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Effect of genotype and crop management systems on the content of antioxidants in hulless and covered spring barley

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Abstract

This paper deals with studies of the content of some antioxidants in barley (*Hordeum vulgare* L.), which is one of the major cereal species with extensive application in food products with increased nutritional value. We studied the effect of genotype and environment on the content of α-tocopherol and total polyphenol content in grain and grain oil and phenolic compounds in grain of two covered and four hulless barley genotypes grown under one organic and three conventional management systems with increasing agrochemical input during 2011–2012. α-Tocopherol in grain and oil during both years ranged between 1.49–14.51 mg kg^{-1} and 9.24–88.32 mg 100 g^{-1}, respectively, with particularly low values in comparatively cooler and wetter year 2012. Total polyphenol content in grain and oil ranged between 81.66–140.13 and 0.19–8.52 mg gallic acid equivalents (GAE) 100 g^{-1}, respectively. We identified 13 phenolic compounds with the highest concentration for ferulic acid, followed by *p*-coumaric and syringic acids. No clear significant effect of crop management systems on the content of antioxidants was found. Conditions of the growing year had the greatest effect on the content of α-tocopherol, total polyphenol content and most phenolic compounds. α-Tocopherol content in barley grain and oil was generally higher under conventional management with higher input level; higher mean content was found for some hulless genotypes, although there was no significant difference between hulless and covered types. Higher total polyphenol content in grain was generally found under organic and lower input conventional management systems. Total polyphenol content was higher for covered barley genotypes in comparison to hulless genotypes. Higher total polyphenol content concentration in oil was found under medium intensive conventional management with covered genotypes being superior in 2011. The content of most phenolic compounds tended to increase with decrease of agrochemical input level and higher content was in covered than in hulless genotypes with some exceptions.

Key words: α-tocopherol, barley grain oil, conventional crop management, organic crop management, phenolic compounds, total polyphenol content.

Introduction

Barley (*Hordeum vulgare* L.) is one of the major cereal species and besides animal feed which is its main application, it can be successfully used in food production, e.g., bread baking. Partial substitution of wheat flour with barley flour increases the overall antioxidant properties in bread and makes the bread healthier due to significant amount of dietary fibre (Holtekjølen, Knutsen, 2011). It is recommended to use barley in a range of other products like healthy muffins which contain 2.4 times higher amount of phenolics than those made of wheat surpassing also oat, corn and rice and therefore possessing the highest antioxidant activity (Soong et al., 2014).

Barley oil has been recognized as potential functional oil. The extracts derived from barely grain were found to be quite effective towards suppressing the primary and secondary oxidation products in sunflower oil suggesting that barley grain might be used for protection of vegetable oils from oxidation (Anwar et al., 2010). It is demonstrated that barley grain oil can be used for improving oxidative stability of rapeseed, flax and hemp oil (Ivdre et al., 2011). Barley grain extract in 70% acetone shows similar scavenging activity to one of the most commonly used synthetic antioxidants and therefore can be used as a source of natural antioxidants and as a possible food supplement or in pharmaceutical industry (Liu, Yao, 2007). Tocols in most cases show better results than synthetic antioxidants butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) (Seppanen et al., 2010).

Barley is rich in vitamin E if compared to other major cereal species. Vitamin E is a complex of eight isomers, four tocopherols and four tocotrienols called tocols. Tocols act as antioxidants and are able to reduce neurodegenerative, cancer and cardiovascular diseases and cholesterol level. Compared with other cereals, barley is richer in α-tocotrienol but has moderate amount of α-tocopherol (Idehen et al., 2017). Žilić et al. (2011) reported that α-tocopherol content in hulless barley is lower than in hulless oat and rye but higher than in wheat. α-Tocotrienol has the largest content proportion among the tocol isomers in barley grain, contributing about 48%; for α-tocopherol it is 18–34% (Idehen et al., 2017). α-Tocotrienol and α-tocopherol are highly significantly

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correlating with vitamin E in contrast to the other tocol isomers (Ehrenbergerová et al., 2006). Do et al. (2015) find α-tocotrienol as the only vitamin E isomer significantly correlating with antioxidant capacity.

Barley is found to be richer in total polyphenol content and subsequently with higher antioxidant potential if compared to einkorn, wheat, rye, triticale and oat (Menga et al., 2010; Žilić et al., 2011; Fogarasi et al., 2015) ensuring protection against heart diseases and cancer (Idehen et al., 2017). A number of phenolic compounds have been reported in barley grain with ferulic acid being the dominant one and followed by *p*-coumaric acid (Žilić et al., 2011; Gamel, Abdel-Aal, 2012; Zhu et al., 2015; Gangopadhyay et al., 2016; Idehen et al., 2017). Positive relationships are found in barley between antioxidant activity and total polyphenol content, caffeic, vanillic and chlorogenic acids, epicatechin and catechin, but contradictory results are published regarding ferulic acid (Žilić et al., 2011; Gamel, Abdel-Aal, 2012; Lahouar et al., 2014).

A number of studies find significant effect of barley genotype on the concentration of tocols, their isomers or vitamin E (Peterson, Qureshi, 1993; Cavallero et al., 2004; Ehrenbergerová et al., 2006; Do et al., 2015). Limited research results are published on genotype effect on total polyphenol content in barley: significant effect is reported by Menga et al. (2010), whereas Eticha et al. (2010) found genotype significant in only one of the two testing years. More studies are done on wheat showing significant effect of genotype on total phenolic (Mpofu et al., 2006; Menga et al., 2010; Bellato et al., 2013) and phenolic acid content (Mpofu et al., 2006).

