

## THE IMPACT OF EXTRUSION ON THE CONTENT OF POLYPHENOLS AND ANTIOXIDANT ACTIVITY OF RYE GRAINS (*SECALE CEREALE* L.)

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**Background.** Polyphenols which are included in a group of food antioxidants have a beneficial impact on human organism, as they prevent the occurrence of life style diseases, including cardiovascular diseases and cancer. Cereals are the main source of polyphenols in a human diet, and especially rye is characterized by high level of these compounds. Many technological processes applied in food production cause a decrease of polyphenols in rye and reduce their antioxidative activity. The aim of the study was to estimate quantitative changes of polyphenols in rye grains subjected to extrusion, under varying process conditions and establish the antioxidant activity of the obtained rye extrudates.

**Material and methods.** The materials were extrudates prepared from grains of three rye cultivars, namely Amilo, Rostockie and Agrikolo. Extrusion was performed in a single-screw laboratory extruder Brabender 20 DN. Contents of phenolic acids and apigenin in analysed samples was checked by HPLC. Antioxidant activity was measured by FRAP and EPR methods.

**Results.** All rye extrudates contained ferulic acid levels (53-104 mg/100 g d.m.) approximately 112-316% higher as compared to raw material (25 mg/100 g d.m.). The highest antioxidant activity (using of FRAP method) was measured in extrudates prepared at extrusion parameters: 14% moisture of raw material and 180°C but the lowest at 20% moisture and 120°C. The analysis of spin label reduction kinetics (in EPR method) allowed to conclude, that its reduction was greater for extrudates (except extrudates obtained at moisture content 20% and 120°C) as compared to raw material.

**Conclusions.** Content of polyphenols and antioxidative activity of rye extrudates is highly dependant on the moisture content of raw material and extrusion temperature.

**Key words:** antioxidant activity, EPR, FRAP, phenolic acids, rye extrudates

## INTRODUCTION

Modern science of food and nutrition aims to define the “optimal” diet, considering these food components, which help to preserve good health and wellbeing. Among them the special role is played by antioxidants, as they are involved in suppression of cardiovascular diseases and several forms of cancer [Baublis et al. 2000, Kaur and Kapoor 2001, Astley 2003, Scalbert et al. 2005].

Antioxidants form a heterogeneous group of chemicals, including both endogenic superoxide dismutase, glutathione, tocopherols, as well as compounds of plant origin – polyphenols. Polyphenols include 5 groups of compounds: phenolic acids (benzoic and cinnamic acid derivatives), flavonoids, tannins and stilbenes [Oszmiański 1995, Rice-Evans et al. 1997]. Their action may be based on the scavenging of free radicals, that initiate oxidation processes; chelating metal ions, that catalize oxidation; inhibiting oxidating and activating antioxidating enzymes [Joseph et al. 2005, Lambert et al. 2005, Vita 2005].

Whole, unprocessed grains of wheat, rye, barley, oat and other cereals are, among other plant raw materials, the excellent source of bioactive compounds (dietary fibre, resistant starch, vitamins, minerals), including antioxidants from the polyphenol family [Andreasen et al. 2000, Weidner et al. 2000, Karamać et al. 2002, Peterson et al. 2002]. This is why cereals grains are recommended in the prophylactic of chronic diseases, including CHD [Willett 1998, Liu et al. 1999, Richardson 2003] and several types of cancer [Adlercreutz 1990]. Among cereals, rye grains have an average level of polyphenols, i.e. low molecular weight compounds, that exhibit antioxidant properties [Zieliński 2002]. There are five main phenolic acids present in the rye grains: ferulic, sinapic, caffeic, *p*-coumaric and vanillic acids [Weidner et al. 1999, Zieliński et al. 2001]. The presence of polyphenols as well as their activity depends on the plant species, cultivar and state of maturity and changes under technological treatment of raw material [Nicoli et al. 1999, Weidner et al. 2000, Zieliński et al. 2001].

The aim of the study was to estimate quantitative changes of polyphenols in rye grains subjected to extrusion, under varying process conditions and establish the antioxidant activity of the obtained rye extrudates.

