**BLACK WHEAT BRAN AS A PROMISING SOURCE OF FOOD FIBRES WITH AN EXPANDED SPECTRUM OF FUNCTIONALITIES**

**Abstract**
Modern requirements of nutritiology determine the enrichment of a person’s daily diet with food fibres. Dietary supplements and cereal-based ingredients are widely used to achieve this goal. Wheat as a food crop traditionally occupies a leading position in food production. Currently, new varieties of wheat with colored grains are being given increasing attention as a source of high-activity phytochemical compounds, which can initiate a positive synergistic physiological effect in the complex. The black-grain wheat of the domestic variety "Chornobrova" belongs to the functional species among the new valuable colored varieties of wheat. It contains an increased amount of biologically active components concentrated in the husk and germ of the grain. At grain processing plants by-products are formed in the production of flour and cereals, among which the hard shells of grain release in the form of bran, that have a rich source of dietary fibres. The paper describes the breaking bran and grinding bran of black-grained wheat "Chornobrova". They contain up to 78.0% of polysaccharides, among which hemicelluloses and cellulose predominate. Both types of black wheat bran are protein-rich (13.0-15.3%), and the crude fat content does not exceed 2.1%. The non-hydrolyzed residue, represented primarily by lignin, reaches 3.8%. Bran is rich in phenolic compounds – powerful antioxidants with the mass fraction 310.0 mg/100 g. Both types of bran have a water retention and sorption capacity towards toxicants (phenol, Pb²⁺), cholic acid, methylene blue. As a result of acid treatment of bran, dietary fibre concentrates were obtained, in which non-starch polysaccharides predominate. They are characterized by modified physicochemical properties, namely improved water holding capacity, sorption activity against Pb²⁺, not inferior to bran in terms of the ability to bind cholic acids and methylene blue. "Chornobrova" wheat bran and dietary fibre concentrates are highly active enterosorbents with antioxidant activity, which can be considered as dietary supplements and food ingredients that should be included in recipes in the development of new functional foods.

**Keywords:** black wheat, bran, dietary fibre, enterosorbents, phenolic antioxidants.

**Introduction**

One of the effective ways to strengthen human health is to introduce dietary fibres (DFs) into the diet, that are mainly represented by complex carbohydrates (structural or non-starch polysaccharides) – cellulose, hemicellulose, pectin, β-glucans, resistant starches, polyfructans, oligosaccharides (degree of polymerization more than 3) – oligofructans, galactooligosaccharides, lignin and related substances. DFs are not digested in the upper sections of gastrointestinal tract, in particular resistant to digestion and absorption in the small intestine, fully or partially fermented in the colon, resulting in the release of short-chain fatty acids, which have anti-carcinogenic properties, inhibit the cholesterol synthesis (in particular propionate) and reduce the postprandial glucose response. Also, they play a crucial role in the composition and metabolic activity of the intestinal microbiome (prebiotic activity), which, in turn, affects intestinal health and, ultimately, the immune system, and subsequently the body’s ability to resist some chronic disease. In addition, during fermentation in the colon soluble DFs produces two hormones – glucagon-like peptide (GLP-1) and peptide YY (PYY), which stimulate the feeling of satiety and reduce weight gain. DFs as natural enterosorbents have a significant sorption and detoxifying effect: well absorb water, bind some substances that forms in cells and tissues of the body (anti-inflammatory cytokines, C-reactive protein, antigens, estrogens), some metabolic products of the body (bile acids, lipid complexes, glucose), sorb endo- (excess urea, bilirubin) and exogenous toxic substances of various natures (phenol, salts of heavy metals, radionuclides, food allergens – more often glycoproteins, less polypeptides and haptens), pathogenic bacteria. This provides a manifestation of a wide range of important physiological effects with preventive and curative direction: activation of motor function of the digestive organs (DFs change the rate of gastric emptying, and, consequently, satiety and loss of appetite, promote the intestinal motility), enable to regulate energy consumption thereby increasing the loss of body mass, and prevent obesity, the risk reducing development of coronary vascular diseases (arterial hypertension, stroke, ischemic heart disease), bile-like disease and certain cancers such as colon carcinoma, small intestine cancer, oral cavity carcinoma, laryngeal cancer and breast cancer. Furthermore, DFs contribute to the
reducing of development type II diabetes by decrease of the glycemic index and acute and chronic intoxications of various origins (soluble DFs increase in a volume in the gastrointestinal tract and form a viscous material, which reduces the duration of contact between potential carcinogens and cells of the small intestinal mucosa), acute seasonal and chronic allergic reactions.