Few results are published on the effect of environment and crop management systems, on tocols and phenolics in barley. Positive effect of chemical treatment and fertilization on the content of vitamin E and tocols has been reported by Ehrenbergerová et al. (2006). Significant effect of growing location for barley α-tocotrienol with similar percentage of total variance to that for genotype is shown by Peterson and Qureshi (1993). Cavallero et al. (2004) found significant effect of growing location and genotype × location interaction for most of tocol isomers. Similar results are obtained for tocols in wheat genotypes (Lampi et al., 2010; Lv et al., 2013). Most of the investigations do not find significant differences in tocopherol content in crops grown under conventional and organic management systems (Johansson et al., 2014). However, Tsochatzis et al. (2012) report decrease in content of tocopherols and increase in content of tocotrienols in organically grown barley grain compared to conventional grain. In respect of total polyphenol content the effect of environment is shown to be larger than that of genotype for wheat and barley (Mpofu et al., 2006; Menga et al., 2010; Bellato etal., 2013). Most of the studies report significantly higher level of various phenolic compounds in organically grown crops in contrast to those produced under conventional farming (Johansson et al., 2014). Konopka et al. (2012) found increase in total polyphenol content but decrease in phenolic acids in wheat grain grown under organic fertilization if compared to mineral fertilization.

The aim of our study was to find out the effect of genotype and environment including growing year, conventional farming system with three crop management systems aimed to achieve different yield levels and organic farming system on concentration of α-tocopherol, total polyphenol content and phenolic compounds in grain and grain oil of hulless and covered spring barley.

Materials and methods

Barley genotypes. Spring barley (*Hordeum vulgare* L.) six genotypes were selected for this study, two of them were recently released covered barley cultivars 'Jumara' and 'Rubiola', one recently released hulless barley cultivar 'Irbe' and three advanced hulless breeding lines. The lines were chosen considering their potentially elevated content of health promoting biologically active compounds. Lines PR-4651 (pedigree Merlin/Sw-1291// Danuta/3/Merlin/Sw-1291) and PR-5099 (Washonubet/ Sw-1291//Heris) are waxy barley with relatively high concentrations of β-D-glucans. Line PR-5099 derives from cross with waxy cultivar 'Washonubet' providing high concentration of tocols as reported by Ehrenbergerová et al. (2006). Line PR-3808 (Sw-1291/3/Tolar//Linga/ CIMMYT 112) contains in its pedigree a source with very high content of protein and lysine.

Growing conditions. The trial was carried out in Priekuļi (lat. 57°19′ N, long. 25°20′ E), Latvia in 2011 and 2012 under conventional (C) crop management system with three agrochemical input levels aiming to obtain potential yield of 4 t ha^{-1} (C1) and 6 t ha^{-1} (C2 and C3) and under organic (O) crop management system. In C3 foliar fertilizer was applied in addition to the same input of agrochemicals as in C2. Under conventional system 10.5 m^2 plots were arranged according to split-plot design; under organic system plot size was 12.3m^2 with randomized complete block design, all in four replications. The trials were arranged on loamy sand *Luvisol* (*LV*) (Table 1). Under organic system in 2012 the harrowing was followed by strong rainfall and therefore hindered plant development and possibly caused plant density and yield reduction.

Weather conditions were relatively warmer and drier (especially in June and beginning of July) in 2011 and a bit cooler and with precipitation above the long-term average in 2012 (Fig. 1).

Grain chemical composition analysis. The grain was combine-harvested on the whole plots, dried and cleaned with 1.7 mm sieve. One composite grain sample was assembled from all replications for analysis. The grain moisture content ranged between 10.2–12.5%. For all analysis barley grain was ground to pass a sieve (d < 0.065 mm).

Preparation of barley oil. Flour was refluxed in petroleum ether (ratio flour:solvent 1:3 to 1:5, g:ml) for 1.5 h, followed by filtration through celite. Solvent was removed by rotary evaporator (~40°C, water aspirator).

Analysis of α-tocopherol. The oil (17–20 mg) was dissolved in hexane (1 ml). High-performance liquid chromatography (HPLC) analysis was performed by 1200 series chromatograph (Agilent Technologies, USA) with ZORBAX RX-SIL column (4.4 × 250 mm, 5 μm) according to the method described previously (Mieriņa et al., 2013).

Total polyphenol content (TPC) analysis. Barley grain flour (10 g) was stirred in 80% ethanol (50 ml) at room temperature for 24 h and followed by filtration. Ethanol extract (1 ml) was diluted with 80% ethanol (4 ml); the obtained solution was used for further analysis. To detect TPC in grain oil the oil (80–90 mg) solution in hexane (5 ml) was extracted with 80% ethanol (5 ml). The extraction was done for 0.5 h on orbital shaker OS 10 (Biosan, Latvia). Further the mixture was centrifuged; ethanol layer was collected. TPC both for barley grain and oil ethanol extracts was determined according to the method described by Singleton et al. (1999). TPC analyses were done on single beam scanning UV/visible spectrophotometer M501 (Camspec, UK). Each sample was analysed in triplicate. TPC was expressed as gallic acid equivalents per 100 g grain (mg GAE 100 g^{-1} grain) or as gallic acid equivalents per 100 g oil (mg GAE 100 g^{-1} oil).