## MATERIAL AND METHODS

### Materials

The material consisted of extrudates prepared from grains of 3 rye cultivars: Amilo (ZA), Rostockie (ZR) and Agrikolo (ZEA). The rye grains was subjected to extrusion in a single-screw laboratory extruder Brabender 20 DN (Duisburg, Germany) equipped with a 3:1 screw and a 3 mm die. Screw speed was maintained at 190 rpm while two temperature profiles, 80-100-120°C and 120-160-180°C, were applied. Prior to extrusion, the moisture of the rye grains to be processed was equilibrated to 14% or 20%.

## Methods

**Determination of phenolic acids and flavonoids.** The HPLC analysis of phenolic acids and flavonoids were carried out on a HPLC apparatus consisting of Merck-Hitachi L-7455 diode array detector (DAD) and pump L-7100 equipped with D-7000 HSM Multisolvent Delivery System (Merck-Hitachi, Tokyo, Japan). The separation was performed on a Li ChroCART® 125-3 Purospher® RP-18 (5 µm) Merck column. Column oven temperature was set to 30°C. 80% acetonitrile in 4.5% formic acid (reagent A) and 2.5% acetic acid (reagent B) were used as an eluent. The flow rate was 1 mL/min. The concentration of reagent A was stepwise increased to reach 15% after 7 min, 20% after 15 min and 100% after 16 min. After 10 min of elution the concentration of reagent A was reduced to 0% to stabilize the column. During analysis the solvent were degassed in Merck degasser. Data logging were monitored at the following wavelengths: phenolic acids (sinapic, ferulic, diferulic, caffeic and *p*-coumaric acids) at 320 nm, vanillic acid at 280 nm and apigenin at 340 nm. Retention times and spectra were compared to those of pure standards within 200-600 nm.

**Determination of antioxidant activity – FRAP method (*Ferric Reducing Ability of Plasma*).** The FRAP (*Ferric Reducing Ability of Plasma*) assay was performed according to Benzie and Strain [1996] and modification by Barton et al. [2005]. To 10 mL test-tubes, 3.3 mL of acetate buffer (pH = 3.6), 0.330 mL of FeCl<sub>3</sub> (20 mmol/L) and 0.330 mL of tripyridyltriazine (10 mmol/L in 40 mmol/L HCl) were added and heated in a water bath at a temperature of 37°C for 5 min. Then, 0.330 mL of the methanol-acetone extracts of analysed material were added. Absorbance at 593 nm was measured after 15 min in disposable plastic absorption cells using a spectrophotometer UV-530 (Jasco, Japan). The blank determination was performed in the same way with a blank extract. The method was calibrated by the use FeSO<sub>4</sub> standard solution at the concentration range 0-1.5 mM/L.

**Electron paramagnetic resonance (EPR) measurement of antiradical activity.** Measurements were obtained using a home-made EPR L-band (1.2 GHz) spectrometer constructed in cooperation with Dartmouth Medical School, Hanover, New Hampshire, USA. The set up of the spectrometer was as follows: maximum power of microwaves 16 mW, modulation amplitude 2.2 G, time constant of the phase discriminator 20 ms, field modulation frequency 33 kHz. The magnetic field scan was adjusted to 100 G. The antiradical activity was determined using stable free radical – DPPH (2,2-diphenyl-1-picrylhydrazyl) (Sigma). The 0.250 mL of the extract was added to 0.750 mL of 33 mM DPPH methanol solution. The time of a scan was set at 20 s. Each spectrum was the average of four individual scans. Measurements were performed twice at room temperature.

The spectra have been measured, stored and manipulated using custom-designed software. The computer program for data acquisition was written in the C programming language. It collects and stores up to 32 arrays of 1024-4096 data points, which contain the observed spectra. Further details are given in Walczak et al. [2005].

**Statistical analysis.** The results were statistically compared basing on the Duncan's test, at the significance level 0.05, with the use of computer programme Statistica 8.0PL. All the measurement were done at least in duplicate.