In most countries of the world the level of DFs consumption is much lower (less than half) than the recommended values, although the consumption of products that are rich in DFs such as fruits, vegetables and whole grains increases. An important way to solve the problem of deficiency of DFs in the daily diet is to develop functional foods by using DFs in them from various traditional and unusual sources, including by-products of agricultural processing.

**Literature review**

Cereals are important among all foodstuffs and play a key role for a healthy diet. Among cereals, wheat is the leader in terms of gross grain harvest and consumption (bakery, cereals and pasta) [1-3]. It is not only a source of essential nutrients such as carbohydrates, proteins, vitamins, trace elements, but also a source of DFs and antioxidants of phenolic nature [4-8].

Widespread traditional varieties of wheat throughout the world are red and white [1-3, 9, 10]. However, for several years now, pigmented varieties with dark and light purple, blue, black and green color of grain have appeared in the world grain market, which have the increased biological value and great market potential [9]. Colored wheat, rich in anthocyanins, attracts the attention of scientists and food producers around the world due to its potential as a bright food dye, nutraceutical ingredient and functional food [10-15]. It can be consumed by making whole-wheat bread, chapati, roti, parata, cookies, cakes, pizza base, burgers, fried snacks, etc. [13, 15].

White wheat is a rich source of phenolic acids. It has the highest content of ferulic acid, which has low solubility in water, but it is a powerful antioxidant (antioxidant activity includes the removal of reactive oxygen species and nitrogen, reducing the ability of metals to interact with chelating agents, inhibition of oxidative enzymes), which actively eliminates or inhibits the processes of free radical oxidation, help curb the aging process, reduce the risk of cancer, cardiovascular disease, diabetes, malaria, rheumatoid arthritis, neurodegenerative diseases, obesity and other disorders [9, 15, 17]. In colored wheat, an additional contribution to antioxidant activity belongs to the high content of anthocyanins, which, in turn, provide the color of black, blue and purple wheat [9-15, 18, 19]. Anthocyanins are water-soluble pigments-polyphenols related to the class of flavonoids. Among the multi-colored wheat species, there is a certain tendency in the total content of anthocyanins: black > blue > purple > white [9, 15, 19]. The white wheat has a very low content of anthocyanins and the purple ones differ by significant fluctuations. The chromatographic profiles of blue and black wheat were similar (they identified five species of anthocyanins – pelargonidin-3-glucoside, cyanidin-3-glucoside, cyanidin-3-rutinoside, peonidin-3-galactoside and cyanidine chloride) and varieties of purple wheat differed significantly from the previously mentioned ones. This indicates that the plants, their growing area and environmental conditions affect the accumulation and quality content of anthocyanins. There are controversial views on the predominant anthocyanins in colored wheat. Some scientists argue that cyanidin-3-glucoside is the dominant anthocyanin in purple wheat [9, 15], while delphinidin-3-glucoside is the main component in blue wheat [15]. The publications show that the main anthocyanin in purple wheat is cyanidin-3-glucoside, while other publications state cyanidin-3-rutinoside. Other results suggest that cyanidin-3-rutinoside contributes more to the color of blue wheat and cyanidin-3-glucoside – to purple wheat. These bioactive compounds are mainly located in the outer membrane of the grain. The purple color of the grain is due to the localization of pigments in the amniotic sac (pericarp), while the blue color is due to the concentration of biocolorants in the aleurone layer [9, 19]. Black wheat is obtained by combining genes of both purple and blue colors [9, 18]. Purple and black wheat varieties have a high protein content and antioxidant activity due to the presence of phenolic substances (phenolic acids and anthocyanins) and vitamin C [9]. Antioxidant activity of colored wheat varieties increased in order: white < blue < purple < black. Although purple wheat had a low total anthocyanin content, they showed higher inhibitory effects on the production of proinflammatory cytokines. This fact may be associated with a higher concentration of acylated anthocyanins with higher stability and bioavailability (acylated anthocyanins have a very low concentration compared to non-acylated forms and are often not considered) [9].

Black wheat has appeared in the agricultural market relatively recently. The main producing countries are China, the United States and India [10-13]. The volume of black wheat growing depends on the demand. Black wheat varieties are especially valued in China due to its high biological activity [12, 18]. Every year the production of black wheat increases worldwide. This wheat variety has a higher content of crude protein, but the quality of gluten is lower than others [20]. The carbohydrate complex of mature black wheat (about 65-75% of dry grain weight) consists of mono- (small amounts of D-glucose, D-fructose and their phosphated forms) and oligosaccharides (low content of maltose, sucrose, fructooligosaccharides, raffinose and stachyose), polysaccharides (amylopectin starch, inulin, arabinoxylactan, (1,3; 1,4)-β-D-glucan, arabinoxylan, cellulose, glucomannan). The cell wall of the aleurone layer of wheat grain includes insoluble (cellulose, part of the hemicellulose component and lignin) and soluble (1,3, 1,4)-β-glucans and often esterified with ferulic acid arabinoxylans) biopolymers [21].