Analysis of phenolic compounds. The grains were defatted before the extraction of phenolic compounds: flour (10 g) was mixed with petroleum ether (50 ml) for 1 h at room temperature and filtered. Acid hydrolysate: defatted barley grain (1.6 g) in 6 M HCl (10 ml) was heated for 1 h at 75–80°C and then filtered. Further 6 M potassium hydroxide (KOH) solution was added to filtrate until pH ~ 2 was reached. Solution was extracted with ethyl acetate (2 × 25 ml); ethyl acetate layer was dried with Na_2SO_4, filtered and evaporated. Ethanol (80%) extract: defatted grain (2.5 g) in 80%

Table 1. Soil properties, fertilization, weed control and disease prevention measures under organic (O) and conventional (C1, C2, C3) crop management systems in 2011 and 2012

Treatment		Crop management system							
		O	C1	C2	C3	O	C1	C2	C3
		2011				2012			
P_2O_5 mg kg^{-1}			183		173		160		208
K_2O mg kg^{-1}			137		201		93		215
pH KCl			5.9		5.0		5.7		5.8
Organic matter %			1.7		2.9		2.3		2.3
Precrop			Green manure (pea)		Bare fallow		Green manure (pea)		Pea
Mineral fertilizer kg ha^{-1}	N		–	90	140		–	90	140
	P		–	35	49		–	30	60
	K		–	70	98		–	45	90
Foliar fertilizer			–	–	–	Cristalon* 5 kg ha^{-1}	–	–	– Cristalon 5 kg ha^{-1}
Weed control			Harrowing in tillering stage		Sekator OD (amidosulfuron 100 g l^{-1} and iodosulfuron-methyl-sodium 25 g l^{-1}) 0.15 l ha^{-1} and Estet 600 EC (2.4 D 600 g l^{-1}) 0.6 l ha^{-1}	Harrowing in tillering stage		Sekator OD 0.1 l ha^{-1} + Estet 600 EC 1.0 l ha^{-1}
Disease management			–	–	Tango Super (84 g l^{-1} epoxiconazole 250 g l^{-1}, fenpropimorph) 1.5 l ha^{-1}		–	–	Tango Super 1.5 l ha^{-1}

* – content of mineral elements (%): N – 13, Fe – 0.07, P – 2.2, Mn – 0.04, K – 21.7, Mo – 0.004, Mg – 1.9, Zn – 0.025, S – 9, B – 0.025, Cu – 0.01

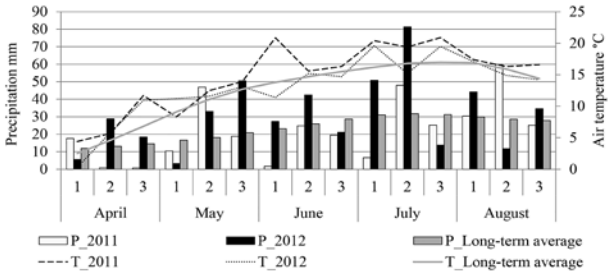


Figure 1. Sum of precipitation (P), average air temperature (T) and long-term average data in Priekuļi, Latvia during barley vegetation (in 2011 and 2012)

ethanol (50 ml), was stirred and refluxed for 1 h, followed by filtration and evaporation of ethanol. The remaining water solution was acidified with 6 M hydrochloric acid until pH ~ 2 was reached. The solution was extracted with ethyl acetate and prepared analogous to the acid hydrolysate. Alkali hydrolysate: defatted grain (2.5 g), was stirred in 2 M KOH solution (30 ml) for 1 h at a room temperature in dark and then filtered. The filtrate was acidified with 6 M hydrochloric acid until pH ~ 2. The solution was extracted with ethyl acetate similarly as described above. HPLC analysis: each extract (~10 mg) was dissolved in 1 ml methanol and HPLC analyses was performed by 1200 series chromatograph (Agilent Technologies), Phenomenex Gemini NX C18 column, 3 µm, 4.6 × 100 mm under the conditions described by Mierina et al. (2013). Result was expressed as mg kg^{-1} of defatted grain. We report results in acid hydrolysate with the exception of catechin and quercetin which were found in 80% ethanol and/or alkali hydrolysates only.

Statistical analysis. Analysis of variance, Pearson correlation and *t*-test were used for data statistical analysis. To estimate stability of component concentration ecovalence (W_i) was computed as described by Becker and Leon (1988) and expressed in percentage of the total interaction sum of squares; values close to zero indicate high stability.

Results

α-Tocopherol. Significant difference was found among α-tocopherol concentrations in barley grain in both years (Table 2); the ranges were 9.11–14.51 and 1.49–6.81 mg kg^{-1} in 2011 and 2012, respectively.

The effect of barley genotype on the concentration of α-tocopherol in grain was significant in 2012 with the highest mean value for hulless breeding line PR-4651, which was superior in three crop management systems. High concentrations of α-tocopherol were also for hulless cultivar 'Irbe' with the exception of organic management and for covered cultivar 'Rubiola' under C3 management system. Covered cultivar 'Jumara' had relatively low and stable values in both years. No significant difference ($p < 0.05$) was between hulless and covered genotypes; however, the average values in both years were slightly higher for hulless genotypes. Genotype and year interaction was significant and as a result the correlation between both year data was insignificant. The impact of the conditions related to the growing year was radically different for hulless line PR-3808 providing the highest mean α-tocopherol concentration among all genotypes in 2011 and the lowest one in 2012. Instability of this line with respect to α-tocopherol in grain is demonstrated by the highest ecovalence value (Table 3). The effect of crop management was not statistically significant; however, a general trend to increase of α-tocopherol content with increasing the mineral fertilizer amount can be observed. The exception was only hulless line PR-3808 with an opposite trend in both years. Comparing data from conventional and organic crop management systems, significant difference between the average of samples was in 2012 ($p = 0.009$).

