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## COMPOSITION OF ALKYLRESORCINS IN GRAINS OF VARIOUS SPECIES AND VARIETIES OF CEREALS

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Key words: 5-alkylresorcin, cereal grains, paper chromatography.

The paper chromatography method was used for separation and quantitative determination of composition of the group of 5-alkylresorcins present in acetone extracts from the grains of wheat, rye, triticale and barley. In all the examined cereal plants, the presence of six 5-alkylresorcins was stated. The quantitative composition of these substances was the characteristic feature of each of the cereal species.

Some components of cereals, appearing most frequently in trace amounts, reveal the antinutritional properties. The phenol compounds, among which 5-alkylresorcins seem have an inhibitory effect on growth rate of young animals, also belong to this group [7, 8, 10, 11, 15].

5-alkylresorcins, appearing in wheat and rye were identified as a mixture of six homologic components which are: 5-n-pentadecyl-resorcin, 5-n-heptadecyl-resorcin, 5-n-nonadecyl-resorcin, 5-n-heneicosoresorcin, 5-n-tricosoresorcin and 5-n-pentacosoresorcin [3, 14, 15]. The so-far determinations of quantitative composition of 5-alkylresorcin group isolated from the grains of wheat and rye had only indicative character. The reason for difficulties in determination of actual composition of these substances are differences in solubility and volatility of 5-alkylresorcins, resulting from the different length of their alkyl chains what, depending on the specific method of isolation and separation of these compounds [5, 6, 12, 14], causes changes in their mutual quantitative and sometimes also in qualitative relationships [1, 13, 15].

In connection with this fact, the studies were undertaken with the aim to define more precisely the natural quantitative composition of 5-alkylresorcins present in grains of wheat, rye, triticale and barley.

## MATERIAL AND METHODS

The grains of five varieties of rye *Secale cereale*, of eight varieties of wheat *Triticum vulgare*, of four unidentified varieties of wheat *Triticum durum* from Canada, Turkey, Soviet Union and the United States, of three species *Triticale* and three varieties of barley *Hordeum sativum*, were used as the material for the experiments.

The content of 5-alkylresorcins in grains of cereals was determined by a colorimetric method, applying the measurements of azo-dye absorbance, resulting from the reaction of conjunction of 5-alkylresorcin and p-nitrobenzendiazofluoroborate [12].

The separation of 5-alkylresorcins was conducted on Whatman's paper 3, by the ascending separation chromatographic method. The hydrophobic stationary phase was paraffine oil (E. Merck) and the mobile polar fraction was constituted by the system of solvents: acetone-water. In these conditions of separation, the rate of migration of the particular homologues decreased gradually with the increase of their molecular weight what caused differentiation of 5-alkylresorcins on chromatograms acc. to the quantity of carbon atoms in side hydrocarbonic chain.

In order to make the precise characteristics of the natural composition of 5-alkylresorcins found in various types of cereals, this content was examined directly in acetone extracts from the grains. For this purpose, 5 g grains were dried for 3 h at 60°C, put into tight-sealed test tube with 25 cc capacity, 10 cc acetone were added and left at a room temperature for 16 h. Then, the content of the tube was shaken for 15 minutes, the acetone extract was filtrated on a ceramic filter and solvent was evaporated under the decreased pressure. The obtained sediment was diluted again in 1 cc acetone and put onto properly cut paper strips [9], twice impregnated in 20% solution of paraffine oil and dried at 60°C for 30 minutes. Depending on the type of cereal plant, the following solutions of acetone extracts from grains were taken for separation: 10 mm<sup>3</sup> (wheat), 6 mm<sup>3</sup> (rye), 8 mm<sup>3</sup> (triticale) and 20 mm<sup>3</sup> (barley). The strips were developed by the system of solvents acetone-water: first (3:2) and second (2:1) during 8-10 h at 25°C ± 0.5°C. After drying at 60°C during 30 minutes, chromatograms were immersed in fresh 0.1% water solution of p-nitrobenzenediazo fluoroborate for 1 minute and as a result of the reaction with 5-alkylresorcins, yellow azo dye was formed. The developed chromatograms were washed for 20 minutes in a current water, then they were washed with distilled water and dried at 60°C. The separated 5-alkylresorcins appeared in a form of yellow-stained bands. On the chromatogram developed with the acetone-water system, ratio 3:2, four first constituents of mixture of 5-alkylresorcins were separated very well, beginning from the front of solvent and the components with higher molecular weight remained near the initial point. On the chromatogram