In Genetic Selection Institute (Odessa, Ukraine) scientists created and declared the first middle-early variety of black wheat "Chornobrova" in Ukraine, which was included in 2014 in the State Register of plant varieties suitable for distribution in Ukraine as a common wheat variety for cereals direction with improved nutritional (biological) value of grain. This wheat variety originated from the cross-breeding of cultivated wheat and wild wheatgrass, known in folk medicine. The last one is a
donor of chromosomal translocations of black grain pigmentation. Due to this, the plant has an increased number of biologically active components and, accordingly, the best botanical indicators: moderately bushy, high drought resistance and resistance to lodging, frost, disease. "Chornobrova" wheat has a solid consistency of endosperm. It is characterized by a high content of easily soluble, complete and digestible proteins (up to 15.3%), vitamins (B₁, B₂, C, E), trace elements (Phosphorus, Calcium, Iron, Zinc, Selenium), antioxidants and resistant starch. Healthy grain components of this variety are concentrated in the husk and germ. This wheat is characterized by a low content of crude gluten (23.0%). Also, it has a minimum content of gluten, which is suitable for people suffering from celiac disease [10-13].

"Chornobrova" wheat can be used to make cereals, flour, breakfast cereals, muesli, porridge, different pastries, bread from germinated wheat (without flour and yeast) and healing juice from green 8-9-day-old seedlings. Using it, to make wholemeal flour with high biological value is appropriate [10-13]. Making bread, this flour with the addition of Top Bake Ban Bread 0.5% or in a rye-wheat mixture should be used, which will not only improve the traditional color of rye bread, but also its properties [22].

In the production of high-quality flour, the endosperm is significantly grinded, and the embryo, shell and aleurone layer are isolated in the form of bran. This by-product of cereal processing is an important source of DFs in diets. Today, they are enriched by such consumer products as bakery products, various food concentrates, meat products, salads, sauces, etc. "Chornobrova" wheat bran due to their high content of valuable components can have a synergistic effect in theory and become highly effective bioregulators of human body functions.

**Purpose and objectives of the study**

The aim of the work is to characterize the bran of black wheat variety "Chornobrova" in the context of use as a physiological and functional ingredient, which can become a promising ingredient in the food matrix in the development of new healthy products.

In order to achieve the objective, the following tasks should be solved:
- to establish the chemical composition and characterize the biopolymer composition of black wheat bran;
- to study the physico-chemical properties of black wheat bran, which determine their physiological effects;
- to obtain enterosorbents from black wheat bran with an expanded spectrum of biological activity.

**Materials and methods**

In the work bran was used formed during the processing of wheat "Chornobrova" into flour. In both types of bran, we determined mass fraction of moisture by drying at 105 °C to constant weight [23], ash – by burning followed by calcination of the mineral residue at 500-600 °C [23], Nitrogen – by Kjeldahl method [23], protein – by multiplying the nitrogen content by a factor 5.7, lipids – by exhaustive extraction with hexane [23], easily hydrolyzed polysaccharides (EHP) – by reducing capacity of solutions obtained after hydrolysis of bran with 2% HCl solution [24], hardly hydrolyzed polysaccharides (HHP) – by reducing capacity after hydrolysis of the residue (after removal of EHP) with 80% solution of H₂SO₄ [24], reducing substances (monosaccharides) – by the Hagedorn-Jensen micromethod [24], phenolic substances – by spectrophotometric method in 70% ethanolic extracts with 1% HCl with reagent Folina-Chokalteu at λ = 725 nm in terms of gallic acid [23], mineral elements – atomic emission method [23]. The monosaccharide composition of EHP hydrolysates was determined by paper chromatography [25]. Sorption properties of bran were studied for their ability to bind water (method of soaking samples in water and subsequent centrifugation) [5], to sorb phenol (bromide-bromate method) from aqueous solution [26] and Pb²⁺ ions (trionometric method) [27], cholic acid [28] and methylene blue [29] are analyzed by spectrophotometric method.