## RESULTS AND DISCUSSION

Table 1 demonstrates the content of phenolic acids: sinapic, diferulic, ferulic, caffeic, *p*-coumaric and vanillic acid, as well as one flavonoid: apigenin in the grains of three rye cultivars: Amilo, Rostockie and Agrikolo, as well as in the extrudates prepared from these rye cultivars. At the same time the total amount of polyphenols was analysed by summing up all the identified phenolic acids and apigenin. Among the analysed rye cultivars, the highest amounts of those phenolic compounds was observed for Agrikolo cultivar (47.04 mg/100 g d.m.) and the lowest for Amilo (38.7 mg/100 g d.m.). In accordance to earlier studies of other authors [Weidner et al. 1999, 2000, Andreasen et al. 2000, Zieliński et al. 2001] it was found, that ferulic, sinapic, caffeic, vanillic and *p*-coumaric acids are the main antioxidants of rye grains, and their content depends on the cultivar. Moreover it was stated, that the ferulic acid is the dominant phenolic acid in rye, which corresponds to the studies of others [Rybka et al. 1993, Weidner et al. 1999, 2000, Andreasen et al. 2000, Zieliński et al. 2001].

Table 1. Phenolic acids and apigenin content of rye grains before and after extrusion (mg/100 g d.m.)

Samples	Sinapic acid	Ferulic acid	Diferulic acid	Caffeic acid	p-coumaric acid	Vanillic acid	Apigenin	Total
ZA	5.91 c*	25.01 a	0.77 a	2.79 a	1.35 a	1.78 a	1.06 a	38.70
ZA14/120	2.63 a	56.47 b	0.91 a	2.66 a	2.59 b	2.80 b	1.82 ab	69.86
ZA14/180	2.95 ab	63.60 bc	1.14 a	2.81 ab	2.59 b	1.82 a	1.46 a	76.40
ZA20/120	3.09 ab	59.71 b	0.72 a	2.82 ab	1.76 ab	2.76 ab	1.64 ab	72.50
ZA20/180	5.33 b	104.38 c	1.14 a	5.02 c	3.66 c	3.19 c	3.33 c	126.04
ZR	6.41 d	25.34 a	0.94 a	2.61 a	1.93 a	2.97 c	1.82 a	42.02
ZR14/120	3.11 ab	57.46 c	1.01 a	3.19 b	3.39 c	2.08 a	1.86 a	72.08
ZR14/180	3.41 c	58.88 d	0.93 a	3.58 c	3.41 c	1.90 a	2.11 ab	68.60
ZR20/120	2.94 a	53.26 b	0.83 a	2.73 a	2.77 b	2.39 b	1.84 a	70.33
ZR20/180	3.26 bc	56.82 c	0.89 a	3.27 bc	3.62 cd	2.31 b	1.88 a	74.11
ZEA	7.02 b	28.43 a	0.89 a	2.80 b	1.79 a	3.53 d	2.59 b	47.04
ZEA14/120	7.53 bc	54.09 bc	1.69 b	2.68 ab	3.46 bc	0.90 a	1.67 a	72.01
ZEA14/180	9.19 d	65.31 d	1.89 b	3.21 bc	3.67 c	1.35 b	2.06 ab	86.70
ZEA20/120	5.73 a	51.69 b	1.79 b	2.23 a	3.11 b	1.80 c	1.84 a	68.18
ZEA20/180	8.30 cd	56.45 c	1.71 b	2.53 a	3.09 b	1.71 c	1.71 a	75.50

ZA, ZR, ZEA – rye grains cv. Amilo, Rostockie and Agrikolo, respectively, constituting the raw material for extrusion.

ZA14/120 – rye extrudate of Amilo cv. obtained from the raw material of 14% moisture at 120°C (other symbols are built in the same manner).

\*Different letters denote mean values that statistically differ from one another (Duncan test, at  $\alpha = 0.05\pm$ ) within selected cultivars.

