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Antioxidant Potential and Phenolic Acid Profiles in Triticale Grain under Integrated and Conventional Cropping Systems

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Abstract: Cereals are a valuable source of biologically active compounds. Phenolic compounds, of which the phenolic acids (PA) found in cereal grains constitute a significant proportion, are characterized by health-promoting properties largely due to their antioxidant capacity. PA, located mainly in the outer parts of the grain, play an important role in preventing environmental stresses. Triticale is a cereal species of increasing economic value, and also value for human consumption. The aim of this study was to demonstrate the effect of conventional (CONV) and integrated (INTEG) cropping systems on antioxidant activity and content of selected PA in triticale cultivars (Meloman, Panteon, Belcanto) grain. The experiment was conducted in seasons from 2019/2020 to 2021/2022. Among the PA tested, ferulic acid (FER) had the highest contribution to total PA content (TPAs), with 519, 99, and 1115 μg g^{-1} in whole grain, flour, and bran, respectively. The unfavorable hydrothermal conditions occurring in the seasons (rainfall deficit) increased TPA, mainly in whole grain. Grain cv. Meloman had the highest PA content in whole grain, flour, and bran and cv. Belcanto had the lowest, with differences of 22.7, 18.2, and 15.7% respectively. Cultivation of triticale under the CONV vs. INTEG cropping system resulted in reduced amounts of TPAs in flour and bran and PA: p-hydroxybenzoic acid (p-HB) in flour, syringic acid (SYR) in whole grain and bran, and ferulic acid (FER) and sinapic acid (SIN) in bran. The CONV cropping system also caused a decrease in antioxidant activity (AOA) in flour and bran. In most of the cases analyzed, the highest antioxidant activity and content of PA were found in bran, and the lowest were found in flour. The high presence of PA in triticale grain indicates that this cereal, especially when grown under the INTEG cropping system, can be destined for consumption and provide a source of valuable antioxidants for various food and nutraceutical purposes.

Keywords: x *Triticosecale* Wittmack; phenolic acids; antioxidant property; whole grain; bran; flour; cropping systems

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1. Introduction

Cereals play an important role in human nutrition [1,2]. Cereal grains are a rich source of naturally occurring phytochemicals, which include phenolic compounds such as benzoic and cinnamic acids, anthocyanidins, quinones, flavonols, chalcones, flavonones, and amino-phenols. The role of phenolic compounds as natural antioxidants has attracted considerable interest because of their pharmacological function. Phenolic compounds are products of secondary metabolism in plants [1,3]. Many phenolic compounds exhibit strong antioxidant properties as they scavenge or neutralize reactive oxygen species (ROS) and therefore have the effect of reducing or minimizing oxidative damage to proteins, DNA, and lipids [4,5].

Numerous phenolic compounds exhibit antioxidants, anticancer, antibacterial, cardioprotective agents, anti-inflammation, immune system-promoting, and skin protection from UV radiation [6–8]. Most phenolic acids (PA) are bound by ester bonds and with cell-wall polysaccharides [9]. Ferulic acid (FER) is the most common PA found in cereal grains. Approximately 75% of phenolic compounds are found in the grain bran and 15% are found in the grain endosperm, with the remainder present in the aleurone layer [10]. A high content of phytochemicals, especially phenolic antioxidants, is an important quality parameter for cereal grains [11,12]. Phenolic acids, including ferulic acids, are important in the human diet because they attenuate oxidative stress by blocking free radicals, for example resulting from alcohol toxicity or polyunsaturated fatty acids (PUFA) [13].

Plants are exposed to various stress factors during the growing seasons. Phenolic compounds accumulate in response to ROS under stress conditions. Phenols provide resistance to host plants, providing resistance to agrophages, and also act as indicators of mineral deficiencies at various stages of plant growth and development. The action of resistant plants apparently consists of increasing the level of phenol synthase enzymes or their activity, leading to increased phenol production [14–16]. According to Stuper-Szablewska et al. [17], variable, unfavorable weather conditions are also factors inducing the biosynthesis of PA.

The content of phenolic compounds in triticale grain depends on the genotype, environmental conditions, agrotechnical factors, and their interactions. Jaśkiewicz and Szczepanek [18] showed that they affect the growth, development, yield, and quality parameters of grain, including the phenolic compound content.

Among the phenolic compounds present in cereal grains, PA are the best understood, exhibiting many biological properties [19] and influencing the antioxidant capacity of triticale [20,21]. Triticale (x *Triticosecale* Wittmack) is a self-pollinating cereal resulting from the crossing of wheat (*Triticum*) and rye (*Secale*). The main objective of its creation was to obtain a new species that combines the best agro-morphological and grain quality characteristics of wheat (suitability for obtaining a wide range of food products) and rye (resistance to unfavorable growing conditions resulting from various environmental stresses). Triticale, therefore, has greater adaptability than wheat and is better suited to a wide range of environmental conditions (e.g., drought, climate change, disease) [22–25]. Triticale grain has a higher protein content than rye grain. It has also been shown that the biological value of triticale protein is higher than that of wheat. In addition, triticale is a species adapted to growing in more marginal environments than wheat [23]. An increase in the importance of triticale cultivation is noted worldwide, with Poland being the leading producer. In 2021, triticale production was 14.8 million tons worldwide and 5.3 million tons in Poland. By comparison, wheat production at that time was 220.8 million tons worldwide and 2.4 million tons in Poland. In the case of rye, production was much lower and amounted to 4.3 and 0.8 million tons in the world and in Poland, respectively [26].

Triticale is mainly used as animal feed (pigs, poultry, and ruminants) in different forms: grain, forage, silage, hay, and straw [23,27]. Recently, the cultivation of triticale for human consumption is also gaining in popularity [28]. Given the nutritional and agronomic value of triticale and the increasing level of consumer interest in products made from alternative cereal species, it is believed that triticale may have the necessary characteristics to become an important food for humans in the future [20].

Triticale grain has both special nutritional properties and technological stability. Flour obtained from milling triticale grain can be used for bread-making [29]. Factors limiting the widespread use of triticale grain for bakery products are the grain's unfavorable quality characteristics—high amylolytic activity and low gluten content, which have a negative impact on the bread-making process [30,31]. However, the baking properties of triticale flour can be improved through use of various additives (e.g., bran), and also through breeding and genetic enhancement [23,29,32]. The grain quality of cultivated cereal species is largely influenced by the cultivar used, the growing environment, and the fertilizer applied, which determines not only yield but also grain quality [33,34]. Cultivation conditions greatly modify the content of phenolic compounds [35].

The conventional (CONV) system of cultivation aims to maximize profits by applying high doses of nitrogen fertilizer and crop protection products [36,37]. The range of nitrogen application in CONV in cereal cultivation is usually in the range of 50 to 140 kg N ha^{-1} and they should not exceed 160 kg N ha^{-1}, while the maximum doses of N can be from 180 to 200 kg N ha^{-1} [38,39]. In triticale cultivation, higher grain quality was obtained in the CONV system compared to INTEG in which 150 kg N ha^{-1} was applied and crop protection included the application of three herbicides (diflufenican + iodosulfuron-methyl-sodium + mesosulfuron-methyl; 2,4 D + dicamba; clopyralid), two fungicides (flusilazole + carbendazim; difenoconazole + paclobutrazol), and an insecticide (deltamethrin + dimethyl-cyclopropanecarboxylate) [18]. However, due to the threat of environmental pollution, alternative cropping systems to CONV farming are increasingly being used to protect the soil by aiming to reduce the use of inputs, thus contributing to a decline in ecosystem disturbance [37]. In an integrated (INTEG) system, the use of pesticides and fertilizers is limited to the minimum (based on an assessment of soil fertility). The main aim of the INTEG system is thus to reduce the negative impact of agriculture on the natural environment [36,40]. The use of the INTEG system resulted in a higher efficiency of nitrogen use compared to CONV in the cultivation of winter wheat (165 and 208 kg·ha^{-1}, respectively) and barley (138 and 168 kg·ha^{-1}, respectively). In years with high variability of weather conditions and high pressure of diseases, limiting the use of fungicides from three treatments in the CONV system to only one in the INTEG system resulted in a decrease in the yield of these cereal species [41].

