 13.2%, 4.0% (winter wheat); 14.3%, 14.1%, 9.1% (spring barley); 12.8%, 8.4%, 7.2% (oat). The farming system did not significantly affect the grain absorbance of individual cereals. However, a statistically significant interaction was found in the situation of oat cultivation in the organic system—reduction potential of 0.239. By including grain fractions in the interaction, a statistically significant triple interaction was obtained, whereas the highest grain reduction potential (0.260) was found in the bran of oat cultivated organically (Table 2).

The ability of extracts obtained from cereal grains to quench DPPH$^{\bullet}$ free radicals is shown in Table 3. Significant differences were found between the cereal species in question. Oat grain showed, independently of the other test factors, significantly the highest free radical scavenging capacity, with an average of 32.07%. This value was 5 percentage points "p.p." higher than that recorded in spring barley and 5.63 p.p. higher than that found in winter wheat. Grain fractions had a significant effect on the trait determined. Methanol–acetone extracts obtained from cereal bran as well as extracts of whole cereal grains showed a significantly higher ability to quench DPPH$^{\bullet}$ free radical than dehulled grain (by 10.63 p.p. and 8.89 p.p., respectively) or flour obtained from grain endosperm (by 11.34 p.p. and 9.6 p.p., respectively). Grain dehulling had the biggest effect on reducing free radical elimination capacity compared to whole grain for spring barley (−12.00 p.p.) and winter wheat (−11.92 p.p.). The cultivation system did not significantly affect this quality parameter. However, a statistically significant interaction was found between the farming system and the cereal species—oat grown under the organic system showed a free radical quenching capacity of 32.88%. A statistically significant interaction between farming system and grain fractions was also reported—the highest free radical DPPH$^{\bullet}$ quenching capacity was shown by cereal bran in the organic system (35.55%). A significant triple interaction was also found—bran from oat grain grown in the organic system had a free radical DPPH$^{\bullet}$ quenching capacity of 37.11% (Table 3).

The total antioxidant potential of the extracts obtained from the grain of the analysed cereals, irrespective of the other experimental factors (Table 4), was, respectively, winter wheat (28.80%), spring barley (31.39%), oat (32.65%). The cited data show that the total antioxidant activity of winter wheat grain was significantly lower (by 2.59 p.p.) than that found in barley grain and 3.85 p.p. lower than that found in oat grain.

Table 1. Effect of cereal grain milling on total polyphenol content (mg g^{-1} DM of catechin)—2017–2019 average.

Grain Fractions	Winter Wheat			Spring Barley			Oat			Mean for the Farming System		Mean
	Org. System	Conv. System	Mean	Org. System	Conv. System	Mean	Org. System	Conv. System	Mean	Org. System	Conv. System	
Entire grain	1.94 ± 0.02 *	1.99 ± 0.03	1.96	2.23 ± 0.02	2.15 ± 0.02	2.05	2.35 ± 0.03	2.27 ± 0.03	2.31	2.17	2.13	2.15
Dehulled grain	1.75 ± 0.02	1.80 ± 0.02	1.77	1.80 ± 0.01	1.77 ± 0.01	1.78	2.26 ± 0.04	2.18 ± 0.02	2.22	1.93	1.91	1.92
Flour	1.86 ± 0.01	1.92 ± 0.01	1.89	1.90 ± 0.01	1.85 ± 0.02	1.87	1.93 ± 0.04	1.87 ± 0.04	1.90	1.89	1.88	1.88
Bran	2.01 ± 0.03	2.09 ± 0.03	2.05	2.36 ± 0.02	2.27 ± 0.03	2.31	2.47 ± 0.06	2.39 ± 0.05	2.43	2.28	2.25	2.26
Mean	1.89	1.95	1.92	2.07	2.01	2.04	2.25	2.17	2.21	2.07	2.04	-

* SD—standard deviation. $HSD_{(0.05)}$ cereals = 0.078; farming system = not significant (n.s.); grain fraction = 0.083; cereals × farming system = n.s.; cereals × grain fraction = 0.089; farming system × grain fraction = n.s. cereals × farming system × grain fraction = 0.079.