Until recently it was thought, that technological processes used in food industry are the cause of degradation of native antioxidants [Grela et al. 1999, Nicoli et al. 1999, Viscidi et al. 2004], but the recent reports prove, that their impact on the amounts and quality of polyphenols is ambiguous [Zieliński et al. 2001], which is also supported by the present results. In the effect of extrusion the total amount of identified phenolic compounds increased, in comparison to unprocessed rye grains (Table 1). However the contents of selected phenolic acids and apigenin before and after extrusion can not give univocal conclusions (Table 1). Regarding the grain of Amilo cultivar, it was observed that the amounts of sinapic acid in extrudates were 10-55% lower than before extrusion, while the level of ferulic acid was 2-4 times higher (Table 1). The content of diferulic acid in the grains of this cultivar after extrusion was not changed, while the amounts of caffeic, *p*-coumaric and vanillic acids and apigenin were increased on average by: 27%, 96%, 48% and 94%, respectively. The most significant rise of ferulic (by 320%), caffeic (80%), *p*-coumaric (by 170%) and vanillic (180%) acids and apigenin (by 214%) was observed when the moisture content of extruded material was 20% and the temperature profile of extruder's sections was set to 180°C in comparison to other extrudates prepared from these cultivar and unprocessed grain (Table 1). Similar changes in the amounts of phenolic acids and apigenin were found in extrudates prepared from rye cultivar Rostockie. When the moisture content of extruded grain was 20% and temperature profile was set to 180°C, the increase in the following phenolic acids was observed: ferulic (by 130%), caffeic (by 25%), *p*-coumaric (by 87%), which was less than in case of extrudate prepared at the same conditions from rye cultivar Amilo (Table 1). The exception was vanillic acid, which content was reduced in rye extrudates on average by 30% in comparison to raw material (grain *cv.* Rostockie). The apigenin level was not affected by extrusion. Extrudates prepared from rye grains of cultivar Agrikolo were characterised by increased amounts of sinapic, ferulic, diferulic and *p*-coumaric acids, and the content of other phenolic acids and apigenin was reduced in comparison to the raw material (Table 1). The extrudate obtained at 180°C from grain with 14% moisture content, contained the highest amounts of sinapic (9.2 mg/100 g d.m.) ferulic (65.31 mg/100 g d.m.), caffeic (3.2 mg/100 g d.m.) and *p*-coumaric (3.67 mg/100 g d.m.) acids in comparison to other extrudates prepared from these cultivar and unprocessed grains (Table 1).

Irrespective of the rye cultivar and extrusion parameters, the extrudates contained almost 2-times more ferulic acid than unprocessed rye. This acid was dominating both in extrudates (80% of all identified polyphenols) and raw grains (60% of all identified polyphenols; Table 1, Fig. 1), which is in accordance with studies of other authors [Zieliński et al. 2001]

Zieliński et al. [2001] observed a drastic decrease of vanillic, sinapic and caffeic acid after extrusion of rye, which is in disagreement with the presented data, that suggest dependance of the changes in above mentioned acids on the cultivar of rye and extrusion parameters. It can be concluded that the amount of analyzed polyphenols depends both on the rye cultivar and on the process conditions. Taking into account these parameters, some correlations may be found. All the analysed samples of rye extruded at 180°C contained more sinapic, ferulic and caffeic acid, than extrudates processed at 120°C (Table 1). The amount of *p*-coumaric acid in rye cultivars Amilo and Rostockie conditioned to 14% moisture content, and extruded at 120 or 180°C were not changed, in contrast to Agrikolo cultivar. It was observed that the content of apigenin in all analyzed rye samples extruded at 120°C was not changed, irrespective of the moisture