Many authors describe the characteristics of phenolic compounds in wheat grain, while there is insufficient information on the properties of triticale grain, grown under different production systems, especially in different parts of the grain.

Therefore, the aim of this study was to demonstrate the effect of CONV and INTEG cropping systems on antioxidant activity and content of selected PA in triticale grain. An important element was to compare the values of these parameters in the whole grain milling meal, flour, and grain husk of three cultivars of winter triticale. Such studies may provide valuable information for breeders in developing new triticale cultivars that can be widely used for consumption.

2. Materials and Methods

2.1. Plant Materials and Field Experiments

A field experiment was conducted at the Advisory Center in Boguchwała (49°59′ N, 21°56′ E) in south-eastern Poland, over three growing seasons, from 2019/2020 to 2021/2022. It was carried out using the randomized block method in triplicate, and the area of a single experimental plot to be harvested was 15 m^2.

The experiment included three cultivars of Polish winter triticale (x *Triticosecale* Wittm. ex A. Camus) cv. Belcanto (breeder Danko HH Sp. z o.o.), cvs. Meloman and Panteon (breeder Strzelce HR Sp. z o.o.).

Triticale cultivars were grown under INTEG and CONV cropping systems. In the INTEG system, protection measures were limited, rates of application of NPK mineral fertilizer were reduced, and one stem-shortening treatment was carried out using Moddus 25 EC (trinexapac-ethyl, 0.2 dm^3·ha^{-1}).

In the CONV system, comprehensive plant protection and higher rates of NPK fertilizer application were used (Table 1). One application of fertilizers containing phosphorus (superphosphate, 46%) and potassium (potassium salt, 60%) was applied before sowing triticale in both cropping systems. Application of nitrogen fertilizer was carried out before sowing (CONV system) and in the spring after the start of vegetation growth using ammonium nitrate (60%) and urea (46%) during the growing period of triticale. In addition, two foliar fertilizer treatments using Basfoliar 36 Extra (2.0 and 3.0 dm^3·ha^{-1}) and two stem-shortening treatments using Moddus 25 EC (trinexapac-ethyl, 0.4 dm^3·ha^{-1}) and Cerone 480 EC (ethephon, 0.5 dm^3·ha^{-1}) were carried out in the CONV system. Mineral fertilizer and plant protection products were applied at the respective developmental stages of wheat according to the BBCH scale [42].

Table 1. Mineral fertilization and plant protection products used in farming systems.

Specification	Farming Systems	
	Integrated	Conventional
Nitrogen (N)	90 kg·ha^{-1} (3 applications: 40–start of vegetation; 30–BBCH 32–33; 20–BBCH 54–56)	160 kg·ha^{-1} (4 applications: 20–presowing; 60–start of vegetation; 50–BBCH 32–33; 30–BBCH 54–56)
Phosphorus (P)	50 kg·ha^{-1}	90 kg·ha^{-1}
Potassium (K)	70 kg·ha^{-1}	120 kg·ha^{-1}
Herbicides	Expert Met 56 WG (metribuzin+ flufenacet) 0.35 L·ha^{-1} (BBCH 11–13)	
Fungicides	–	Delaro 325 EC (prothioconazole+ trifloxystrobin) 1.0 L·ha^{-1} (BBCH 32–33); Bukat 500 SC (tebuconazole) 0.5 L·ha^{-1} (BBCH 54–56)
Insecticides	Karate Zeon 100 CS (lambda-cyhalothrin) 0.35 L·ha^{-1} (BBCH 54–56)	

After harvesting the forecrop of broad beans (INTEG system) and winter wheat (CONV cropping system), the straw was chopped and a stubble cultivator was applied (depth 12–14 cm). This was followed by ploughing (depth 18–22 cm) in preparation for sowing, and before sowing, a cultivating unit was applied. Triticale cultivars in both systems were sown in the first decade of October at a rate of 350 seeds·m^{-2}. Triticale cultivars were harvested in late July/early August at full grain maturity (BBCH 89-92).

2.2. Soil Conditions

The experiment was set up each season on Haplic Cambisol (CMha) soil developed from silty clay [43]. In soil samples, the following were determined: soil pH—pH in 1 mol dm^3 KCl—potentiometrically, soil organic carbon content (%) by Tiurin's method [44], and N_{min} (kg·ha^{-1}) in 0.01 $CaCl_2$ solution [45]. The content of available forms phosphorus and potassium by Egner–Riehm's method [46] and magnesium by Schachtschabel's method [47].

2.3. Weather Conditions

Meteorological conditions in the triticale growing seasons from 2019/2020 to 2021/2022 were estimated on the basis of monthly precipitation sums, average air temperatures, and Sielianinov's hydrothermic coefficients (K). The weather data came from the weather station located at the Advisory Center in Boguchwała (49°59′ N, 21°56′ E). The Sielianinov's hydrothermic coefficients (K) were calculated according to the formula $K = p/0.1\Sigma t$, were: K—value of hydrothermal coefficient, p—signifies the monthly sum of rainfall, Σt—monthly sum of air temperatures > 0 °C from a given month [48].

2.4. Analytical Methods

2.4.1. Extraction of Phenolic Acids

The PA were extracted according to the micro-scale method of Zavala-López and García-Lara [49] with modifications: 2.5 mL of 2 M NaOH was added to 0.25 g of samples, and the mixture was homogenized for 2 min at 2500 rpm on a vortex (MSV-3500 Biosan, Riga, Latvia). After hydrolysis, the sample was acidified with 2.5 mL of 2 M HCl at pH 2. Lipids were removed with 4.0 mL of n-hexane. The PA were recovered three times using 4.0 mL of ethyl acetate. The ethyl acetate layer collected was evaporated to dryness (BÜCHI

B-720 Vacuum Controller, Flawil, Germany) and resuspended in 3 mL of 80% methanol and stored at −20 °C until analysis. Sample extraction was performed in duplicate and used for further analysis.

2.4.2. Determination and Quantification of Phenolic Acids (PA) by HPLC

Individual PA in extracts were analyzed using a Series 200 HPLC system (Perkin Elmer, Waltham, MA, USA) coupled with a Kinetex Core-Shell RP-C18 column (150 × 4.6 mm, 100 Å, 5 µm) and a diode array detector (DAD). Prior to HPLC analysis, samples were filtered through a 0.2 µm nylon filter (Ahlstrom GmbH, Helsinki, Finland). The mobile phase for analysis included solvent A (Millipore water acidified with 1% trifluoroacetic acid (*v*/*v*)) and solvent B (acetonitrile acidified with 1% trifluoroacetic acid (*v*/*v*)). Elution was performed using linear gradients from 5–40% B in 40 min, isocratic 90% of B for 5 min, and column equilibration in 5 min. At a column temperature of 30 °C and a flow rate of 1.0 mL/min, peaks were detected at 275 nm. PA were identified by comparison of UV absorption spectra and retention times with those of standards [50], while their quantification was completed using a five-point external calibration curve.

2.4.3. Spectrophotometric Analysis of Total Phenolic Content (TPC) and Antioxidant Activity (AOA)

Total phenolic content was determined by the modified Folin–Ciocalteu method [51]. In brief, 0.1 mL of extract (1:1; *v*/*v* diluted with 80% methanol) was mixed with 1.5 mL of dH_2O and 0.1 mL of Folin–Ciocalteu reagent (1:1; *v*/*v* diluted with water). After 5 min, 0.3 mL of sodium carbonate solution (20%; *w*/*v* diluted with water) was added. The homogenized reaction mixture was left to stand for 30 min in a dark place at room temperature, after which an absorbance reading at 750 nm was taken in a spectrophotometer (Specord 200, Analytik Jena GmbH, Jena, Germany). The content of total polyphenols was expressed as mg of gallic acid equivalents (GAE) per g of dm based on a gallic acid calibration curve. All measurements were performed in duplicate.