Modification of the composition of bran was carried out by treating them with 1.7% H₂SO₄ solution at the boiling point of the reaction mixture to remove components capable of fermentolysis with α-amylase [5]. Then physichemical properties of bran were characterized.

**Results and discussion**

Owing to black wheat has different characteristics of the chemical composition in comparison with traditional varieties of wheat for the flour production, the chemical composition of breaking bran and grinding bran should be determined. Results are presented in table 1.

The dominant components of wheat bran are polysaccharides, counted 78.2%. Among them, the biggest contents are EHP represented by starch and hemicellulososes (HMC). In contrast, breaking bran contains the same proportions of EHP and HHP (cellulose). The mass ratio of galactose: glucose: arabinose: xylose in the products of bran hydrolysis of EHP is tracess: 1.00 : 0.73 : 0.99 respectively, and in the products of bran hydrolysis of EHP – traces: 1.00 : 0.19 : 0.23 respectively. Among the identified hexoses in EHP of both types of bran, galactose contains trace levels, and glucose predominates, part of which apparently belongs to starch, which is digested in the human body and the other part may be relate to undigested (1,3; 1,4)-β-glucan. In breaking bran mass ratio of glucose : arabinose : xylose is quite close. Another trend is observed in the monosaccharide composition of EHP of grinding bran: hexoses predominate. Among pentoses, bran hydrolysates contain slightly more xylose than arabinose. Obviously, the HMC of black wheat bran can be represented by arabinoxylans. Some arabinose residues in arabinoxylan are esterified with hydroxycinnamic acid or its substitutes with ferulic or p-coumaric acids. HMCs of more complex structure are known, in the structure of which, in addition to xylose and arabinose residues, galactose and glucose residues are included. It is possible that the HMC of black wheat husks may include xylloglucans and arabinoxylglucans. Uronic acid was not identified in the products of hydrolysis of EHP of both bran types. The mass fraction of substances in bran had not been hydrolyzed under conditions of EHP and HHP did not exceed 3.8%, which, in particular, included lignin. Both types of black wheat bran were rich in protein.
Table 1 – Chemical composition of black wheat bran

| Parameter                                | Breaking bran | Grinding bran |
|------------------------------------------|---------------|---------------|
| Moisture (W), %                           | 10.7          | 11.9          |
| **On a dry matter basis**                |               |               |
| Mass fraction of total Nitrogen, %       | 2.7           | 2.3           |
| Mass fraction of protein, %              | 15.3          | 13.0          |
| Mass fraction of crude fat, %            | 1.7           | 2.1           |
| Mass fraction of polysaccharides, %:     |               |               |
| EHP, %                                   | 38.5          | 55.7          |
| HHP, %                                   | 38.8          | 22.5          |
| Mass fraction of non-hydrolyzed residue, % | 3.1           | 3.8           |
| Mass fraction of ash,%                   | 2.5           | 2.2           |
| Mass fraction of mineral components, mg/kg: |            |               |
| Mn                                       | 175.9         | 79.2          |
| Fe                                       | 123.0         | 65.9          |
| Si                                       | 47.0          | 18.3          |
| Mass fraction of phenolics (in terms of gallic acid), mg/100 g | 310.0         | 270.0         |

The content of crude fat in grinding bran is slightly higher than in breaking bran, and the content of ash substances was contrary. Bran is rich in such valuable mineral elements as iron, manganese and silicon. The content of manganese and iron in breaking bran was by 1.9-2.2 times higher than in grinding bran, and, on the contrary, the content of silicon was by 2.6 times lower than in grinding bran. Phenolic components are a valuable minor component of black wheat bran with their inherent antioxidant effect.

The next step was to evaluate the sorption properties of black wheat bran. The results of experimental data are shown in table 2.

According to the obtained data, grinding bran absorb and retain water better and their sorption capacity towards cholic acid and phenol is higher comparative to breaking bran. But in terms of the ability to sorb Pb$^{2+}$ ions from the aqueous solution they are inferior to breaking bran. Higher WRC of grinding bran than breaking bran may be due to the greater mass fraction of HMC in them, in particular, arabinoxylans and (1,3; 1,4)-β-glucan, capable of high hydration. Both types of bran have similar values of sorption activity relative to methylene blue, which allows to model *in vitro* and predict *in vivo* their adsorption capacity against *Escherichia coli* bacteria – the most numerous aerobic commensals of the large intestine, which can cause diarrhea and infection if they are in sterile loci of the human body (for example, urinary tract).