Concentration of α-tocopherol in grain oil correlated significantly with α-tocopherol in the grain in both years ($r = 0.63$ and 0.85 in 2011 and 2012, respectively; $p < 0.001$), and the trends were generally similar. Significantly lower concentration was obtained in 2012 than in 2011 (ranges 9.24–39.70 and 49.91–88.32 mg 100 g^{-1} oil, respectively). Significant differences between genotypes were under conventional systems in 2012 with the highest values for hulless cultivar 'Irbe' and line PR-4651. The effect of crop management was significant in 2011 with the highest mean value under C3 system. The difference between crop management systems was significant only for covered cultivar 'Jumara' with higher concentration under C3 system. The difference between conventionally and organically grown samples was significant in 2012 ($p = 0.01$).

Total polyphenol content (TPC). The concentration of TPC in barley grain was significantly different between both years with the range 98.78–140.13 mg GAE 100 g^{-1} in 2011 and 81.66–110.04 mg GAE 100 g^{-1} in 2012.

The effect of genotype was significant in 2012 with the highest mean value for hulless line PR-4651. Hulless cultivar 'Irbe' was of equal value and with the most stable TPC according to ecovalence (Table 3). Significantly higher values ($p = 0.005$) were for hulless samples if compared to covered samples in 2012. In 2011 such trend was only under organic system. Low TPC in all environments was for covered cultivar 'Rubiola', whereas other covered cultivar 'Jumara' was the richest one with polyphenols under conventional system in 2011 and was the most unstable among the tested genotypes. The correlation between both year data was positive but insignificant.

Table 2. Average concentration of α-tocopherol and total polyphenol content (TPC) in grain and oil of covered and hulless barley genotypes under organic (O) and conventional (C1, C2 and C3) crop management systems in 2011 and 2012

Genotype / management	α-tocopherol mg kg^{-1} grain		α-tocopherol mg 100 g^{-1} oil		TPC mg GAE 100 g^{-1} grain			TPC mg GAE 100 g^{-1} oil		
	2011	2012	2011	2012	2011	2012	average	2011	2012	average
Jumara	10.93	2.93 bc	69.59	24.70 ab	124.23	98.62 b	111.42 a	3.68	1.40 a	2.54
Rubiola	12.65	3.80 ab	76.11	26.76 a	107.59	84.52 c	96.05 b	3.19	1.26 a	2.23
Irbe*	12.42	4.90 a	75.81	31.82 a	115.03	105.19 ab	110.11 a	2.56	0.55b	1.56
PR-4651*	12.37	5.50 a	63.67	27.60 a	118.68	106.05 a	112.37 a	5.17	0.65 b	2.91
PR-3808*	13.13	1.75 c	73.04	11.05 bc	111.08	100.34 ab	105.71 a	4.54	0.28 b	2.41
PR-5099*	11.13	3.10 bc	59.80	16.91 b	119.28	102.99 ab	111.13 a	2.94	0.52 b	1.73
Genotype, *p*-value	ns	0.04	ns (0.08)	0.03	ns	0.0002	0.001	ns (0.07)	0.0005	ns
O	11.54	2.59	66.94 b	16.76	123.24	98.61	110.92	2.47 b	0.69	1.58
C1	11.69	4.15	65.98 b	25.23	116.06	101.54	108.80	3.51 b	0.66	2.08
C2	12.38	3.57	69.60 ab	25.30	111.67	99.20	105.43	5.94 a	0.93	3.43
C3	12.80	4.34	76.16 a	25.28	112.95	99.11	106.03	2.81 b	0.84	1.82
Management, *p*-value	ns	ns (0.08)	0.047	ns (0.08)	ns	ns	ns	0.001	ns	ns
Average	**12.10**	**3.66**	**69.67**	**23.14**	**115.98**	**99.62**	**107.80**	**3.68**	**0.78**	**2.23**
Year, *p*-value	<0.0001		<0.0001		<0.0001			<0.0001		
G × Y interaction, *p*-value	0.02		0.03		ns			ns		

Note. * – hulless barley; ns – $p > 0.05$; a, b, c – different letters indicate significant differences ($p < 0.05$) between genotypes or management systems.

Table 3. Stability of α-tocopherol, total polyphenol content (TPC) and phenolic compound concentration in barley genotypes over four crop management systems in 2011 and 2012

Genotype	Ecovalence (W_i) %															
	α-toc in grain	α-toc in oil	TPC in grain	TPC in oil	fer	*p*-co	sin	caf	chl	syr	4-hy	van	gal	3,4-di	cat	ell
Jumara	9.7	15.6	32.7	9.5	26.7	5.6	14.8	14.4	55.7	45.9	18.0	12.6	2.4	18.8	10.1	18.7
Rubiola	9.7	7.2	23.8	11.3	22.5	62.7	18.4	66.3	6.4	11.3	13.7	8.8	5.7	10.6	13.8	24.8
Irbe	11.3	14.3	6.1	6.6	10.2	6.6	18.7	4.3	9.4	7.8	30.1	15.4	52.7	37.4	31.4	15.2
PR-4651	17.4	16.1	13.4	34.6	20.4	8.5	39.5	5.6	18.1	14.1	17.4	3.8	16.2	5.7	12.3	9.1
PR-3808	39.3	36.1	14.1	34.4	10.4	5.4	2.5	2.9	1.7	8.4	11.7	9.6	0.6	2.2	16.7	3.0
PR-5099	12.4	10.7	10.0	3.6	9.8	11.2	6.2	6.3	8.7	12.5	9.2	49.8	22.5	25.2	15.6	29.3

α-toc – α-tocopherol, fer – ferulic acid, *p*-co – *p*-coumaric acid, sin – sinapic acid, caf – caffeic acid, chl – chlorogenic acid, syr – syringic acid, 4-hy – 4-hydroxybenzoic acid, van – vanillic acid, gal – gallic acid, 3,4-di – 3,4-dihydroxybenzoic acid, cat – catechin, ell – ellagic acid