Antioxidant activity (AOA) was measured using a modified version of the DPPH Assay (2,2-diphenyl-1-picrylhydrazyl) by Brand-Williams et al. [52]. In summary, a 0.5 mM methanolic DPPH solution was prepared. The initial absorbance of the DPPH in methanol (control) was measured at 517 nm and did not change throughout the assay. A quantity of 0.2 mL of each extract was mixed with 2 mL of methanol and 1 mL of methanolic DPPH solution. Discolorations were measured at 517 nm (Specord 200, Analytik Jena) after incubation for 30 min at room temperature in the dark. The antioxidant activity was expressed as mg of Trolox equivalent (TE) per g of dm based on a Trolox calibration curve. The percentage of DPPH inhibition was calculated as: %DPPH inhibition = ((Ac − As) × 100)/Ac where Ac is the absorbance of the control, and As is the absorbance of the sample. All measurements were performed in duplicate.

2.5. Statistical Analysis

The results of the analyses of PA, TPC, and antioxidant activity were statistically processed using the TIBCO Statistica 13.3.0 program (TIBCO Software Inc., Palo Alto, CA, USA). The test results were analyzed by analysis of variance (ANOVA) using Tukey's post hoc test at $p \leq 0.05$. In addition, a two-way repeated measures ANOVA test (with part of the grain as a factor) was used to compare the phenolic acid content and antioxidant activity of the different parts of the grain (whole grain, flour, bran).

3. Results

3.1. Weather and Soil Conditions

Both the amount of N_{min} measured before sowing triticale and the soil organic carbon (SOC) content was low, ranging from 57.3 to 60.1 kg·ha^{-1} and 1.12 to 1.31%, respectively. The soil was slightly acidic and had very high phosphorus content, very high (2021/2022) and medium (2019/2020 and 2020/2021) potassium content, and very high magnesium content (Table 2).

Table 2. Soil properties before setting up the experiment (0–35 cm).

Parametr	2019/2020	2020/2021	2021/2022
pH in 1 mol dm^{-3} KCl	5.40	5.30	5.45
Soil organic carbon (%)	1.12	1.19	1.31
N_{min} (kg·ha^{-1})	57.3	59.4	60.1
Phosphorus (mg·kg^{-1} soil)	102	135	125
Potassium (mg·kg^{-1} soil)	140	160	273
Magnesium (mg·kg^{-1} soil)	136	152	147

The 2019/2020 season in the three-year study period was warmer during the growing season, with average temperatures 1.9 °C higher than the multi-year period (Figure 1A). By contrast, the 2020/2021 and 2021/2022 seasons also had air temperatures 0.9 °C higher than the multi-year period. A high precipitation deficit of 277.8 mm (43.2%) occurred in 2021/2022, while in 2019/2020 the amount of precipitation was 20.4% lower than the multi-year total. The 2020/2021 season had a relatively even distribution of precipitation among the individual months compared with the multi-year total; however, there was a deficit of precipitation in November and March and an excess in August.

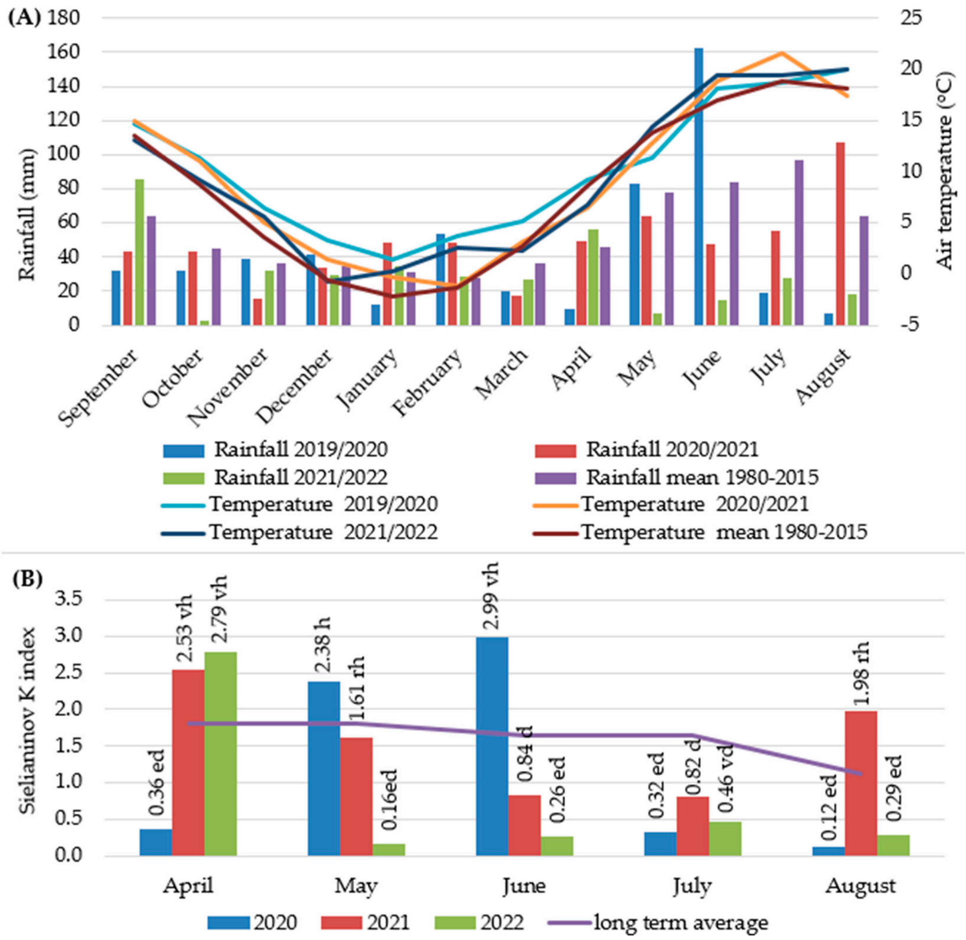


Figure 1. (**A**) Mean monthly air temperature and rainfall in 2019/2020–2020/2021; (**B**) Sielianinov's hydrothermic coefficients (K) in the growing seasons. K ≤ 0.4 extremely dry (ed), 0.4 < K ≤ 0.7 very dry (vd), 0.7 < K ≤ 1.0 dry (d), 1.6 < K ≤ 2.0 relatively humid (rh), 2.0 < K ≤ 2.5 humid (h), 2.5 < K ≤ 3.0 very humid (vh).

The hydrothermal conditions in the triticale crop during the spring-summer growing season were defined as rather dry (K = 1.23) in 2020, relatively humid (K = 1.97) in 2021, and dry (K = 0.79) in 2022. The most unfavorable extremely dry conditions were in April, July and August 2018 and May, June, and August 2022, while the months of April 2021 and 2022 and June 2020 were very humid (Figure 1B).

