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### Variability in chemical composition and biologically active constituents of cereals

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ABSTRACT: Whole grain flours of diverse wheat species (*Triticum* sp.) and botanical varieties of barley (*Hordeum vulgare*), oat (*Avena sativa*) and rye (*Secale cereale*) were analysed for their chemical composition, with particular regard to dietary fibre and polyphenols. A considerable variation was observed between the cereal crops. Ancient wheats einkorn and emmer exhibited highest protein contents and lowest levels of dietary fibre. Rye showed highest contents of dietary fibre and intermediate ranges of total phenol content and reducing power. Barley revealed high contents of  $\beta$ -glucan, total phenol and reducing power. Oat contained the highest amount of total fat and represents also a valuable source of  $\beta$ -glucan. High contents of carotenoids were observed for einkorn, while blue and purple grain common wheats were significantly higher in their content of anthocyans. The results indicate that cereals represent a valuable source of biologically active constituents, which can profoundly affect the health-enhancing potential of a functional food. However, it is a challenge for food technologists that the physiological effects of these compounds are not altered significantly during certain processing techniques and that they bring them into palatable products, considering eventual negative effects on flavour and processing quality of single constituents.

Key words: Dietary fibre – functional food –  $\beta$ -glucan – health-benefit – secondary metabolites

#### Introduction

Apart from energy intake nutrition is taking on new meanings in the 21<sup>st</sup> century. Emphasis is now given on foods which can promote well-being and health, and help to reduce the risk of diseases. Responsible for these effects are certain food components that act on the body beyond or in addition to vitamins and minerals. Although these newly recognized food components have not been classified as essential compared to traditional nutrients, they are acting on the body to promote and improve health. The concept of 'functional foods' has become popular in recent years, first in Japan, and later in other developed countries. For foods with a specific health claim the physiological benefit must be well documented scientifically and approved by the respective administration.

Cereal based foods represent the bulk of all foods consumed and their contribution to human nutrition and health should be considered cumulative, immediate and significant. Cereals can and do contribute a significant amount of these new food ingredients in the diet. Biologically active constituents of cereals that promote beneficial physiological effects are dietary fibre, starch and polyphenols. Dietary fibre is defined as that portion of plant foods that can not be digested and absorped in the human small intestine, but are completely or partially fermented in the large intestine. Dietary fibres include poly- and oligosaccharides, lignin, and associated plant substances. The actions of cereal dietary fibre on the body are varied and highly beneficial, e.g. reduction of plasma cholesterol and postprandial glycaemic response, which decrease the risk of cancer, heart disease, hypertension and obesity in the long term. The relationship between consumption of foods rich in soluble fibre, especially  $\beta$ -glucan, and reduced risk of heart disease resulted in the first health claim for a specific food in

North America in 1997. Resistant starch resists enzymatic activity *in vivo* and *in vitro*, and therefore shows similar physiological effects as dietary fibre. Polyphenols constitute a large group of secondary plant metabolites (flavonoids, phenolic acids, lignins, etc.) found in the outer layers of cereal seeds. Phenolic compounds are effective antioxidants with the potential therapeutic value to reduce the risk for cardiovascular disease and cancer.

In the presented study the variability in the chemical composition of diverse cereals was investigated. Besides ash, starch, crude protein, total fat and crude fibre, special account was taken to dietary fibre and phenolic compounds.

#### Materials and methods

#### Plant material

The following cereals were grown in 2003 at the experimental farm Groß-Enzersdorf, northeast of Vienna: einkorn wheat (*Triticum monococcum*), emmer wheat (*T. dicoccum*), Oriental wheat (*T. turanicum*), durum wheat (*T. durum*), spelt wheat (*T. spelta*), common wheat (*T. aestivum*), barley (*Hordeum vulgare*), oat (*Avena sativa*), and rye (*Secale cereale*). Within some species diverse biotypes were analysed, i.e. red, blue, and purple grain coloured common wheats, hull-less, hulled and hulled black barley, hull-less and hulled oats, and common and semi-perennial rye (var. *multicaule*). Generally, grains with a kernel size between 2.2 and 2.5 mm were analysed.

#### Chemical analysis

Whole grain flour was milled using a ZM 100 ultra-centrifugal mill (Retsch Gmbh & Co KG, Haan, Germany) equipped with a 0.5 mm sieve. Afterwards the samples were analysed for moisture content (ICC Standard Method 110/1), ash content (ICC 104/1), crude protein content (ICC 105/1), total fat content (ICC 136), starch content (ICC 123/1), crude fibre content (Fibertec<sup>TM</sup> 2021/2023 Fibercap system; Foss Tecator AB, Höganäs, Sweden), total dietary fibre content (112979 Bioquant<sup>®</sup> Total Dietary Fiber Reagent Kit; Merck, Darmstadt, Germany), total  $\beta$ -glucan content (ICC 166; Beta-Glucan (Mixed-linkage) Assay Kit; Megazyme, Bray, Ireland), total yellow pigment content (ICC 152), total anthocyan content (modified after Abdel-Aal & Hucl 1999), total phenol content by means of the Folin-Ciocalteu reagent (Singleton et al. 1974), and reducing power according to the method of Oyaizu (1986) based on the chemical reaction of Fe(III)  $\rightarrow$  Fe(II). The reported values are means of triplicate and/or quadruplicate measurements, and on a dry weight basis. Hulled wheats (einkorn, emmer, spelt) were dehulled before analyses, whereas hulled barleys and oats were not dehulled and, therefore, whole grain flours contained the husk part of the grain.