developed with acetone-water system, ratio 2:1, last four components of mixture of 5-alkylresorcins were developed very well, beginning from the start point while the first constituents with lower molecular weight were near the front of the solvent. Thus, totally, on both chromatograms all the components of the examined mixture of 5-alkylresorcins in a form of distinctly separated bands, were obtained. For identification of the particular bands, the separation of standard mixture of 5-alkylresorcins isolated from rye grains was simultaneously carried out in the same conditions and its qualitative and quantitative determination was previously performed by the gas chromatography and mass spectrometry [13].

In order to determine the quantitative composition of 5-alkylresorcin group present in cereals, the particular bands were cut out from the chromatograms, put into the tight-sealed test tubes and 5 cc acetone were added to each of them. After 24 h, the tubes were shaken for 15 minutes, and the obtained solutions of azo dye of 5-alkylresorcins filtrated on a ceramic filter. The absorbance was measured at wavelength  $\lambda = 423$  nm. Then, the percentage share of the particular 5-alkylresorcins in the examined mixture [13] was calculated, taking into consideration their molecular weight.

## DISCUSSION OF RESULTS

The content of 5-alkylresorcins in the grains depended mainly on the type and species of the examined cereal plant (Table 1). The highest level of 5-alkylresorcins was found in the rye and the lowest one in barley. What *T. vulgare* contained more resorcin than *T. durum*. The content of these substances in triticale was on the intermediate level between wheat and rye.

Table 1. Mean content of 5-alkylresorcins in grains of wheat, rye, triticale and barley

Type (species) of cereal	Content of 5-AR, mg/100 g	Standard deviation $\pm$ mg/100 g
Wheat		
<i>T. vulgare</i> n = 8	85.9	9.4
<i>T. durum</i> n = 4	63.4	6.8
Rye		
<i>S. cereale</i> n = 5	139.9	3.9
Triticale		
n = 3	100.0	10.3
Barley		
<i>H. sativum</i> n = 3	33.0	3.0

In the samples of all examined varieties of cereal plants, the presence of six homological 5-alkylresorcins containing respectively 15, 17, 19, 21, 23 and 25 carbon atoms in hydrocarbonic chain and of small quantities of unidentified compound with the properties of alkylresorcins, marked as 5-AR(X), was stated.

The quantitative composition of 5-alkylresorcins present in the grains depended very much on the type and species of the examined cereal (Table 2). The particular varieties in the frames of one species of the cereal were characterized by a similar quantitative composition of 5-alkylresorcins present in the grains.

Table 2. Mean percentage composition of 5-alkylresorcins present in the grains of rye, wheat and barley

Type of 5-alkylresorcins	Rye	Wheat		Barley
		<i>T. vulgare</i>	<i>T. durum</i>	
5-AR (X)	1.0	1.2	0.8	1.3
5-AR (15)	6.5	1.6	0.8	0.2
5-AR (17)	26.3	9.5	3.1	1.4
5-AR (19)	26.5	31.8	14.8	14.6
5-AR (21)	18.7	42.2	50.4	28.9
5-AR (23)	10.4	10.3	21.0	16.6
5-AR (25)	10.6	4.4	9.1	37.0

The main components of the mixture of 5-alkylresorcins in the examined varieties of *T. vulgare* were 5-nonadecylresorcins and 5-heneicosoresorcins (Table 3) while in *T. durum* variety, 5-heneicosoresorcins and 5-tricosoresorcins (Table 4) had the greatest share. For both species of wheat, the mentioned compounds constituted above 70% of total content of 5-alkylresorcins in the grains. Within each species of wheat, the quantity of 5-alkylresorcins was similar for the particular varieties. The mean absolute error of determinations of the quantitative composition of the discussed substances in wheat, varied from  $\pm 0,1$  to  $\pm 0.8\%$ .