3.2. Effect of Cultivar and Cropping System on Phenolic Acids (PA) Concentration in Triticale Grain

A three-factor ANOVA showed that triticale cultivar (C) had a significant influence on the differential content of total phenolic acids (TPAs) and most of the PA analyzed (Table S1). Only for p-HB (whole grain) and SYR (whole grain and bran) acids was no significant effect of cultivar shown. The cropping system determined the content of TPAs and PA to a lesser extent than cultivar. A significant effect of the cropping system was found in total PA (flour and bran), p-HB (flour), SYR (whole grain and bran), FER (whole grain and bran), and SIN (flour and bran). The years of the experiment had a significant influence on the content of the PA studied in most cases. The effect of years on total PA (flour), p-HB (whole grain), and p-COU (whole grain and flour) was not found. In the research conducted, a statistically significant interaction between the experimental factors in all the parts of the grain that were analyzed was only found for FER. The interaction of year with cultivar (CxY) had a more significant effect on determining the values of the parameters studied than the interaction of the years with the cropping system (CxCS). The only parameters for which a significant effect was not found in the CxY interaction were total PA (flour), p-HB (grain), SYR (bran), and p-COU (flour). The interaction of experimental factors and years CxCSxY significantly influenced the content of most PA tested. Only with p-HB, p-COU, and SIN in flour was no statistically significant interaction observed.

The experiment showed a significant effect of cultivar (C), year (Y), and interaction between the factors CxCS and CxY on the TPC and antioxidant activity (AOA) in all parts of the grain analyzed (Table S2). For CS, a significant effect was only found for TPC (flour) and AOA (flour and bran). The CSxY interaction did not significantly determine the TPC (whole grain and bran), while the CxCSxY interaction did not affect AOA (bran).

The highest values of TPAs were found in the whole grain of cv. Meloman cultivated under the CONV system, in the flour of cv. Meloman under the INTEG system, and in bran in cv. Panteon under the INTEG system (Figure 2). The cultivation of triticale using the INTEG technology resulted in an increase in TPAs content compared to the CONV technology. However, only in flour and bran, the increase in TPAs content was statistically significant (by 5.4 and 6.8%, respectively). Cv. Meloman had the highest TPAs content relative to the other cultivars when measured in whole grain and flour. In the case of the bran measurement, in addition to cv. Meloman, the highest values for this parameter were also achieved by cv. Panteon. Cultivation of triticale in the 2019/2020 season resulted in the highest TPAs content in whole grain, while in the 2021/2022 season, this was in bran.

In the flour, the highest p-HB content was observed in the INTEG system for all cultivars, while in bran this was found in cv. Belcanto grown under the INTEG system and cv. Meloman under the CONV system (Figure 3). Triticale cultivation using the INTEG system only resulted in higher p-HB contents for flour Belcanto and Meloman than those of cv. Panteon. Cultivation of triticale in 2021/2022 resulted in the highest values for this parameter in bran, while in 2020/2021, this was only in flour.

Triticale cultivation under the INTEG system resulted in higher SYR values in grain and bran (Figure 4). Cvs. Belcanto and Panteon had a higher SYR content in flour than cv. Meloman by 12.4 and 21.0%, respectively. The 2019/2020 season influenced the obtaining of the lowest SYR values during the years of the study. The other years of the study were more favorable in terms of this acid content, with the exception of the 2021/2022 season in which the SYR content of whole grain was obtained at a similar level to that of the 2019/2020 season.

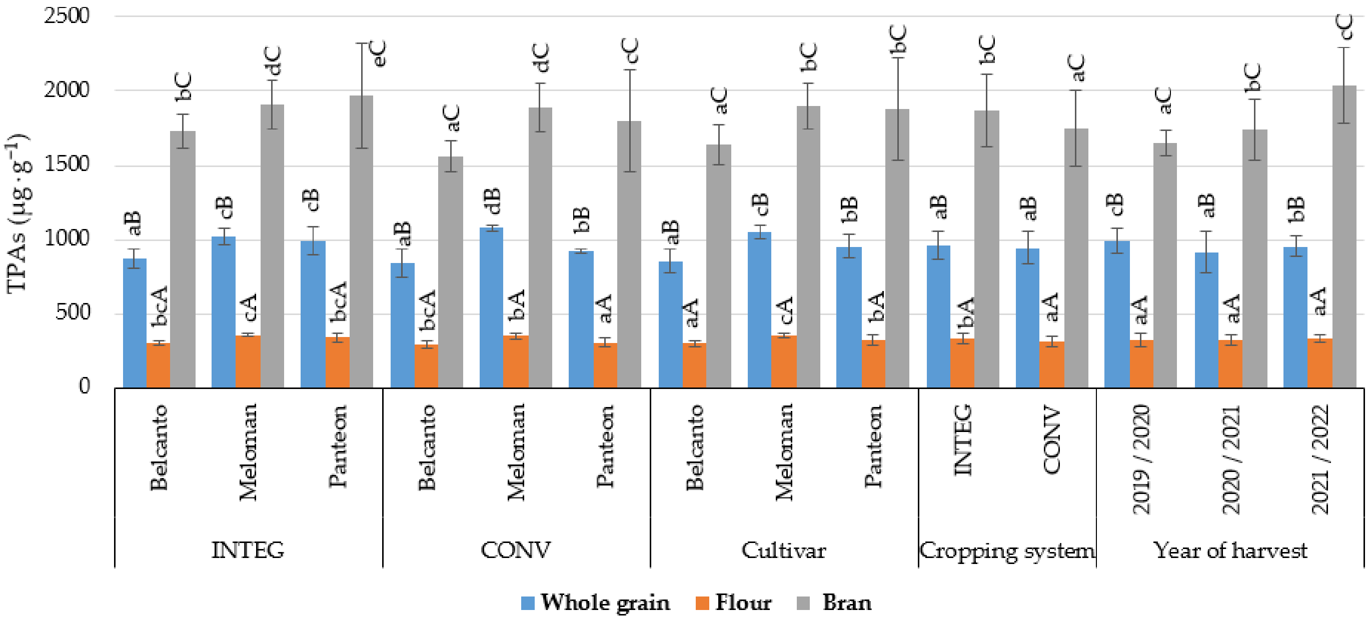


Figure 2. Total content of phenolic acids (TPAs) content on triticale grain and grain parts. Capital letters indicate significant differences between the means (whole grain, flour, and bran), lowercase letters indicate significant differences between the means within experimental factors.

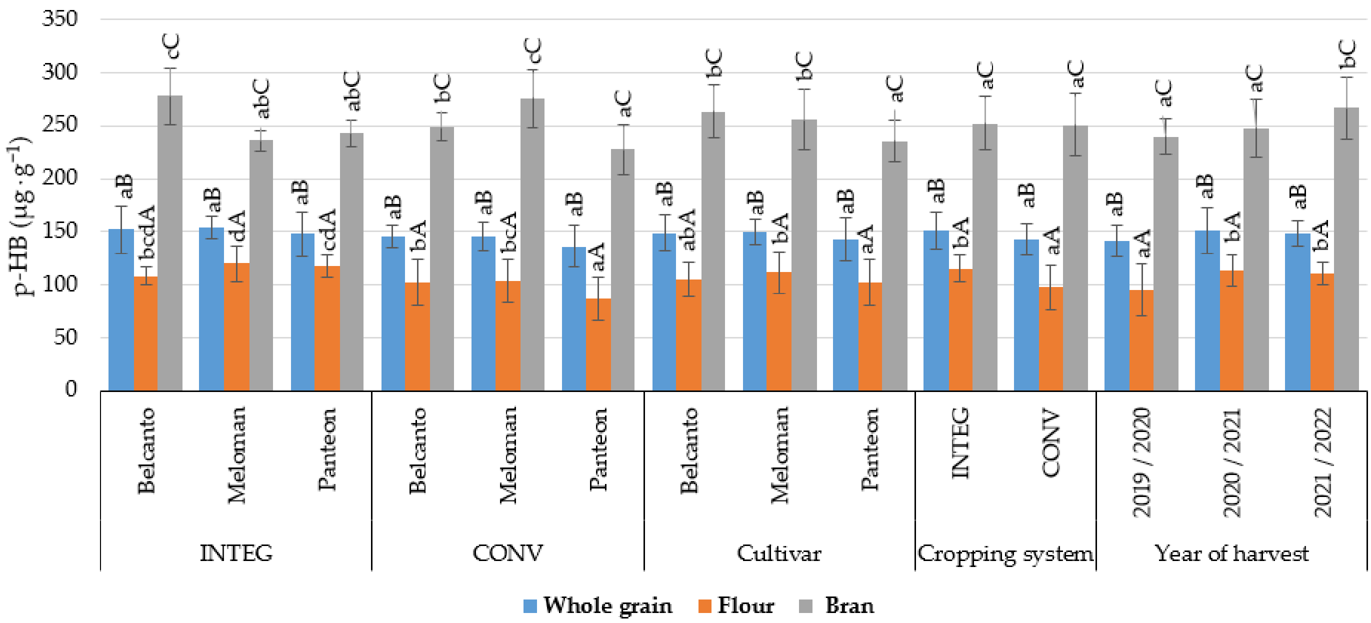


Figure 3. P-hydroxybenzoic acid (p-HB) content on triticale grain and grain parts. Capital letters indicate significant differences between the means (whole grain, flour, and bran); lowercase letters indicate significant differences between the means within experimental factors.