Table 2. Effect of cereal grain milling on grain absorbance (%) (FRAP method)—2017–2019 average.

Grain Fractions	Winter Wheat			Spring Barley			Oat			Mean for the Farming System		Mean
	Org. System	Conv. System	Mean	Org. System	Conv. System	Mean	Org. System	Conv. System	Mean	Org. System	Conv. System	
Entire grain	0.215 ± 0.005 *	0.224 ± 0.005	0.219	0.222 ± 0.004	0.219 ± 0.003	0.220	0.238 ± 0.003	0.229 ± 0.004	0.233	0.225	0.224	0.224
Dehulled grain	0.197 ± 0.006	0.200 ± 0.005	0.198	0.211 ± 0.005	0.206 ± 0.004	0.208	0.234 ± 0.005	0.226 ± 0.006	0.230	0.214	0.210	0.212
Flour	0.193 ± 0.003	0.198 ± 0.002	0.195	0.209 ± 0.006	0.201 ± 0.005	0.205	0.225 ± 0.006	0.214 ± 0.004	0.219	0.209	0.204	0.206
Bran	0.225 ± 0.007	0.231 ± 0.007	0.228	0.249 ± 0.007	0.235 ± 0.006	0.242	0.260 ± 0.008	0.243 ± 0.007	0.251	0.244	0.236	0.240
Mean	0.207	0.213	0.210	0.222	0.215	0.218	0.239	0.228	0.233	0.223	0.219	-

* SD—standard deviation. $HSD_{(0.05)}$ cereals = 0.012; farming system = not significant (n.s.); grain fraction = 0.013; cereals × farming system = 0.011; cereals × grain fraction = 0.090; farming system × grain fraction = n.s.; cereals × farming system × grain fraction = 0.090.

Table 3. Effect of cereal grain milling on DPPH• free radical quenching capacity (% RSA; RSA = AG, 516 nm (start)—AB, 516 nm (6 min))—2017–2019 average.

Grain Fractions	Winter Wheat			Spring Barley			Oat			Mean for the Farming System		Mean
	Org. System	Conv. System	Mean	Org. System	Conv. System	Mean	Org. System	Conv. System	Mean	Org. System	Conv. System	
Entire grain	31.25 ± 0.05 *	31.78 ± 0.06	31.51	32.18 ± 0.06	31.96 ± 0.07	32.07	35.03 ± 0.05	34.02 ± 0.07	34.52	32.82	32.58	32.70
Dehulled grain	19.25 ± 0.0.37	19.94 ± 0.41	19.59	20.12 ± 0.39	20.02 ± 0.22	20.07	32.05 ± 0.51	31.90 ± 0.55	31.97	23.80	23.83	23.81
Flour	20.79 ± 0.30	21.06 ± 0.26	20.92	22.51 ± 0.09	21.78 ± 0.08	22.14	27.35 ± 0.27	25.12 ± 0.22	26.23	23.55	22.65	23.10
Bran	33.65 ± 0.41	33.82 ± 0.37	33.73	34.89 ± 0.40	33.19 ± 0.33	34.04	37.11 ± 0.38	34.04 ± 0.39	35.57	35.21	33.68	34.44
Mean	26.23	26.65	26.44	27.42	26.73	27.07	32.88	31.27	32.07	28.84	28.21	-

* SD—standard deviation. $HSD_{(0.05)}$ cereals = 1.972; farming system = not significant (n.s.); grain fraction = 1.984; cereals × farming system = 1.602; cereals × grain fraction = 1.826; farming system × grain fraction = 1.528; cereals × farming system × grain fraction = 1.988.

Table 4. Effect of grain milling on antioxidant activity (%) in the β-carotene/linoleic acid system—2017–2019 average.