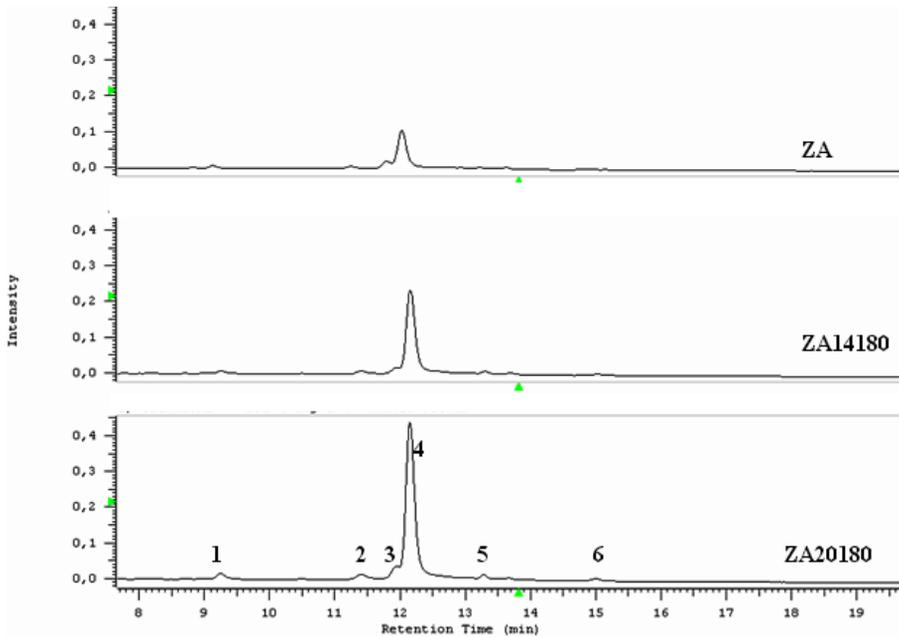


Fig. 1. The comparison between HPLC (320 nm) chromatograms of phenolic compounds present in the extracts of unprocessed (ZA) and extruded (ZA14180; ZA20180) rye samples: 1 – caffeic acid, 2 – p-coumaric acid, 3 – sinapic acid, 4 – ferulic acid, 5 – diferulic acid, 6 – apigenin, ZA – rye grains cv. Amilo, ZA14/180 – rye extrudate of Amilo cv. obtained from the raw material of 14% moisture at 180°C (other symbols are built in the same manner)

content in the raw material (Table 1). It should be noted, that the total amount of identified polyphenols was higher when extrusion was performed at 180°C, irrespective of rye cultivar, with the exception of cv. Rostockie (Table 1). The moisture content of raw material was not directly corresponding to the amounts of polyphenols identified in extrudates. The rise in phenolic compounds (polyphenols), and especially ferulic acid in the processed material after extrusion (extrudates) may be explained as the effect of their release from cell walls during extrusion, which could result in elevated antioxidant (and antiradical) activity of the product.

Antioxidant activity of methanol-acetone extracts, prepared from rye extrudates was established by means of FRAP (Table 2). It was found, that all the applied extrusion parameters resulted in enlargement of antioxidant activity of the processed material. The only exception was 20% moisture content of the raw material and 120°C, when antioxidant activity was decreased on average by 30% in comparison to the raw grains (Table 2). Low antioxidant activity of such extrudates may be caused by low extrusion temperature and high moisture content, which according to Nicoli et al. [1999] causes the formation of pro-oxidizing agents, that could diminish antioxidant activity of the product.

It was also observed, that irrespective of the rye cultivar, the highest antioxidant activity was found for extrudates obtained at 180°C from the grains with 14% moisture

Table 2. Antioxidant activity (FRAP) of rye grains before and after extrusion

Extrusion parameters	Grain of rye cultivar		
	Amilo (ZA)	Rostockie (ZR)	Agrikolo (ZEA)
	FRAP, mM Fe/kg d.m.		
Raw materials	10.90 b*	11.71 ab	11.98 b
14/120	10.30 b	14.28 bc	13.65 c
14/180	18.08 c	17.26 c	16.55 d
20/120	6.62 a	9.19 a	8.55 a
20/180	11.13 bc	14.49 bc	13.68 c

\*Different letters denote mean values that statistically differ from one another (Duncan test, at  $\alpha = 0.05 \pm$ ) within selected cultivars.

content. The rise in antioxidant activity was in this case: 66%, 45% and 40% for Amilo, Rostockie and Agrikolo cultivars, respectively in comparison to the raw materials (Table 2). The other conditions (14%/120°C and 20%/180°C) resulted in the same antioxidant activity of all the examined rye cultivars. Irrespective of the analysed rye cultivar, the application of extrusion temperature 180°C positively affected activity of rye extrudates, which could be explained by higher amount of total polyphenols (Table 1) in extrudates obtained at this temperature. According to Pulido et al. [2000] the efficiency of phenolic acids, measured by FRAP, is as follows: galic acid > caffeic acid > ferulic acid, which is in accordance with the results showing the highest antioxidant activity of rye extrudates obtained at 14% moisture content of raw material and 180°C, only in case of cultivars Rostockie and Agrikolo, which was characterised by highest amounts of ferulic and caffeic acids (Tables 1, 2). High antioxidant activity of rye cultivar Amilo, obtained at 14% moisture content and 180°C may be explained by formation of other biologically active compounds, that were not identified in this work, but exhibit antioxidant properties for example: tannins, tocopherols nad proteins [Nicoli et al. 1999].