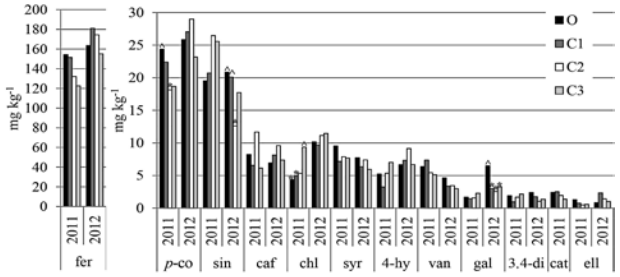
Crop management did not affect the TPC in barley grain significantly. An increase of TPC with the decrease of synthetic fertilizers with the highest average value under organic system was observed in 2011 (Table 2); however, it existed for hulless genotypes only for which the mean content of polyphenols under organic management exceeded significantly that under conventional management by 19.47 GAE 100 g^{-1} ($p = 0.005$). TPC correlated positively among crop management systems (some of correlations significant, $p < 0.05$) with the exception of correlations between organic and conventional management in 2011.

Negative correlations were obtained between TPC in barley grain and barley grain oil (significant in 2012, $p < 0.05$). Polyphenols in grain oil ranged between 1.40–8.52 and 0.19–1.92 GAE 100 g^{-1} in 2011 and 2012, respectively, and the effect of the year was significant. Significantly higher average values were found for both covered cultivars if compared to the hulless genotypes in 2012 (differences significant under C2 and C3 management systems), whereas in 2011 hulless line PR-4651 provided the highest average TPC in oil. Crop management influenced significantly TPC in barley grain oil in 2011. The values obtained under C2 surpassed those under other management systems for all genotypes. In 2012 there was similar trend mostly for covered cultivars. The TPC in oil was lower in organically grown samples if compared to those grown conventionally (difference significant in 2011, $p = 0.009$).

Phenolic compounds. We identified 13 phenolic compounds: ferulic, *p*-coumaric, syringic, chlorogenic, 4-hydroxybenzoic, sinapic, vanillic, gallic, caffeic, 3,4-dihydroxybenzoic and ellagic acids, quercetin and catechin. The highest concentration was for ferulic acid followed by *p*-coumaric and sinapic acids (Fig. 2, Table 4). The concentration of most of the phenolic compounds was significantly affected by the conditions of the growing year and differed between the compounds in which year the concentration was higher.

Covered cultivars had significantly higher concentrations of ferulic, *p*-coumaric and syringic acids if compared to the hulless genotypes in both years. Genotype and year interaction was significant in several cases (Table 4) mainly because of different reaction between the years for both covered cultivars. Hulless line PR-3808 had the most stable concentration for majority of the phenolic compounds (Table 3). However, it contained comparatively low amounts of all compounds. Covered cultivar 'Jumara' was unstable for ferulic, chlorogenic and syringic acids with high means and some extreme values, and covered cultivar 'Rubiola' was unstable for *p*-coumaric and caffeic acids. Hulless cultivar 'Irbe' was relatively stable for ferulic acid with the highest values among hulless genotypes and for syringic acid but unstable for several compounds with smaller concentrations.

3,4-Dihydroxybenzoic acid was in all covered samples except one but was not in most of hulless samples; however, the maximum values were in organically grown hulless genotypes in both years. In contrast to previously mentioned compounds, catechin was identified only in 80% ethanol extracts and not in acid hydrolysates. In 2011 it was determined in most of the samples but in 2012 only in a few. Ellagic acid was found only in five samples in 2011 and in almost half of the samples in 2012 (ranges 0–4.67 and 0–5.12 mg kg^{-1}, respectively). The two-year mean of covered grains was



Note. fer – ferulic acid, *p*-co – *p*-coumaric acid, sin – sinapic acid, caf – caffeic acid, chl – chlorogenic acid, syr – syringic acid, 4-hy – 4-hydroxybenzoic acid, van – vanillic acid, gal – gallic acid, 3,4-di – 3,4-dihydroxybenzoic acid, cat – catechin, ell – ellagic acid; ^ * – significant differences ($p < 0.05$) between differently marked management systems within a year.

Figure 2. Average content of phenolic compounds over six genotypes as affected by crop management systems (O – organic, C1, C2, C3 – conventional with increasing agrochemical input level) and year (2011 and 2012)

significantly higher than that of hulless ($p = 0.03$), covered barley cultivar 'Jumara' reached the highest mean value of 2.37 mg kg^{-1}; however, the maximum values in both years were reached by hulless line PR-5099. Quercetin was identified only in 2011 in three samples of alkali hydrolysates (1.32–2.94 mg kg^{-1}) and in two samples of 80% ethanol extracts (2.49–4.51 mg kg^{-1}), but not in acid hydrolysates. Both extracts of line PR-3808 under organic management system contained quercetin.