Grain Fractions	Winter Wheat			Spring Barley			Oat			Mean for the Farming System		Mean
	Org. System	Conv. System	Mean	Org. System	Conv. System	Mean	Org. System	Conv. System	Mean	Org. System	Conv. System	
Entire grain	33.62 ± 0.65 *	34.91 ± 0.66	34.26	38.35 ± 0.77	37.25 ± 0.56	37.80	39.44 ± 0.82	36.78 ± 0.65	38.11	37.13	36.31	36.72
Dehulled grain	31.89 ± 0.49	32.96 ± 0.52	32.42	36.22 ± 0.47	35.16 ± 0.44	35.69	37.85 ± 0.58	38.12 ± 0.46	38.48	35.32	35.41	35.36
Flour	11.61 ± 0.67	11.87 ± 0.70	11.74	12.19 ± 0.86	12.02 ± 0.75	12.10	13.74 ± 0.91	12.50 ± 0.85	13.12	12.51	12.13	12.32
Bran	36.25 ± 0.79	37.34 ± 0.55	36.75	40.11 ± 0.70	39.87 ± 0.61	39.99	41.88 ± 1.02	40.96 ± 1.08	41.42	39.41	39.39	39.40
Mean	28.34	29.27	28.80	31.71	31.07	31.39	33.22	32.09	32.65	31.09	30.81	-

* SD—standard deviation. $HSD_{(0.05)}$ cereals = 2.003; farming system = not significant (n.s.); grain fraction = 2.006; cereals × farming system = n.s.; cereals × grain fraction = 2.011; farming system × grain fraction = n.s.; cereals × farming system × grain fraction = n.s.

The farming system did not significantly modify the antioxidant activity of cereal grain extracts in the β-carotene/linoleic acid system. Interactions of this factor with the other experimental factors were also not statistically significant. The trait in question was significantly altered by the grain fractions determined in the study. Significantly, the highest antioxidant potential of grain extracts (relative to the other grain fractions), irrespective of grain species, was recorded in the fraction bran (39.40%). The other grain fractions showed lower antioxidant activity, respectively, by an average of −2.68 p.p. (whole grain), −4.04 p.p. (dehulled grain) and as much as −27.08 p.p. (flour from the endosperm of the grain). The obtained data show that methanol–acetone extracts obtained from the endosperm of all the cereals studied showed a significantly ($p < 0.05$) lower ability to inhibit oxidative changes occurring in the β-carotene/linoleic acid emulsion compared with the other cereal fractions (especially bran and whole grain).

The calculated Pearson's correlation coefficients (r) (Table 5) confirm in most cases a significant relationship between the total polyphenol content of cereal grain extracts and the ability of extracts obtained from cereal grains to quench DPPH$^{\bullet}$ free radicals. The strongest relationship was for the bran fraction, especially for oat grown in an organic system (r = 0.925), but also in the conventional system (r = 0.887). A highly significant correlation between TPC content and DPPH$^{\bullet}$ scavenging activity was also found for whole oat grain (r = 0.860—organic cultivation; r = 0.738—conventional cultivation). High correlation coefficients (r) TPC × DPPH$^{\bullet}$ characterized bran from organic spring barley (r = 0.871), as well as from conventionally grown spring barley (r = 0.746). The process of dehulling the grain (with the exception of oat) and, in particular, milling the endosperm into flour, resulted in a reduction of the TPC content of the cereal grain and, consequently, in a reduction of DPPH$^{\bullet}$ scavenging activity. For wheat grain flour, Pearson's correlation coefficients (r) were statistically insignificant.

Table 5. Pearson's correlation coefficients (r) between total phenolic content (TPC) and DPPH$^{\bullet}$ scavenging activity.

Cereals	Grain Fractions	Organically Grown Grain	Conventionally Grown Grain
Winter wheat	Whole grain	0.621 *	0.633 *
	Dehulled grain	0.473 ^{ns}	0.521 *
	Flour	0.423 ^{ns}	0.434 ^{ns}
	Bran	0.677 *	0.694 *
Spring barley	Whole grain	0.724*	0.709 *
	Dehulled grain	0.601 *	0.586 *
	Flour	0.564 *	0.532 *
	Bran	0.871 *	0.746 *
Oat	Whole grain	0.860 *	0.738 *
	Dehulled grain	0.710 *	0.698 *
	Flour	0.622 *	0.613 *
	Bran	0.925 *	0.887 *

* significant correlation coefficient (r); ^{ns}—not significant correlation coefficient.

4. Discussion

The mechanical processing of cereal grains includes the processes of surface cleaning, hulling (separation of undesirable parts or separation of parts of the grain, such as germ or bran) and milling into flour.