The analysis of reduction kinetics of spin marker (DPPH) by methanol – acetone extracts (EPR studies) of grains of three rye cultivars showed, that the initial rate of DPPH free-radical scavenging was forming in the following order: Agrikolo, Rostockie and Amilo (reduction by 46%, 40% and 22% after 5 min, and 76%, 60% and 57% after 10 min, respectively). After 15 min the reduction of spin marker by those three extracts was comparable and from 20 min to the end of the experiments almost identical (after 60 min the reduction of spin marker was as follows: Agrikolo – 91.5%, Rostockie – 90%, Amilo – 92%; Fig. 2 A). According to Samotyja et al. [2002] and Goupy et al. [1999] the antioxidant activity (and antiradical activity) does not only depend on the total content of polyphenols, but also on the individual composition of the compounds (in plant), which display various activity in respect to specified radical [Karamać et al. 2005]. Karamać et al. [2005] evaluated the scavenging activity of free radical DPPH by selected acids: caffeic, sinapic, ferulic, vanillic and *p*-coumaric to be respectively: 49.58%, 32.73%, 25.57%, 0.16%, and 0.04%. The highest initial reduction of DPPH by extracts from rye cultivar Agrikolo should probably be explained by highest content of identified polyphenols, as well as higher content of acids with high efficiency of DPPH scavenging

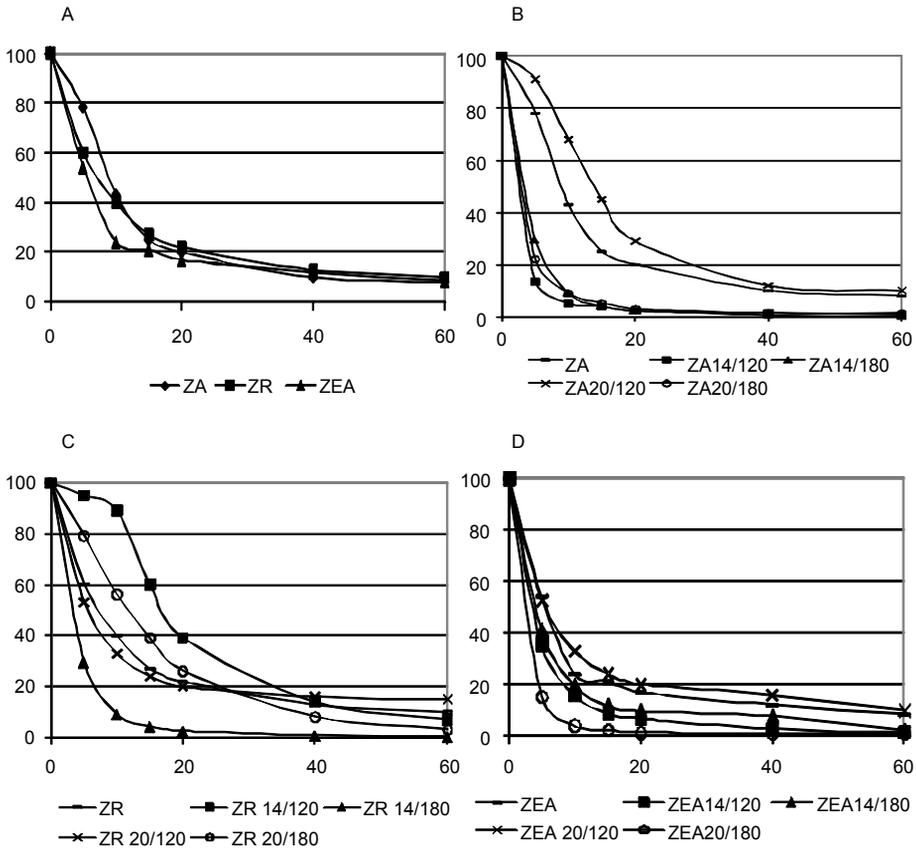


Fig. 2. Kinetics of the spin marker (DPPH) reduction by the extracts of rye grains and extrudates: X – time, min, Y – efficiency of spin marker reduction, %; A – extracts of grains of three rye cultivars, B – extracts of extrudates prepared from rye grains cv. Amilo, C – extracts of extrudates prepared from rye grains cv. Rostockie, D – extracts of extrudates prepared from rye grains cv. Agrikolo; ZA, ZR, ZEA – rye grains cv. Amilo, Rostockie and Agrikolo, respectively, constituting the raw material for extrusion; ZA14/120 – rye extrudate of Amilo cv. obtained from the raw material of 14% moisture at 120°C (other symbols are built in the same manner)