The highest p-COU content was found in cv. Meloman grown under the CONV system (Figure 5). The cultivation systems did not significantly affect the differences in the values of the test parameter. Cultivation of cv. Meloman resulted in the highest p-COU values for grain, flour, and bran. Only in the case of bran was a significant impact of seasons 2020/2021 and 2021/2022 found on the increase in the content of p-COU.

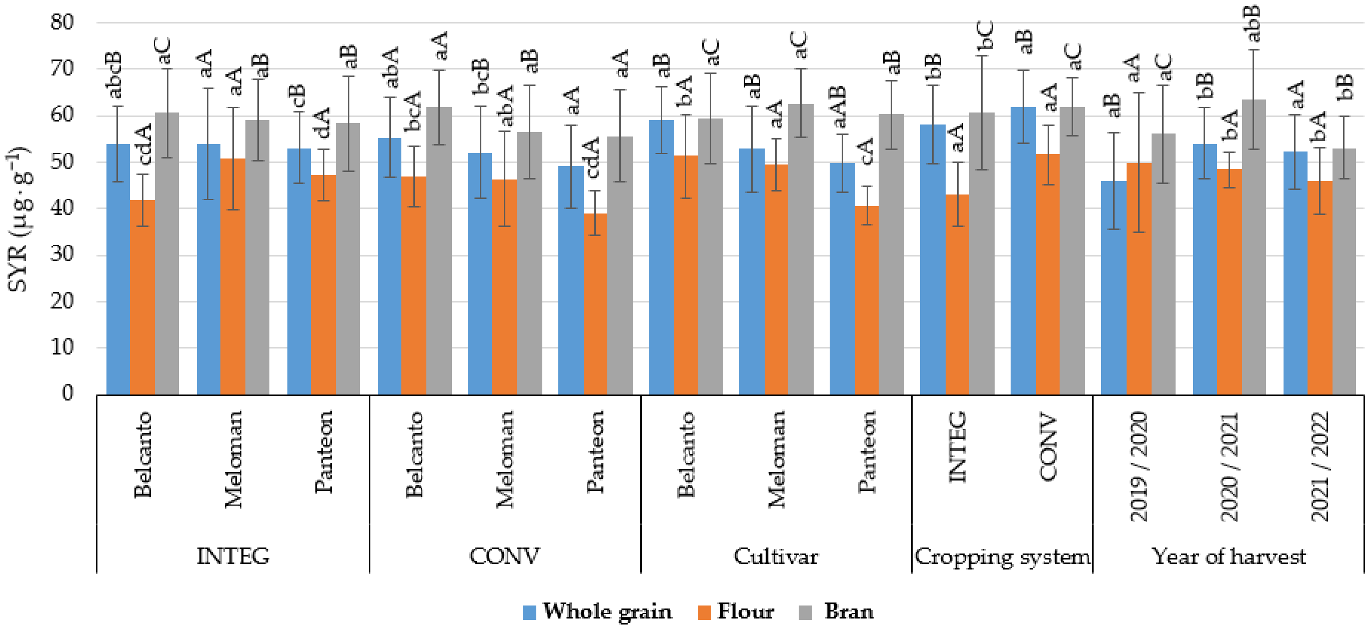


Figure 4. Syringic acid (SYR) content on triticale grain and grain parts. Capital letters indicate significant differences between the means (whole grain, flour, and bran); lowercase letters indicate significant differences between the means within experimental factors.

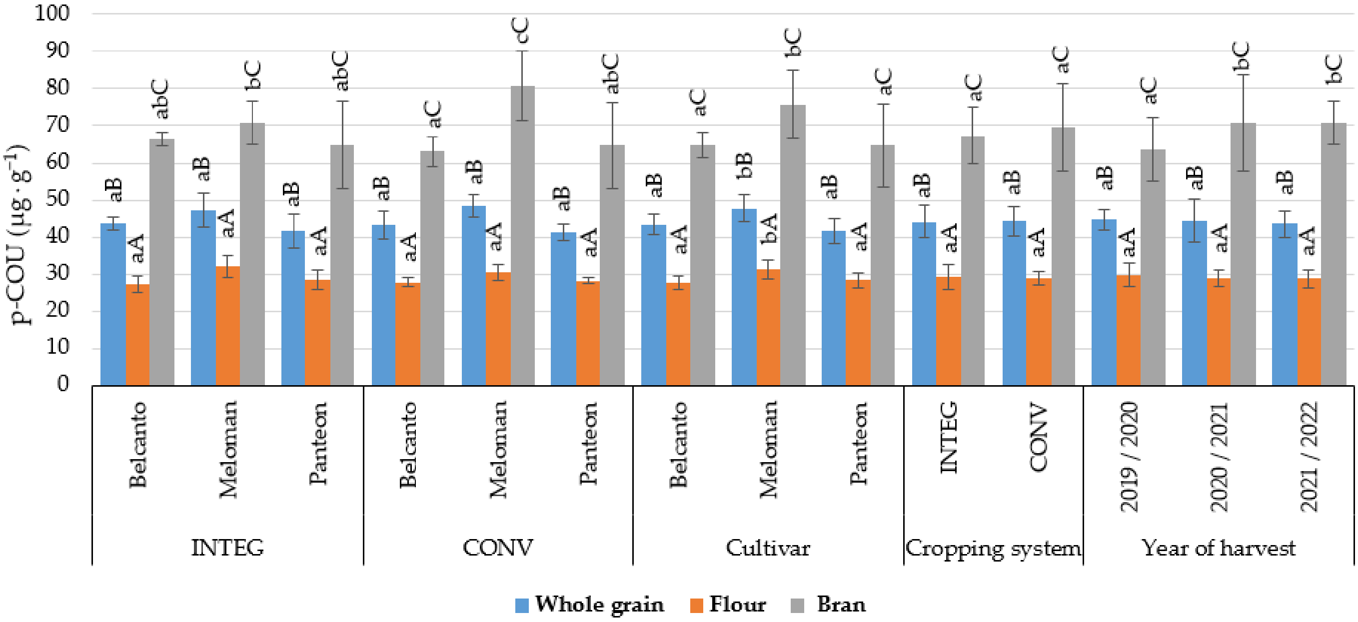


Figure 5. P-coumaric acid (p-COU) content on triticale grain and grain parts. Capital letters indicate significant differences between the means (whole grain, flour, and bran); lowercase letters indicate significant differences between the means within experimental factors.

The significantly highest FER content was found for cv. Meloman grown in the CONV system (1247 µg·g^{-1}) (Figure 6). Triticale cultivation in the CONV system resulted in an increase in FER content in the whole grain (by 1.2% with respect to cultivation in the INTEG system), while an opposite relationship was found for bran. Cultivation of triticale under the INTEG system resulted in a 3.5% higher FER content compared to CONV. Meloman had the highest content of FER in all parts of the grain tested by a significant margin when compared to other cultivars.