#### **Results and discussion**

The results of the chemical analyses are presented in Tables 1 and 2. Significantly higher contents of crude fibre and ash, and lower contents of starch were determined for hulled barleys and oats. This is not astonishing, since these cereals were analysed with the husk of the grain (oats: 25 - 30 %; barley: 6 - 15 %), which is known to contain more than two-thirds of the grain's cellulose. Very high protein contents ( $\geq 19$  %) were determined for the 'ancient wheats' einkorn, emmer and Oriental, as well as for hulled black barley, whereas the lowest level (11 %) was observed for common rye. As for total fat content, oats contain about twice the amount than other cereals. All values reported in Table 1 are within the ranges known from literature, e.g. somewhat higher ash contents and significantly higher protein contents for ancient wheats compared to modern durum and/or common wheats were reported by D'Egidio et al. (1993) and Løje et al. (2003). In Table 2 mean values of some biologically active constituents are presented. Except for hulled barleys and oats, both forms of rye turned out to have highest contents of total dietary fibre ( $\approx 17$  %), while grains of the hulled wheat

species einkorn, emmer and spelt showed the significantly lowest values ( $\leq 10$  %). Similar results were obtained by Løje et al. (2003). In regard to β-glucan the lowest levels were observed for wheats (0.3 - 0.9 %), while rye contained about 2 %, and the highest levels were obtained for barley and oats (3 - 4.5 %). These results are very similar to those reported by Wagner and Kuhn (1996) for German-grown cereals. Variation in polyphenolic compounds was considerable. Einkorn, durum and purple grain common wheat contained highest values of yellow pigment (carotenoids). Abdel-Aal et al. (2002) report somewhat lower values of lutein, the major yellow pigment in wheat, for Canadian einkorn and durum genotypes, while D'Egidio and Vallega (1994) and Grausgruber et al. (2004) found contents of yellow pigments between 12 and 23 ppm. The high value for hulled oats must be neglected, since this value is most likely influenced by the co-analysed husk. Astonishing, however, is the high content for hulled black barley, which is similar to einkorn, durum and purple wheat, and nearly the double amount of hulled 'yellow' barley. Highest contents of anthocyans were observed for blue and purple grain common wheat. Somewhat higher contents than for the rest were also observed for black barley and rye. Total phenol content and reducing power were responsible for the significantly higher antioxidant activity of barley, especially of black barley. In addition, purple grain wheat and semi-perennial rye had somewhat higher contents than the other cereals.

	1		$\mathcal{O}$		
Sample	$ASH^1$	TS	СР	TF	CF
Wheat					
Einkorn	2.21	50.46	20.03	2.44	1.32
Emmer	2.10	59.97	19.05	2.01	1.71
Oriental	2.38	57.96	19.68	1.40	2.22
Durum	1.93	61.12	16.79	2.26	2.97
Spelt	2.04	52.38	19.07	2.19	2.56
Red grain	1.90	59.73	15.74	1.83	3.05
Blue grain	1.61	61.97	14.95	2.07	3.13
Purple grain	1.77	60.66	14.14	1.52	3.38
Barley					
Hull-less	2.06	58.55	17.76	2.26	1.88
Hulled	2.44	54.66	15.03	2.20	4.02
Hulled black	2.54	49.55	18.83	2.07	5.20
Oats					
Hulled	2.75	33.61	13.19	3.88	12.77
Hull-less	2.15	56.61	17.59	4.82	2.01
Rye					
Common	1.81	59.71	10.84	1.52	2.17
Semi-perennial	1.68	55.51	15.76	1.62	2.41

**Table 1.** Composition of whole grain flours (%, db)

<sup>1</sup> ASH, ash content; TS, total starch content; CP, crude protein content; TF, total fat content; CF, crude fibre content

Summarizing, there exists a considerable variability of biologically active constituents in cereals, and especially barley has great potential for healthy human food products. However, besides the potential therapeutic value, some compounds can negatively affect the flavour of products, e.g. phenolic acids, or the processing of the raw material, e.g. poor mixing characteristics of einkorn, barley and oat flour. Hence, it is a great challenge for food technology not to alter the active ingredients during certain processing techniques and to bring them into a palatable form.

Sample	$\mathrm{DF}^1$	BG	YP	CYAN	PHEN	RP
Wheat						
Einkorn	9.68	0.32	1.15	0.75	102.27	15.69
Emmer	8.89	0.31	0.66	0.78	105.85	20.45
Oriental	12.72	0.53	0.47	0.50	95.49	11.91
Durum	13.25	0.53	1.10	0.68	109.64	15.63
Spelt	10.16	0.74	0.51	1.23	110.77	13.46
Red grain	14.28	0.90	0.39	0.91	108.04	15.77
Blue grain	14.53	0.88	0.48	6.01	118.50	19.26
Purple grain	15.66	0.67	1.05	7.45	143.96	25.16
Barley						
Hull-less	12.32	3.51	0.57	0.49	171.35	44.47
Hulled	20.54	3.46	0.64	1.45	114.50	44.00
Hulled black	21.24	4.62	1.13	2.13	197.15	49.15
Oats						
Hulled	41.64	2.76	1.30	1.17	101.51	27.87
Hull-less	14.68	4.51	0.43	0.43	128.41	17.35
Rye						
Common	17.33	2.21	0.64	2.22	118.51	20.63
Semi-perennial	16.96	1.87	0.62	1.76	132.41	24.54

Table 2. Contents of biologically active constituents of whole grain flours

<sup>1</sup> DF, total dietary fibre (%); BG, total beta-glucan (%); YP, total yellow pigment (mg  $\beta$ -carotene equivalent/100 g, db); CYAN, total anthocyan (mg cyan-3-O-glucoside equivalent/100 g, db); PHEN, total phenol (mg ferulic acid equivalent/100 g, db); RP, reducing power (mg ascorbic acid equivalent/100 g, db).

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