No significant effect of crop management was found for any phenolic compound in both years. However, the average values over genotypes differed significantly between the management systems in a single year for four compounds (Table 4). The highest values of these compounds were in samples grown under organic system with the exception of chlorogenic acid, which increased with the increase of mineral fertilizer. There were no significant differences between organically and conventionally grown samples; however, a general trend of increased concentrations under organic system or with the decrease of mineral fertilizer amount applied was observed in both years for ferulic, syringic, vanillic and

Table 4. Range, significance of genotype (G), crop management system, year (Y), genotype and year interaction (G × Y), difference between hulless and covered barley and correlation between years for content of phenolic compounds in grain in 2011 and 2012

Phenolic compound		Range mg kg^{-1}	G	Management	Y	G × Y	Hulless / covered	Correlation
Ferulic acid	2011	63.21–270.93	<0.0001	ns	<0.001	ns	0.02	$p < 0.01$
	2012	109.09–308.82	<0.0001	ns			<0.001	
p-coumaric acid	2011	3.83–70.64	<0.0001	<0.05	<0.001	ns	<0.001	$p < 0.01$
	2012	6.39–92.31	<0.0001	ns			0.002	
Sinapic acid	2011	0–49.96	ns	ns	ns (0.08)	ns	ns	ns
	2012	1.84–28.31	ns	<0.05			ns	
Caffeic acid	2011	0.87–42.17	ns	ns	ns	0.03	ns	ns
	2012	3.91–17.37	<0.001	ns			<0.01	
Chlorogenic acid	2011	0–15.90	<0.01	0.03	<0.001	<0.0001	ns	ns
	2012	0–34.68	0.001	ns			0.001	
Syringic acid	2011	1.96–16.07	<0.0001	ns	0.03	<0.01	<0.0001	$p < 0.01$
	2012	4.29–12.30	<0.001	ns			<0.01	
4-hydroxybenzoic acid	2011	0–12.56	ns	ns	0.01	ns (0.07)	ns	ns
	2012	2.86–15.40	0.01	ns			ns	
Vanillic acid	2011	1.25–18.53	ns	ns	0.001	ns	ns	ns
	2012	0–7.34	ns	ns			ns	
Gallic acid	2011	0–5.71	ns (0.07)	ns	<0.001	ns	<0.001	ns
	2012	0.63–13.18	ns (0.07)	<0.01			ns (0.07)	
3,4-dihydroxybenzoic acid	2011	0–5.56	0.03	ns	ns	ns	<0.001	ns
	2012	0–8.67	ns	ns			ns	
Catechin	2011	0–4.73	ns	ns	<0.0001	ns	ns	ns
	2012	0–0.56	ns	ns			ns	

p – *p*-value; ns – not significant ($p > 0.05$)

ellagic acids. For *p*-coumaric and sinapic acids opposite trends were observed in both years with respect to increase / decrease of values with increase of amounts of mineral fertilizer applied (Fig. 2).

Discussion

We studied concentration of α-tocopherol although α-tocotrienol is the major tocol isomer in barley (Idehen et al., 2017) with the highest antioxidant capacity (Do et al., 2015). However, significant positive correlation between α-tocotrienol and α-tocopherol was shown by Peterson and Qureshi (1993) and Ehrenbergerová et al. (2006) reported significant positive correlations between vitamin E and both isomers. The concentrations of α-tocopherol found by us were close to those reported for barley in other studies (Peterson, Qureshi, 1993; Cavallero et al., 2004; Ehrenbergerová et al., 2006; Žilić et al., 2011; Tsochatzis et al., 2012; Do et al., 2015) except for very low values in 2012 for majority of samples. Moreau et al. (2007) reported α-tocopherol concentration in oil obtained from different hulless scarification fractions in range 56.3–128.9 mg 100 g^{-1} oil, which is comparable to our results in 2011 but noticeably higher than in 2012. However, our results were obtained from whole grain, which can have lower values. Our results (especially from 2011) presented the barley grain oil as an important source of α-tocopherol in comparison to some well-known vegetable oils (e.g., sunflower, corn, oilseed rape, etc.) (Saini, Keum, 2016).

The range of total polyphenol content in grain found by us was generally lower than reported in some other studies (Dabina-Bicka et al., 2011; Holtekjølen, Knutsen, 2011; Lahouar et al., 2014; Fogarasi et al., 2015). The phenolic compounds determined by us were reported in barley by other authors (Kim et al., 2007; Gamel, Abdel-Aal, 2012; Žilić et al., 2011; Kandil et al., 2012; Gangopadhyay et al., 2016) with the exception of ellagic acid. Yet the extraction methods used are different, thus it is hard to compare the results. Ferulic acid was the major phenolic compound with a range 63.2–308.8 mg kg^{-1} followed by *p*-coumaric acid (3.8–92.3 mg kg^{-1}). That is in agreement with some other studies (Gamel, Abdel-Aal, 2012; Kandil et al., 2012). We found catechin in around half of the samples in a comparatively little amount (0.14–4.73 mg kg^{-1}), whereas Žilić et al. (2011) reported it as a major free phenolic compound with 20-fold higher concentration than ferulic acid. The negative correlation between total polyphenol content in barley grain and oil can be explained by dominance of different compounds in ethanol extracts and grain oil because different extraction solvents were used.

Concentrations of α-tocopherol and total polyphenol content were significantly affected by barley

genotype only in 2012 when it was lower than in 2011. Genotype is a significant factor affecting α-tocopherol concentration in barley (Peterson, Qureshi, 1993; Cavallero et al., 2004; Ehrenbergerová et al., 2006; Do etal., 2015); however, the impact of environment is larger than that of genotype for α-tocopherol but not for total tocols and most of other tocol isomers (Peterson, Qureshi, 1993; Cavallero et al., 2004) approving the instability between the environments for this particular isomer. Similarly to our results, Eticha et al. (2010) also found significant effect of genotype only in one of two trial years while testing a collection of 86 barley genotypes for total polyphenol content, as well as no significant correlation between genotypic values in both years was observed. Growing environment has larger effect than genotype for total polyphenol content, ferulic, vanilic and syringic acids in hard spring wheat (Mpofu et al., 2006). In respect of phenolic compounds we found the effect of genotype highly significant for ferulic, *p*-coumaric and syringic acids which had clear significant differences between covered and hulless samples indicating association with presence or absence of hulls.