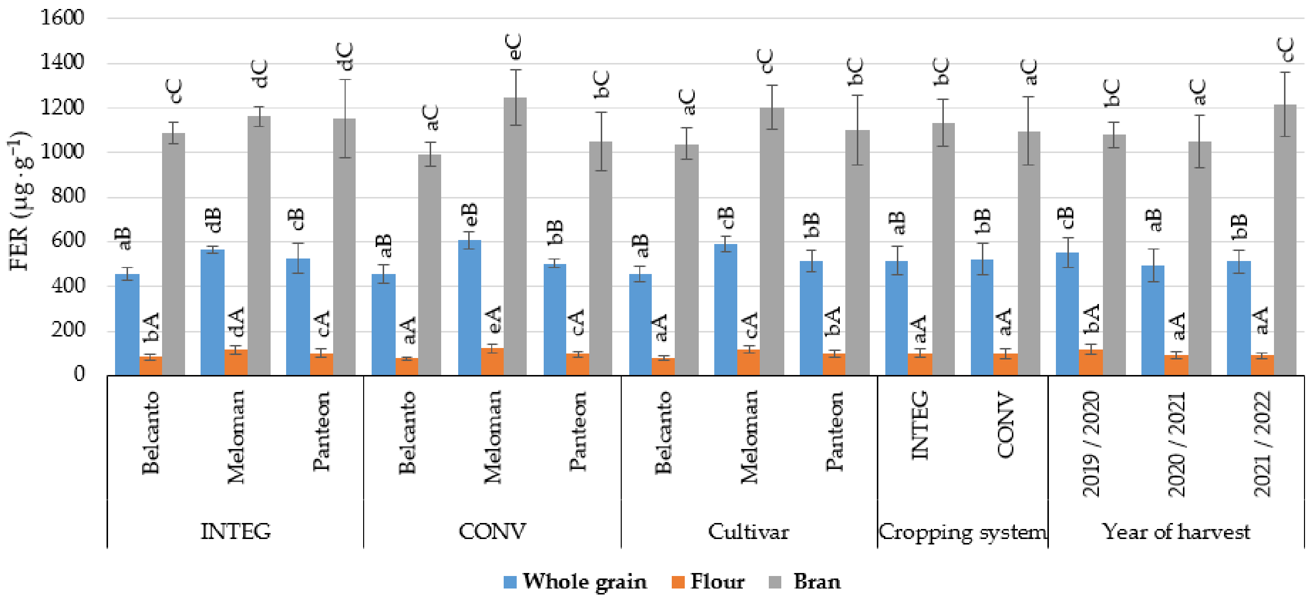


Figure 6. Ferulic acid (FER) content on triticale grain and grain parts. Capital letters indicate significant differences between the means (whole grain, flour, and bran); lowercase letters indicate significant differences between the means within experimental factors.

Under both cropping systems the highest SIN content in cvs. Meloman and Panteon was found in the whole grain (Figure 7). A similar relationship was also observed for bran, but the highest SIN content was only found to be significant for cv. Panteon cultivated under the INTEG system. The cropping system only produced differences in the SIN content only for flour and bran. Cultivation using the INTEG system resulted in higher (by 27.8%) SIN content for bran than cultivation using the CONV system, and lower (by 7.4%) for flour. Among the test cultivars, the lowest content of SIN was found in the cv. Belcanto in all types of samples. The 2021/2022 season was conducive to obtaining the highest SIN contents in all grain parts analyzed. For whole grain, however, its high content was also obtained in the 2019/2020 season.

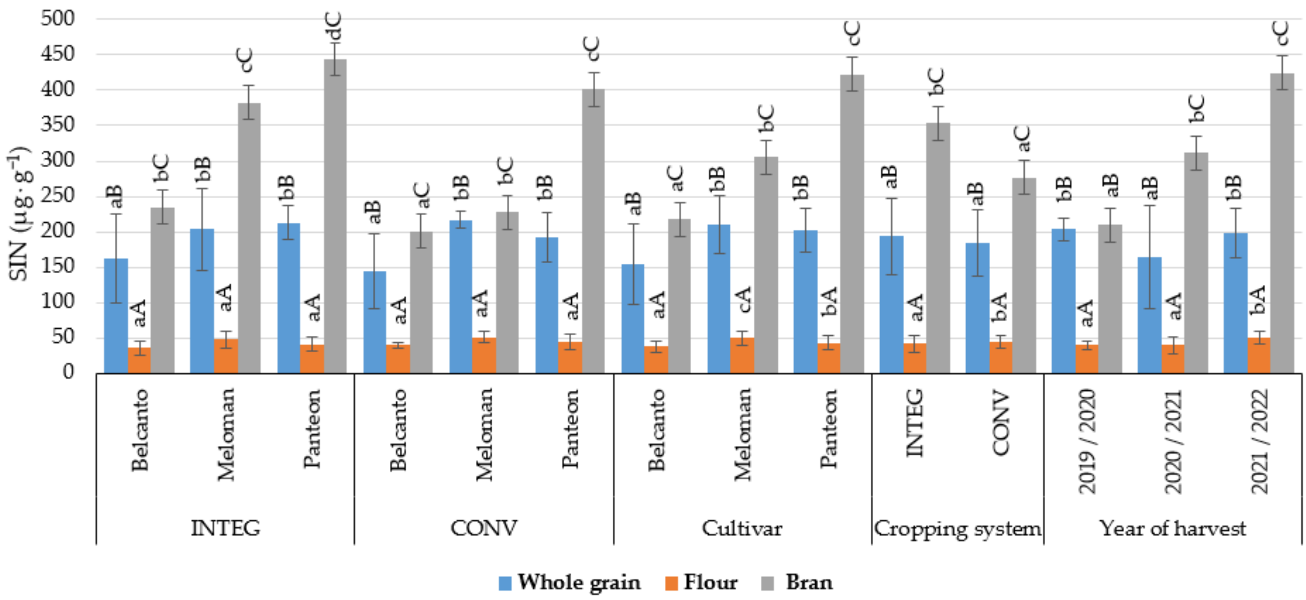


Figure 7. Sinapic acid (SIN) content on triticale grain and grain parts. Capital letters indicate significant differences between the means (whole grain, flour, and bran); lowercase letters indicate significant differences between the means within experimental factors.

3.3. Effect of Cultivar and Cropping System on Total Phenolic Content (TPC) and Antioxidant Activity (AOA) in Triticale Grain

The highest total phenolic content (TPC) was obtained in whole grain and bran for cvs. Meloman and Panteon regardless of cultivation system, and in flour for cv. Panteon cultivated under the INTEG and CONV system and cv. Belcanto under the INTEG system (Figure 8). Cvs. Meloman and Panteon had the highest TPC values in whole grain and bran, while cv. Panteon had the highest TPC in flour. The lowest values of the test parameter were found in the 2020/2021 season in whole grain, in the 2021/2022 season in flour, and in the 2019/2020 and 2020/2021 seasons in bran.