The determination of the reduction potential ($Fe^{+3} \rightarrow Fe^{+2}$) of the extracts analysed allows the potential ability of the polyphenols present in the extracts to transfer protons to be assessed. In all analysed cereal species, the whole grain, with a higher polyphenol content, had a higher reduction potential. Losses of polyphenols (less than −4%) found during the dehulling of oat grain did not significantly reduce the reduction potential of extracts obtained from these fractions. In contrast, losses of polyphenols resulting from the dehulling of wheat and barley grains (amounting to −9.7% and −13.2%, respectively)

significantly ($p > 0.05$) affected the reduction potential of the extracts obtained from these fractions. The results of studies by other authors show that endosperm obtained from dehulled cereal grains show different reduction potentials, which is probably due to the different composition of polyphenols in specific cereal species. In oat, avenanthramides A, B and C are present, showing antioxidant properties. The avenanthramides are evenly distributed in the oat grain, so there is not as much loss during the dehulling process [35–38]. The above thesis is reflected in the results of our own study.

A study by Zieliński et al. [39] showed that the highest content of phenolic compounds was found in buckwheat kernels (2.69 mg g^{-1} of catechin), followed by oat kernels (1.64 mg g^{-1} of catechin) and rye (1.39 mg g^{-1} of catechin), while by far the lowest content of these components was found in wheat (0.53 mg g^{-1} of catechin). Phenolic acid derivatives are the main antioxidants of cereal grains [3,8,13,40–42]. A study by Zieliński et al. [12] shows that the content of free and ester-bonded phenolic acids in oat grains was higher than in wheat and barley. Similar correlations in favour of oat kernels were noted in this study. Tian et al. [3], using the example of wheat, proved that phenolic acid profiles are affected by genotype, field management and environment, and their interactions. Intensified field management, in particular, may lead to a decreased concentration of wheat phytochemicals. The level of naturally occurring nitrogen in the soil may also affect the accumulation of wheat phytochemicals. In a subsequent article by Tian et al. [43] notes that the health benefits of whole wheat consumption can be partially attributed to wheat's phytochemicals, including phenolic acids, flavonoids, alkylresorcinols, carotenoids, phytosterols, tocopherols and tocotrienols.

The differences found in the content of polyphenols and their potential reducing properties may have been due to the individual composition of polyphenols showing differential activity [34,44–46]. Individual phenolic acids have different antioxidant activities [4]. Other compounds present in cereal grains, the levels of which have not been determined in these fractions, also show potential antioxidant properties [17,47–50]. Tian et al. [51] demonstrated that nitrogen fertilizer usage was not a major factor affecting wheat phenolic acid composition. Wheat variety was the predominant factor determining wheat phenolic acid composition. The effect of environmental factors was also dependent on the wheat variety.

The lower polyphenol levels of dehulled grain, compared to whole grain, reduced the free radical quenching capacity of $DPPH^{\bullet}$ by an average of approximately 8.8 percentage points (p.p.). Peterson et al. [5] showed that as oat grain is dehulled, there is a decrease in polyphenol content and a decrease in the ability to eliminate the free $DPPH^{\bullet}$ radicals. The method of extraction of the test material also has an important influence on the determination of antioxidant activity [7]. The results of our study show that, although dehulling oat grain caused a decrease in polyphenol content, it was insignificant (−2.5 p.p.) compared to wheat and barley.

Of the cereal grain fractions analysed, bran showed the strongest antioxidant activity in our study, compared to the starting material (whole grain). This may be due to a change in the composition of the pool of phenolic acid compounds during germination and to the presence of other biologically active components showing antioxidant properties [2,8,33]. Emmons and Peterson [4] report that the ability of phenolic acids to eliminate the free radical $DPPH^{\bullet}$ is dependent on the site and amount of hydroxyl (-OH) and methoxyl (-OCH3) groups.

In our own research, we found a higher content and activity of antioxidants in grain (and its fractions) of oat and barley from organic cultivation compared to conventional cultivation. This is reflected in other scientific articles [24,29,52,53]. In the case of wheat, the opposite trend was noted in our study; more favourable antioxidant properties were obtained in the conventional system. A different view is presented by Zrcková et al. [54]. According to them, the variability of antioxidant compounds in wheat grain depends on the genotype, weather conditions and cultivation system. Organic cultivation may help to increase antioxidant levels in wheat grain.