Table 3. Percentage composition of 5-alkylresorcins present in grains of various varieties of wheat *T. vulgare*

Type of 5-alkylresorcins	Grana	Dana	Jana	Alcedo	Mironowska	Bezostaja	Mexico White	Topbas
5-AR (X)	1.0	0.8	1.3	1.2	2.2	0.9	1.2	1.4
5-AR (15)	3.1	1.3	1.7	0.6	1.4	2.2	1.5	1.1
5-AR (17)	9.0	7.0	8.4	7.8	9.1	9.5	9.0	8.6
5-AR (19)	30.0	35.6	29.4	35.8	30.8	33.4	30.6	29.1
5-AR (21)	41.9	43.5	42.2	42.6	41.5	41.9	40.3	43.0
5-AR (23)	10.2	8.8	11.5	8.5	10.4	8.7	12.1	11.6
5-AR (25)	4.8	3.0	5.5	3.5	4.6	3.4	5.3	5.2

Table 4. Percentage composition of 5-alkylresorcins present in the grains of various varieties of wheat *T. durum*

Type of 5-alkylresorcin	<i>T. durum</i> deriving from:			
	USA	Soviet Union (SU)	Canada	Turkey
5-AR (X)	0.6	1.2	0.6	0.8
5-AR (15)	1.0	traces	0.9	1.4
5-AR (17)	3.6	1.8	3.5	3.4
5-AR (19)	14.6	13.3	13.6	17.8
5-AR (21)	51.1	50.0	50.6	49.7
5-AR (23)	19.2	23.5	21.8	19.7
5-AR (25)	9.9	10.2	9.0	7.2

In the mixture of 5-alkylresorcins present in the grains of the examined rye varieties, 5-heptadecylresorcin and 5-nonadecylresorcin were in the largest quantities and it amounted totally to about 49-55% (Table 5). The percent composition of 5-alkylresorcins in the examined varieties of rye were only slightly differentiated. The mean absolute error of determinations of quantitative composition of these compounds in the rye was  $\pm 0.2$ - $\pm 0.7\%$ .

Table 5. Percent composition of 5-alkylresorcins present in the grains of various varieties of rye *S. cereale*

Type of 5-alkylresorcin	Dańkowskie				Pancerne
	Nowe	Selekcyjne	Srebrne	Złote	
5-AR (X)	1.3	0.8	1.2	0.8	0.9
5-AR (15)	6.3	6.6	6.6	6.7	6.1
5-AR (17)	26.0	23.8	27.2	28.1	26.4
5-AR (19)	26.7	24.0	27.6	27.3	26.9
5-AR (21)	18.4	20.6	18.5	18.4	17.9
5-AR (23)	10.7	11.7	9.8	9.1	10.6
5-AR (25)	10.6	12.5	9.1	9.6	11.2

Table 6. Percentage composition of 5-alkylresorcins present in the grains of various strains of triticale and varieties of barley *H. sativum*

Type of 5-alkylresorcin	Triticale			Barley		
	B-093	B-193	B-2061	Dura	Aramir	B-577
5-AR (X)	0.5	1.0	0.6	1.4	1.3	1.2
5-AR (15)	1.5	1.0	2.1	0.5	traces	traces
5-AR (17)	11.5	4.6	14.5	1.9	0.7	1.7
5-AR (19)	28.8	18.2	32.0	14.9	14.6	14.4
5-AR (21)	33.4	38.4	33.0	30.0	28.4	28.3
5-AR (23)	16.0	24.0	12.7	17.1	16.2	16.5
5-AR (25)	8.3	12.8	5.1	34.2	38.8	37.9

The grains of triticale were characterized by the greatest quantities of 5-nonadecylresorcin, 5-heneicosoresorcin and in B-193 strain — also of 5-tricosoresorcin (Table 6). The share of two main components in the mixture of 5-alkylresorcins varied from 57 to 65%. As it regards the percent composition of 5-alkylresorcins, the particular strains of triticale differed distinctly each other. The mean absolute error of determinations of quantitative composition of the discussed substances in triticale amounted from  $\pm 0.1$  to  $\pm 0.6\%$ .

The main components in the mixture of 5-alkylresorcins in the examined varieties of barley were 5-tricosoresorcin and 5-pentacosoresorcin, constituting totally about 66% of these substances content in the grains (Table 6). The quantity of 5-alkylresorcins in the particular varieties of barley were similar. The mean absolute error of determinations of these compositions varied from  $\pm 0.1$  to  $\pm 0.6\%$ .