(sinapic and ferulic acids) in this rye cultivar, in comparison to other cultivars of this cereal (Table 1). After 60 min of experiments, the scavenging of DPPH by all extracts of rye cultivars was set to stable level, which can be connected to the constant content of the most effective phenolic acid – caffeic acid in analysed extracts.

It was found, that extracts obtained from rye extrudates were characterised by higher initial rate of reduction of spin marker in comparison to raw material (Figs 2 B-2 D). It was probably caused by the release of polyphenols from the cell walls of plant tissues at high temperature. In the extrudates from Amilo cultivar the reduction of paramagnetic signal (after 10 min) was 94.7, 90.9 and 91% for extrusion parameters: 14%/120°C, 14%/180°C and 20%/180°C, respectively. The extrudate obtained at parameters

20%/120°C was significantly different from others (32% reduction of the marker; Fig. 2 B). The highest antiradical activity of the extrudates was found for extrudate obtained at 20% moisture of raw material and 180°C (Table 3), which could be due to the highest content of identified polyphenols (126.04 mg/100 g d.m.), especially with high scavenging activity: caffeic (5.02 mg/100 g d.m.), sinapic (5.33 mg/100 g d.m.) and ferulic (104.38 mg/100 g d.m.) in comparison to other extrudates and raw material (Table 1). In case of extrudates from Rostockie cultivar the low rate of DPPH scavenging (until 10 min) was observed for extrudate processed at 14% moisture and 120°C (the degree of DPPH reduction – 11%) and the highest rate of scavenging was displayed by extrudate obtained at 14% moisture and 180°C (the degree of DPPH reduction – 90.9%; Fig. 2 C). The extrudates from Rostockie cultivar prepared at extrusion parameters 14 and 20% of moisture of raw material and 180°C displayed high (and comparable) antiradical activity (Table 3), which could be connected to the large amounts of most effective phenolic acids: caffeic, ferulic and sinapic (Table 1). Such a high activity of this type extrudates may be caused by presence of other compounds that possess antiradical activity, and were not evaluated, such as tannins. Lower rates of free radical scavenging were found in case of rye cultivar Agrikolo, at extrusion parameters 20% moisture and 120°C (47-90%), in comparison to other parameters (70-98%; Fig. 2 D). In analogy, the highest antiradical activity for Agrikolo extrudates was observed, when the material was processed at 14 and 20% moisture and 180°C (Table 3).

Table 3. Antiradical activity (EPR) of rye grains before and after extrusion

Extrusion parameters	Grain of rye cultivar		
	Amilo (ZA)	Rostockie (ZR)	Agrikolo (ZEA)
	mg Trolox/g d.m.		
Raw materials	20.50 ab*	20.61 c	20.64 ab
14/120	22.01 b	20.51 b	21.78 c
14/180	22.11 bc	21.98 d	21.80 c
20/120	20.05 a	18.96 a	20.53 a
20/180	22.16 c	22.05 d	22.20 d

\*Different letters denote mean values that statistically differ one from another (Duncan test, at  $\alpha = 0.05\pm$ ) within selected cultivars.

It was also observed, that the degree of reduction of paramagnetic marker was higher for rye extrudates (except those obtained at 20%/120°C) than for unprocessed material. Rye extrudates were characterised by higher initial rate of DPPH scavenging, which was reduced (less intensive) in the next phase, but all the time higher than for unprocessed rye. High rate of DPPH reduction by rye extrudates was due to the release of large amounts of free-radical scavenging agents – polyphenols, which were active during the whole period of measurement, which resulted in higher activity of rye extrudates in comparison to raw material i.e. unprocessed rye grains (Table 3).

## CONCLUSIONS

1. All the rye extrudates contained almost 2-times more quantities of ferulic acid in comparison to raw material. This acid was found in largest quantities both in raw material (60% of identified polyphenols) and after processing (80% of identified polyphenols).