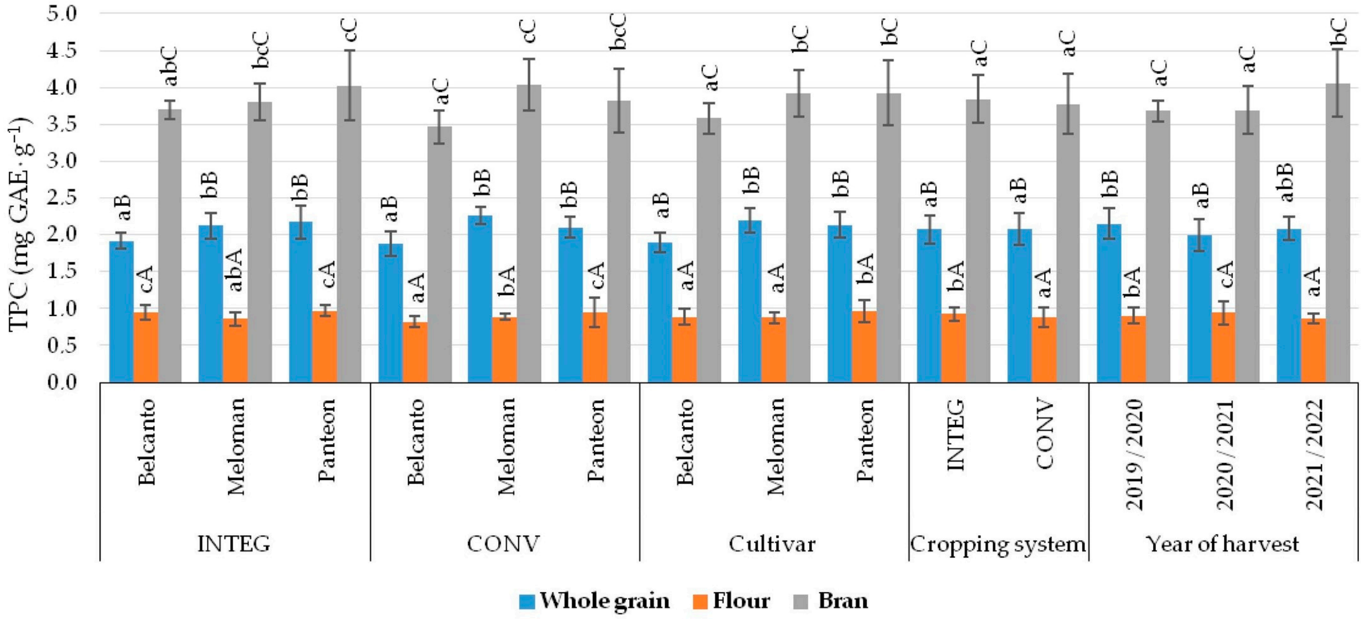
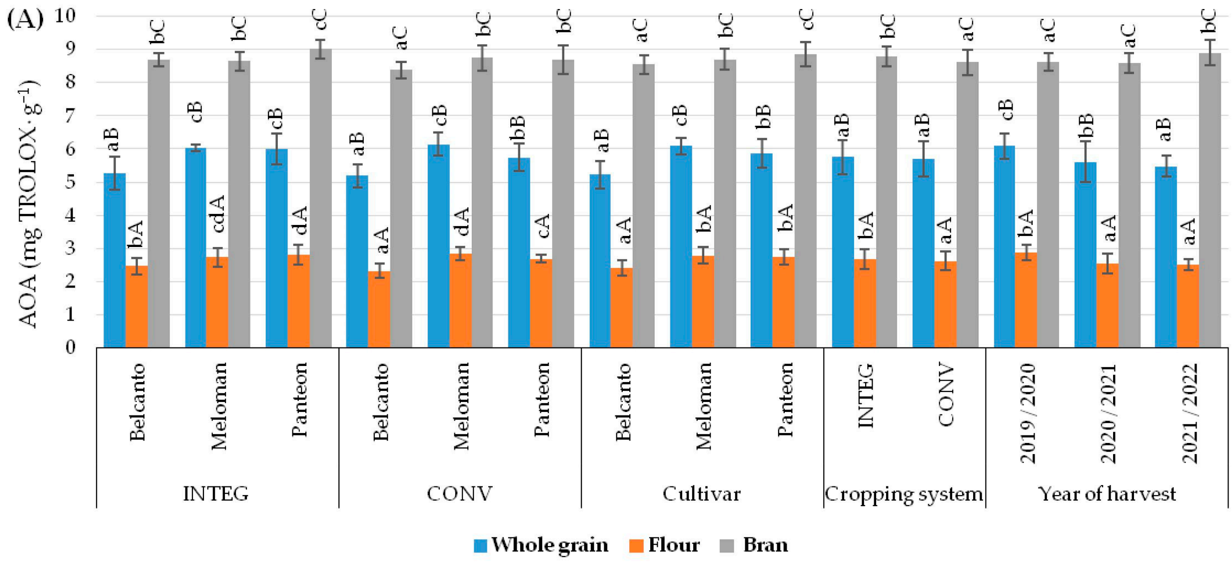


Figure 8. Total phenolic content (TPC) on triticale grain and grain parts. Capital letters indicate significant differences between the means (whole grain, flour, and bran); lowercase letters indicate significant differences between the means within experimental factors.

The highest AOA value in triticale grain determined by the Trolox method was observed in cv. Meloman regardless of the cultivation system used, in cv. Panteon in flour and whole grain grown under the INTEG system, and in cv. Panteon in bran grown under the INTEG system (Figure 9A). The value of the analyzed parameter only in the case of flour and bran was influenced by the cultivation system. The use of the INTEG system resulted in an increase in AOA of 1.9% in flour and 2.1% in bran. The lowest AOA among the test cultivars was found in cv. Belcanto. The cultivation of triticale in the 2019/2020 season resulted in the highest values of this parameter measured in whole grain and flour, while in the bran the highest values were obtained in the 2021/2022 season.

The highest AOA values determined by the DPPH method were obtained in the whole grain and flour of cvs. Meloman and Panteon grown under the INTEG system and cv. Meloman under the CONV system (Figure 9B). When measured in bran, the highest values of this parameter were obtained in cv. Panteon under the INTEG system. When measured in flour, cv. Belcanto had lower DPPH values than cvs. Meloman and Panteon, by 18.9 and 17.3%, respectively. In the grain bran, on the other hand, cv. Panteon obtained higher DPPH values than cvs. Belcanto and Meloman, by 4.1 and 1.7%, respectively. The highest DPPH value for whole grain and flour was obtained in 2019/2020, while for bran it was obtained in the 2021/2022 season.

Similarly to the content of phenolic acids, the highest AOA was found in bran and the lowest in flour.



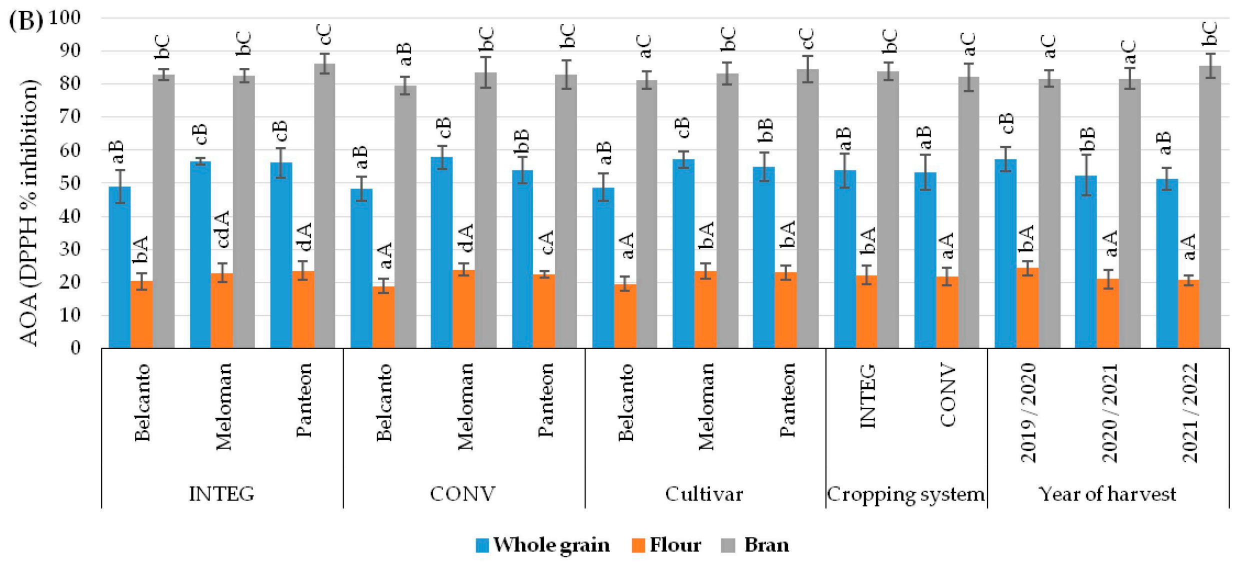


Figure 9. Antioxidant activity (AOA) in triticale grain and grain parts. (**A**) TROLOX, (**B**) DDPH. Capital letters indicate significant differences between the means (whole grain, flour, and bran), lowercase letters indicate significant differences between the means within experimental factors.