## DISCUSSION

The ascending paper chromatography method was applied for separation and determination of quantitative and qualitative composition of 5-alkylresorcins group present in acetone extracts in the grains of wheat, rye, triticale and barley.

It was stated that the examined types of cereals did not reveal the significant differences in the quantity of 5-alkylresorcins which were present as a group of six homological derivatives of resorcin containing uneven number of carbon atoms (from 15 to 25) in the alkyl chain. It may be concluded that the presence of the mentioned 5-alkylresorcins with the composition determined only in wheat and rye [3, 6, 14, 15] and stated also in barley and triticale, is a characteristic feature of grains of the plants belonging to Gramineae family.

The quantitative composition of 5-alkylresorcins present in grains of wheat, rye and barley was very distinctly differentiated for the particular type of cereal and in case of wheat also for its species. Simultaneously it showed only minimal variability in the frames of the species, affected by differences in variety. Data concerning the studies on the variability of this composition were not found in the literature.

Triticale, the strains of which distinctly differed each other in respect of quantitative composition of 5-alkylresorcins, is the exception which can be explained by the fact that this cereal plant contains genome of diploid rye of *S. cereale* species and genomes of wheat deriving most frequently from various species of tetraploid or hexaploid wheat [2, 4]. Thus, different share of these genomes in the construction of triticale could be the reason for variable quantitative composition of 5-alkylresorcins in the examined strains of this cereal.

On the basis of the obtained results, it may be assumed that the quantitative composition of 5-alkylresorcins in grains of cereals is the characteristic feature, determined and controlled genetically for each species of cereal, and independent on the variety factor.

## CONCLUSIONS

1. Ascending paper chromatography method was used for separation of mixture of 5-alkylresorcins present in the grains of wheat, rye, triticale and barley, into six component differentiated acc. to the length of alkyl chain containing respectively: 15, 17, 19, 21, 23 and 25 carbon atoms. The presence of slight quantities of one additional component with the non-established structure.

2. The quantitative composition of 5-alkylresorcins was different in different species of the examined cereals. There was a predominancy of the 5-alkylresorcins with the following number of carbon atoms in side hydrocarbonic chain: 17 and 19 in *S. cereale* rye, 19 and 21 in *T. vulgare* wheat, 21 and 23 in *T. durum*, 19, 21 and 23 in triticale and 21 and 25 in *H. sativum* barley.

3. The qualitative composition of 5-alkylresorcin group in wheat, rye triticale and barley is unchanged while the quantitative content is the characteristic feature for each species of the cereal.

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## SKŁAD ALKILOREZORCYN ZIARNIAKÓW RÓŻNYCH GATUNKÓW I ODMIAN ZBÓŻ

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### Streszczenie

Rozdzielono mieszaninę 5-alkilorezorcyn występujących w ekstraktach acetonowych z ziarniaków pszenicy, żyta, pszenżyta i jęczmienia, stosując technikę chromatografii bibułowej. Fazę stacjonarną stanowił olej parafinowy, a fazą ruchomą był układ rozpuszczalników aceton-woda. Udział procentowy każdej 5-alkilorezorcyny w mieszaninie oznaczano kolorymetrycznie po wyeluwaniu z wywołanych chromatogramów pojedynczych składników. Najwyższą zawartością 5-alkilorezorcyn charakteryzowały się ziarniaki żyta, a najniższą ziarniaki jęczmienia.

Skład jakościowy grupy 5-alkilorezorcyn był jednakowy we wszystkich badanych odmianach zbóż, w których stwierdzono sześć homologicznych pochodnych rezorcyny zawierających w łańcuchu alkilowym 15, 17, 19, 21, 23 i 25 atomów węgla. Natomiast skład ilościowy mieszaniny 5-alkilorezorcyn występujących w ziarniakach był bardzo wyraźnie zróżnicowany dla poszczególnych rodzajów zbóż, a w przypadku pszenicy także dla jej gatunków, nie wykazując przy tym istotnej zmienności odmianowej. Głównymi składnikami badanych mieszanin 5-alkilorezorcyn były: heneikozorezorcyna w pszenicy i pszenżycie, heptadecylrezorcyna i nonadecylrezorcyna w życie oraz pentakozorezorcyna w jęczmieniu.