In general, covered genotypes were more stable for α-tocopherol and hulless genotypes were more stable for total polyphenol content in grain. We did not find significant difference in α-tocopherol content between hulless and covered types while significantly higher α-tocopherol concentration is reported in naked oat genotypes if compared to husked ones (Berga, Zute, 2012). However, we found the highest mean α-tocopherol values for hulless genotypes in both years. It was in agreement with Cavallero et al. (2004) who report higher content of total tocols in covered with positive effect of the hulless trait on tocopherols and negative effect on tocotrienols. Ehrenbergerová et al. (2006) find significantly higher amount of vitamin E, total tocols and α-tocotrienol in waxy hulless cultivar; however, in respect of α-tocopherol covered line is superior.

We found significant advantages of hulless genotypes in comparison to covered for total polyphenol content in a single year. Similarly higher content of total polyphenol content is found in coloured hulless in comparison to coloured covered barley (Kim et al., 2007). However, the content of major phenolic acids was higher in covered genotypes. Our results partially agreed with a finding that cereal hulls contain significantly higher total polyphenol and most phenolic acid content if compared to cereal grain (Kerienė et al., 2015). Gamel and Abdel-Aal (2012) show the highest concentration of phenolic acids (especially ferulic, *p*-coumaric and syringic acids) in covered barley hulls followed by outer layers of grain (pericarp and testa) and decreasing towards endosperm. It explains the superiority of covered over hulless genotypes in respect of several compounds in our study. Significantly higher phenolic acid content is in common oats than in naked oats (Kerienė et al., 2015), whereas Eticha et al. (2010) point to far more important influences of genotype and environment on total polyphenol content than the presence or absence of the hull. Further, it must be considered that for food purposes covered grain needs to be dehulled and thus will lose compounds concentrated in the hulls, outer layer of grain and possibly also germ.

Covered barley was superior for content of ferulic, *p*-coumaric and syringic acids in both trial years and hulless – for caffeic and gallic acids in a single year. It agreed with some other studies, which report higher content of ferulic and *p*-coumaric acids in covered (Holtekjølen et al., 2006; Gamel, Abdel-Aal, 2012) and considerable amount of caffeic acid in hulless genotypes in contrast to covered (Dabina-Bicka et al., 2011). However, the ferulic acid percentage of total phenolic acids is reported to be higher in hulless in comparison to covered barley genotypes (Holtekjølen et al., 2006).

Environmental conditions of the growing year affected significantly most of the antioxidants studied and was the factor with the highest partitioning of sum of squares in the case of α-tocopherol, total polyphenol content, sinapic acid, gallic acid and catechin concentration in barley grain. The effect of conditions of the year differed for compounds: 2011 with somewhat higher mean air temperature and comparably lower amount of precipitation during the time of grain formation (Fig. 1) favoured synthesis of α-tocopherol, total polyphenols, including, syringic acid, vanillic acid, catechin and quercetin, while a bit cooler 2012 with considerable amounts of rainfall promoted higher concentrations of ferulic, *p*-coumaric, 4-hydroxybenzoic, chlorogenic and gallic acids. Weather conditions in 2012 could be characterized as more favourable for barley development due to significantly higher ($p = 0.002$) mean yield level (4.03 and 4.49 t ha^{-1} in 2011 and 2012, respectively). Colder and drier conditions significantly increase accumulation of total tocols including α-tocopherol if compared to hotter and wetter years (Ehrenbergerová et al., 2006). Whereas Lachman et al. (2018) found higher tocol contents at higher rainfall and lower temperatures. Lower content of tocols in wheat genotypes in more rainy seasons is explained by larger grain size and negative correlation between tocol content and thousand grain weight (Lampi et al., 2010). In our study, the difference in thousand grain weight between the years was not significant (data not shown). Higher content of total polyphenols in cereals is associated with drought stress and high temperature during grain filling (Menga et al., 2010). In contrast, Bellato et al. (2013) conclude that high water availability increases total polyphenol content in durum wheat. Considering these findings and our results we assumed that drought can be one of the stress factors stimulating synthesis of α-tocopherol and some other antioxidants. Similarly Eticha et al. (2010) explain higher concentration of total phenolic compounds in one of two trial years by drought stress. The first ten-day period of June 2011 was extremely dry with 6% rainfall of that in 2012 and the first ten-day period of July with 13%, respectively. For synthesis of most of the phenolic compounds more beneficial appeared either cooler or wetter conditions or combination of both, resulting in more favourable environment for barley yield formation.

Genotype and year interactions were significant for concentration of α-tocopherol and three phenolic acids (syringic, caffeic and chlorogenic) content. Genotypes showing different reaction to the growing year were the most unstable with the highest ecovalence values (hulless line PR-3808 for α-tocopherol, cultivars 'Jumara' for total polyphenol content, syringic and chlorogenic acids and 'Rubiola' for caffeic acid). Similarly, differences in wheat genotype sensitivity to impact of the environment in respect of tocols are reported by Lampi et al. (2010) and some relatively stable genotypes were identified. The factor genotype and environment interaction has the largest effect on α-tocopherol concentration of winter wheat genotypes tested in four locations, followed by significant genotype and environment with considerably lower effects (Lv et al., 2013). Menga et al. (2010) report significant genotype and environment interaction for total polyphenol content in wheat but not in barley supporting our results.

No clear significant effect of crop management treatments was found for any of the investigated compounds indicating that crop management was not very important factor in relation to content of antioxidative compounds. The effect of crop management was significant only in a single year for α-tocopherol and total polyphenol content in oil showing trend to higher values at higher agrochemical input, as well as for four phenolic compounds, with higher values at organic system for three of them (Table 4, Fig. 2). No significant interactions between the year and crop management were found.