4. Discussion

In the experiment, the years of research significantly affected the antioxidant activity in the parts of grain tested. The highest TPC and AOA and the content of PA were obtained in the 2019/2020 and 2021/2022 seasons when the least favorable weather conditions occurred. The significant impact of weather conditions on antioxidant activity during the growing season confirms the role of the plant defense system in counteracting environmental stresses [53]. Similar dependencies were obtained by Zrckova et al. [54], Horvat et al. [2], and Laddomada et al. [55] in their research. They obtained higher PA contents in experiments with wheat grown in years with less favorable hydrothermal conditions.

In the experiment that has been conducted, concentrations of phenolic compounds depended on the cultivar and part of the grain. In studies conducted on various species of cereals, Ivanisová et al. [56] showed that the total antioxidant potential in flour fractions was lower than in bran fractions, which was confirmed in our research with triticale. However, lower antioxidant activity and total PA content were noted in flour than in the bran. In this study, the share of total PA in triticale grain ranged from 842–1077 µg·g^{-1} (whole grain), 306–355 µg·g^{-1} (flour), and 1558–1967 µg·g^{-1} (bran). In the grain of the triticale cultivars examined, FER was dominant among PA. Generally, the main hydroxycinnamic acids found in cereals are FER, p-COU, and SIN [21]. FER with the highest antioxidant activity [57] is the most abundant PA in cereals and is present in the aleurone layer, pericarp, and embryo cell walls, but also in smaller amounts in old endosperm [1,21,58].

The cultivar has a large effect on the content of phytochemical compounds in triticale grain [58]. A similar relationship was also demonstrated in our research. The highest content of PA was found in the grain of cv. Meloman, and the lowest was found in cv. Belcanto. The experiment also showed significant differences in the antioxidant activity and the content of phenolic compounds between the triticale cultivars analyzed, which may correspond to the different levels of enzymes involved in the metabolism [17]. Additionally, other studies conducted on wheat showed that the content of phenolic compounds is determined by genetic factors [21,59,60].

In addition to the cultivar, nitrogen fertilization is also an important factor affecting the yield and quality parameters of cereal grains [61]. The cultivation systems used in our research differed in terms of doses of nitrogen fertilizer. Research by Ma et al. [62] showed that fertilization with nitrogen affects wheat phenolic composition. In their research, an increased dose of nitrogen fertilizer (from 180 to 300 kg N·ha^{-1}) resulted in an increase in the concentration of PA. A different finding was presented by Tian et al. [63], who found no effect of N fertilizer application on the accumulation of phenolic compounds in wheat. Buczek et al. [60] observed an increase in the content of PA in wheat grain grown using the organic system (ORG) compared to the INTEG and CONV systems, where higher doses of nitrogen fertilizer were used.

In this study, triticale cultivation using the CONV system resulted in a decrease in the concentration of PA: p-HB (whole grain, bran), SYR (flour), p-COU (all parts of the grain), FER (flour), and SIN (whole grain). However, no effect of cultivation systems on the accumulation of phenolic acids was observed for p-HB (flour), SYR (whole grain, bran), FER (bran), and SIN (bran). The lack of effect of these cultivation systems on the concentration of phenolic compounds in grain may suggest that the level of nitrogen fertilizer use does not affect the modulation of the expression of the enzyme phenylalanine ammonia lyase (PAL), which is considered a key enzyme in the phenylpropanoid pathway converting the amino acid phenylalanine to phenolic compounds [64].

Previous research showed that the intensification of agricultural practices, such as increased application of nitrogen fertilizer, and the use of fungicides and micronutrients leads to a decrease in the concentration of phenolic compounds. However, so far it is not known which of these factors has the greatest impact on the decrease in the level of PA [65]. Research by Stumpf et al. [64] showed that with the increase in nutrients availability, the content of phenolic compounds decreases, which indicates an inverse relationship between the availability of nitrogen and the concentration of phenolic compounds in cereal leaves. This relationship is explained by the dilution effect caused by greater biomass accumulation with increased nitrogen supply, which results in lower concentrations of phenolic compounds. Canopy density usually increases in fields with higher application of nitrogen fertilizer, which increases the mutual shading of plants and may have a negative impact on the concentration of phenolic compounds. It is therefore assumed that plants fertilized with lower doses of nitrogen are more stressed by excess light energy, and therefore they accumulate more antioxidants, protecting themselves against photodamage.

In the present study, triticale cultivars showed a different reaction to the cropping system that is applied in the accumulation of PA. These results can be partly explained by the differences in the ability of the test cultivars to use nitrogen fertilizers in the process of protein accumulation in grain. On the basis of the results obtained, it can be concluded that the content of PA in triticale grain is determined by the genome, but it also depends on the course of weather conditions and the cultivation system and also varies depending on the part of the grain.

5. Conclusions

PA is a group of organic chemical compounds that exhibit diverse biological activities in the human body. These compounds are considered an essential component of the human diet and exhibit antioxidant, anticancer, antimicrobial, cardioprotective, and anti-inflammatory properties. The study carried out showed the influence of genotype, cropping systems, and hydrothermal conditions in individual years on the PA profiles, TPC, and AOA of triticale grains. The unfavorable hydrothermal conditions occurring in the 2019/2020 and 2021/2022 seasons (rainfall deficit) increased TPA, mainly in whole grain. Grain cv. Meloman had the highest PA content in whole grain, flour, and bran and cv. Belcanto had the lowest, with differences of 22.7, 18.2, and 15.7%, respectively. Cultivation of triticale under the CONV vs. INTEG cropping system resulted in reduced amounts of TPAs in flour and bran and PA: p-hydroxybenzoic acid (p-HB) in flour, syringic acid (SYR) in whole grain and bran, and ferulic acid (FER) and sinapic acid (SIN) in bran. The CONV cropping system also caused a decrease in antioxidant activity (AOA) in flour and bran. In most of the cases analyzed, the highest antioxidant activity and content of PA were found in bran, and the lowest in flour.

The presence of PA, In particular in by-products (bran) and in whole triticale grain, indicates that this cereal can be grown using the INTEG cropping system for consumption purposes and serve as a source of valuable antioxidants for various food and nutraceutical applications.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agriculture13051078/s1, Table S1: Three-factor analysis of variance (ANOVA) about the effects of triticale growing seasons (Y; 2019/2020-2021/2022), cultivar (C; Belcanto, Melo-man, Panteon), and cropping systems (CS; integrated (INTEG) and conventional (CONV) system), and their bi-/tri-interactions on phenolic acids (PA) content in triticale (whole grain, flour, and bran) (F/*p* value)—for year averages; Table S2: Three-factor analysis of variance (ANOVA) about the effects of triticale growing seasons (Y; 2019/2020-2021/2022), cultivar (C; Belcanto, Meloman, Panteon), and cropping systems (CS; integrated (INTEG) and conventional (CONV) system), and their bi-/tri-interactions on antioxidant activity in triticale (whole grain, flour and bran) (F/*p* value)—for year averages.

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