In order to activate the physicochemical properties, wheat bran was treated with a dilute solution of sulfuric acid when heated. Under these conditions, there are hydrolysis of easily digestible starch and concentration of structural polysaccharides. As a result, concentrates of DFs have less calories than bran and greater safety (microbiological resistance and absence of harmful substances). As expected, the part of easily hydrolyzed polysaccharides decreases, instead the content of nitrogen-containing biopolymers increases, physicochemical parameters increase, that allows to predict their physiological effect. The decrease of phenolic compounds in the content of DFs concentrates does not exceed 3.2-8.5% that is not significant in comparison with the initial bran. Perhaps, this is explained by the fact that phenolic compounds bind to biopolymers, and as a result, they can retain their physiological activity even under the conditions of acid and heat treatments of bran.

Thus, the abovementioned facts indicate the possibility and expediency of using the studied bran as a source of non-starch polysaccharides in health diets. They differ favorably from bran of traditional wheat varieties in Ukraine by a significant content of phenolic compounds known for a wide range of physiological action, in particular antioxidant, antitumor, immune correction, anti-inflammatory effects. Using them, to obtain concentrates of DFs is possible that are characterized by a high content of non-starch component, high level of safety and extended functional properties due to the content of phenolic component.

### Table 2 – Functional properties of black wheat bran

| Parameter                                | Breaking bran | Grinding bran |
|------------------------------------------|---------------|---------------|
| Water retention capacity (WRC), g H$_2$O/g | 1.5           | 3.1           |
| Sorption capacity                        |               |               |
| Phenol, mmol/g                           | 9.4           | 71.7          |
| Pb$^{2+}$, mg/g                          | 49.4          | 10.3          |
| Cholic acid, mg/g                        | 15.5          | 17.1          |
| Methylene blue, mg/g                     | 4.7           | 4.5           |
| In terms of *E. coli* (not less than a million bacteria) | 49.4          | 48.5          |

### Conclusions

The characteristic of chemical composition and sorption properties of breaking bran and grinding bran of "Chornobrova" wheat variety were presented. The content of biopolymers in bran reaches 94.0-95.7%, of which
77.3-78.2% are polysaccharides. Wheat bran is a source of valuable phenolic antioxidants and minerals. It is characterized by high water retention capacity, sorption activity towards toxicants such as phenol and ions of Pb, metabolites such as cholic acid, bacteria of Escherichia coli group, which proves their powerful potential as essential components of health diets. Concentrates of dietary fibre of black wheat bran with improved physicochemical properties were obtained. This allows them to be considered as a safe dietary supplement or physiological and functional ingredient with further identification of promising directions of their use.

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ВИСІВКИ ЧОРНОЗЕРНОЇ ПШЕНИЦІ ЯК ПЕРСПЕКТИВНЕ ДЖЕРЕЛО ХАРЧОВИХ ВОЛОКОН З РОЗШИРЕНИМ СПЕКТРОМ ФУНКЦІОНАЛЬНИХ МОЖЛИВОСТЕЙ

Анотація
Сучасні вимоги нутриціології встановлюють необхідність збагачення добового раціону харчування людини харчовими волокнами. Для досягнення цієї мети широко застосовують використання дієтичних добавок та харчових інгредієнтів на основі зернової сировини. Пшениця як продовольча культура традиційно займає провідне місце у виробництві харчової продукції. У теперішній час все більша увага приділяється новим сортам пшениці з забарвленим зерном як джерелі високаактивних фітохімічних сполук, які в комплексі можуть ініціювати позитивний синергетичний фізіологічний ефект. Серед нових цінних колорових сортів пшениці на функціональних властивостях зростає вага сортів змішаного забарвлення, зокрема пшениці з чернозерном. На зернопереробних підприємствах при виробництві борошна та крупи утворюються побічні продукти, серед яких тверді оболонки зерна виділяються у вигляді висівок, які є багатим джерелом харчових волокон. У роботі охарактеризовано висівки дертьові та розмельні чорнозерної пшениці «Чорноброва». Насіннєва маса висівок містить 28,0-38,0 % дроблих ядрищ та 52,0-62,0 % оболонок зерна. Висівки сортів пшениці «Чорноброва» мають високу водоутримувальну та сорбційну здатність щодо городів, холевої кислоти, метиленового синього. Висівки пшениці «Чорноброва» і концентрати харчових волокон з них є високоактивними ентеросорбентами з антиоксидантною активністю, які можна розглядати як дієтичні добавки і харчові інгредієнти, що варто включати у рецептури при розробленні нових функціональних продуктів харчування.

Ключові слова: чорнозерна пшениця, висівки, харчові волокна, ентеросорбенти, фенольні антиоксиданти.

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