2. The content of phenolic compounds in rye extrudates depended on the rye cultivar and extrusion parameters. At 180°C the content of total amount of identified polyphenols and selected acids: caffeic, ferulic and sinapic was higher than at 120°C.

3. The highest antioxidant activity (using of FRAP method) was measured in extrudates prepared at extrusion parameters: 14% moisture of raw material and 180°C but the lowest at 20% moisture and 120°C.

4. Higher antiradical activity (using of EPR method) of rye extrudates in comparison to raw material was found in most cases, except the extrusion parameters: 20% moisture and 120°C.

5. Content of polyphenols and antioxidative activity of rye extrudates is highly dependant on the moisture content of raw material and extrusion temperature.

## ACKNOWLEDGMENTS

We greatly appreciate kind and helpful comments of Dr Tadeusz Walczak (Dartmouth Medical School, Hanover, New Hampshire, USA). This project was supported by the Polish Ministry of Science (grant PBZ-KBN-094/P06/2003/29).

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## WPLYW PROCESU EKSTRUZJI NA ZAWARTOŚĆ POLIFENOLI I AKTYWNOŚĆ ANTYOKSYDACYJNĄ ZIAREN ŻYTA (*SECALE CEREALE L.*)

**Wstęp.** Polifenole, które należą do grupy antyoksydantów pokarmowych działają dobroczynnie na organizm człowieka, ponieważ przeciwdziałają różnym chorobom cywilizacyjnym, włączając choroby sercowo-naczyniowe i nowotworowe. Głównym źródłem polifenoli w diecie człowieka są ziarna zbóż, a wśród nich znaczną ilością tych związków charakteryzuje się ziarno żyta. Liczne procesy przetwórcze stosowane w przemyśle spożywczym wpływają jednak na zmianę zawartości tych związków w życie oraz ich aktywność antyoksydacyjną. Dlatego też celem badań było określenie ilościowych zmian związków fenolowych w ziarnie żyta po ekstruzji (w różnych warunkach procesu) oraz oszacowanie aktywności antyoksydacyjnej otrzymanych ekstrudatów żytnich.

**Materiał i metody.** Materiałem do badań były ekstrudaty z ziaren trzech odmian żyta: Amilo, Rostockie i Agrikolo. Ekstruzję przeprowadzono w jednoślismakowym ekstruderze firmy Brabender 20DN. W analizowanych próbkach oznaczono zawartość kwasów fenolowych i apigeniny za pomocą HPLC. Oszacowano również aktywność antyoksydacyjną za pomocą metody FRAP i EPR.

**Wyniki.** Wszystkie ekstrudaty żytnie zawierały o 112-316% (ok. 53-104 mg/100 g s.m.) więcej kwasu ferulowego w odniesieniu do surowca (ok. 25 mg/100 g s.m.). Największą aktywnością antyoksydacyjną (wyznaczoną za pomocą metody FRAP) charakteryzowały się ekstrudaty sporządzone przy parametrach 14% wilgotności materiału wyjściowego i temperaturze 180°C, a najmniejszą przy parametrach: 20%/120°C. Analizując kinetykę redukcji znacznika spinowego (w metodzie EPR), stwierdzono, że stopień redukcji tego znacznika był większy dla ekstrudatów (oprócz ekstrudatów otrzymanych przy wilgotności materiału wyjściowego 20% i temperaturze 120°C) w porównaniu z surowcem.

**Wnioski.** Zawartość polifenoli oraz aktywność antyoksydacyjna ekstrudatów żytnich zależy w dużej mierze od wilgotności materiału wyjściowego i temperatury procesu ekstruzji.

**Słowa kluczowe:** aktywność przeciwutleniająca, EPR, FRAP, kwasy fenolowe, ekstrudaty żytnie

*Accepted for print – Zaakceptowano do druku: 29.07.2010*

*For citation – Do cytowania: Gumul D., Korus J., Czechowska K., Bartoń H., Folta M., 2010. The impact of extrusion on the content of polyphenols and antioxidant activity of rye grains (*Secale cereale L.*). *Acta Sci. Pol., Technol. Aliment.* 9(3), 319-330.*