Chemical treatment and fertilization significantly increase the content of total tocols, vitamin E equivalent and α-tocopherol (Ehrenbergerová et al., 2006), that corresponds to the trends found by us for α-tocopherol with the highest mean values under highest fertilization level and is in agreement also with Bleidere et al. (2013). Similarly Tsochatzis et al. (2012) report significantly higher α-tocopherol in barley cultivars under conventional crop management in contrast to α-tocotrienol which was

higher under organic management system. The application of fungicides decreases content of phenols in hulless genotypes (Abdel-Aal, Choo, 2014). We observed similar trends – a significant difference for hulless samples between conventional and organic system in 2011 and highest values under managements without use of fungicides (C1 or O) for most genotypes in 2012. Similarly, in wheat increase of total polyphenol content is found by using organic fertilization regimes in contrast to mineral fertilizer but significant decrease in individual phenolic acid content at the same time is observed (Konopka et al., 2012), whereas our results in respect of most of phenolic acids did not confirm a decrease under organic management system. The differences between crop management systems can be explained by soil organic matter in organic fields or relation of phenolic compounds to plant defence mechanisms against biotic stress factors (Johansson et al., 2014).

Conclusions

1. No clear significant effect of crop management systems on content of antioxidants was found. Conditions of growing year had relatively larger and significant effect on content of α-tocopherol, total polyphenol content and most of phenolic compounds. Effect of genotype was clearly significant for four phenolic compounds. Significant genotype and year interaction was found for α-tocopherol in grain and oil, syringic, caffeic and chlorogenic acids.

2. α-Tocopherol content in barley grain and grain oil was generally higher, when conventional management with higher input level was used. Higher mean content was found for some hulless genotypes, although there was no significant difference between hulless and covered barley types.

3. Higher total polyphenol content in grain generally was under organic and lower input conventional management systems and in hulless than in covered barley genotypes. Higher total polyphenol content concentration in grain oil was under medium intensive conventional management system and lowest – under organic management with covered genotypes being superior in one of the two years.

4. Most of phenolic compounds tended to increase with decrease of agrochemical input level and higher content was in covered than in hulless genotypes with the exception of gallic and caffeic acids.

5. Relatively high content of α-tocopherol and total polyphenols was in waxy hulless line PR-4651; insignificantly lower but more stable it was in hulless cultivar 'Irbe' indicating suitability for healthy food use. For oil production covered barley can be superior mostly because of higher content of phenolic compounds but hulless line PR-4651 and cultivar 'Irbe' can provide comparable results in respect of α-tocopherol and total polyphenol content.

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Genotipo ir auginimo būdo įtaka antioksidantų kiekiui belukščiuose ir lukštinguose vasariniuose miežiuose

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Santrauka

Siekiant nustatyti kai kurių antioksidantų kiekį miežiuose, kurie yra viena pagrindinių javų rūšių, plačiai naudojamų didesnės vertės produktų gamyboje, 2011–2012 m. buvo atliktas tyrimas. Tirta genotipo ir aplinkos įtaka α-tokoferolio ir suminiam polifenolių kiekiui grūduose bei grūdų aliejuje ir fenolinių junginių kiekis dviejuose lukštinguose ir keturiuose belukščiuose vasariniuose miežių, juos auginant ekologiškai ir taikant tris tradicinio auginimo režimus su didėjančiu kiekiu agrocheminių medžiagų. Abiem tyrimo metais α-tokoferolio kiekis grūduose ir aliejuje svyravo atitinkamai nuo 1,49–14,51 iki 9,24–88,32 mg 100 g^{-1}; itin mažas jo kiekis buvo nustatytas šaltesniais ir drėgnesniais 2012 m. Suminis fenolių kiekis grūduose ir aliejuje svyravo nuo 81,66–140,13 iki 0,19–8,52 mg, išreikštas galo rūgšties ekvivalentais 100 g^{-1}. Nustatyta 13 fenolinių junginių, iš kurių didžiausia koncentracija buvo ferulo rūgšties, mažesnė – p-kumaro ir siringino rūgščių. Nebuvo nustatyta aiškios esminės augalų auginimo būdo įtakos antioksidantų kiekiui. Didžiausios įtakos α-tokoferolio, suminiam polifenolių ir daugumos fenolinių junginių kiekiams turėjo auginimo metų sąlygos. Miežių grūduose ir aliejuje α-tokoferolio kiekis buvo didesnis auginant įprastai su didesnėmis sąnaudomis; jo didesnis vidutinis kiekis nustatytas kai kuriuose belukščiuose miežiuose, tačiau skirtumai tarp lukštingų ir belukščių genotipų nebuvo esminiai. Didesnis suminis polifenolių kiekis grūduose nustatytas miežius auginant ekologiškai ir taikant mažesnių sąnaudų reikalaujantį klasikinį auginimo būdą. Lukštingi miežiai pasižymėjo didesniu suminiu kiekiu polifenolių, lyginant su belukščiais. Didesnė bendra polifenolių koncentracija aliejuje nustatyta taikant vidutinio intensyvumo klasikinį auginimą. Šiuo atžvilgiu 2011 m. lukštingi miežiai buvo pranašesni už belukščius. Daugumos fenolinių junginių kiekis turėjo tendenciją didėti mažinant agrochemijos sąnaudas, o didesnis jų kiekis buvo (su kai kuriomis išimtimis) lukštinguose miežiuose.

Reikšminiai žodžiai: α-tokoferolis, ekologiškas auginimas, fenoliniai junginiai, miežių grūdų aliejus, suminis polifenolių kiekis, tradicinis auginimas.