Knap et al. [25] express the view that, apart from some crops (vegetables, herbs), there are no statistically significant differences in antioxidant activity between organic and conventional seeds/fruits. Nevertheless, the organic system may result in an increased concentration of antioxidants due to nitrogen deficiency stress. Żuchowski et al. [23] believe that organically grown plants contain more secondary metabolites. However, in the cited study by these authors, organic farming did not lead to a significant increase in phenolic acid content. Only a slight, statistically insignificant trend towards higher levels of phenolic acids in organic wheat samples was shown. In contrast, the work of Capouchová et al. [29] showed no statistically significant effect of the cultivation system on the total antioxidant activity of oat and the content of polyphenols. Other publications, similar to the present study, demonstrated the high antioxidant and health-promoting value of oat grain [38,55,56]. The particularly high antioxidant potential of oat grain has also been pointed out by Dimberg et al. [57], Chen et al. [58] and Chen et al. [37].

Our own research confirmed a significant positive correlation ($p < 0.05$) between TPC and DPPH• radical scavenging for all cereal grains tested (with the correlation being stronger for oat and barley in organic grains and for wheat in conventional grains). The strongest correlation (r = 0.887–0.925) was found for oat bran, followed by barley bran (r = 0.746–0.871), while a lower correlation was found for wheat bran (r = 0.677–0.694). Horvat et al. [59] also recorded significant correlations between TPC and DPPH• radical scavenging for wheat (r = 0.598), winter barley and spring barley (r = 0.836 and 0.735, respectively). In addition, the authors mentioned above found the closest correlations in the case of cereal grain bran (as in their own study described above) compared to the other fractions. In addition, the results obtained by Mpofu et al. [45], Gałązka et al. [60] and Yilmaz et al. [61] clearly show that TPC content has a significant effect on the free radical quenching capacity of DPPH•. The significant relationship between TPC and DPPH• radical scavenging is related to the cereal species, as confirmed by the study of Fardet et al. [62], among others. Similarly, Emmons and Peterson. [4] and Adom and Liu [6] showed that free radical scavenging capacity was closely correlated with polyphenol content ($p < 0.0001$, r = 0.677). In contrast, other authors report a lack of significant correlation between Folin-Ciocalteu (F-C) assay and DPPH• activity in cereals [63–65].

Horvat et al. [59] and Tian [51] conclude that the variety and species of cereal, as well as the growing environment (habitat), have a strong influence on the phenolic acid profiles and antioxidant activity of cereal grains. Continued research of this kind in other research centers in different countries could contribute to breeding work to produce cereal grains rich in health-promoting phenolic compounds. Science can then reach out to consumers interested in improving their eating habits or preferences for specific cereal crops [53,54,59,66].

5. Conclusions

The study showed that, of the three forms of cereals compared, oat grain had the highest antioxidant activity, followed by spring barley grain, and winter wheat grain had a lower antioxidant activity.

The results of the research show that the difference in the antioxidant parameters of cereal grains between the organic system and the conventional system is not large. There is only a tendency of more favourable antioxidant properties of grain from organic farming. The significant positive influence of the organic system on the antioxidant properties of grain (DPPH•) is revealed only in the interaction with oat cultivation.

The whole grain of the cereals analysed shows strong antioxidant activity in vitro due to its polyphenol content. The dehulling process of dehulled barley and wheat grain reduces the potential antioxidant properties of the obtained product, resulting from the loss of polyphenols. By contrast, dehulling grain does not significantly affect the antioxidant parameters of oat grain. Similarly, the reduction in the antioxidant potential of cereals concerns the flour facies, relative to whole grain and bran.

The strongest antioxidant properties are shown by bran obtained from organically grown oat, followed by spring barley. Fewer antioxidant properties are found in winter wheat bran from organic, but also from conventional cultivation.

The determined free radical quenching capacity of $DPPH^{\bullet}$ is closely correlated with the polyphenol content of the test material, especially for bran and whole grain organically grown oat.

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