



Anthocyanins in Naked Pigmented Barley Grain as a Source of Antioxidant Activity

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Abstract

Anthocyanins and other phenolic compounds are powerful antioxidants, which reduce risks of many serious human diseases. Anthocyanin contents in naked pigmented barley grain have been determined in numerous studies. In Ukraine, the purpose of the breeding of barley with pigmented grain as a functional food product is biofortification of the grain nutritional value. Published data have demonstrated that it is possible to create high-yielding naked pigmented barley lines.

Keywords: Naked Barley; Pigmented Grain; Anthocyanins; Pigments; Phenolic Compounds; Antioxidant Activity; Functional Nutrition

Introduction

Progressive trends in breeding and production of functional foods include the creation of enriched grain-based products. Due to low costs of raw materials, such products are available to broad segments of the population and capable of compensating for deficits of biologically active substances in diets, enhancing the body's resistance to adverse environmental factors, and thus increasing human life expectancy.

In 2006, the US Food and Drug Administration (US FDA) listed barley grain as a product that reduces the risk of coronary heart disease, that is, as a functional food product. Participants of an ICARDA symposium assessed the food barley value and the need to create domestic and international networks for its research. A global project on food barley was prepared with the following steps:

- Collection of initial information, filling out blind spots
- Reproduction of local food barley cultivars to ensure grain quality and stable performance

- Organization of optimal crop management for stable production
- Improvement of storage of raw materials and enrichment of diets with barley
- Development of small food barley-growing farms
- Improvement of seed production and reproduction

It was decided that recipes of barley dishes should be collected in different regions and compiled into a recipe book to promote food barley [1-3].

The role of grain products in adequate nutrition is scientifically justified, as they are recognized sources of various physiologically active health-ensuring ingredients [4-9]. Bioactive ingredients are found in cereal grains in varying amounts, depending on genotypes. Antioxidant properties are the main factor determining the food value for human health. Antioxidant level in barley is one of the highest ones among cereals. An antioxidant is any substance that neutralizes free radicals, which trigger chain reactions, and thereby delays or prevents the oxidation of target molecules.

The most common are cyanidins, delphinidins, malvidins, pelargonidins, petunidins, and peonidins [5,6]. The main function of antioxidants in the cell is the neutralization of reactive oxygen species and free radicals, which are formed, as a rule, under the influence of adverse environmental factors. Resistance of a plant to oxidative stress is determined by antioxidant content and composition and by how quickly they are synthesized and accumulated, and these processes are genotypically controlled [4,5]. Studies of genetic control of anthocyanin content and variability in barley are very popular worldwide [10-12].

Food Barley Breeding in Ukraine

In different countries worldwide, programs on food barley breeding have been launched; outstanding successes have been achieved in Canada, the USA, Japan, Australia, and European countries. In Ukraine, similar studies are also being conducted: they were initiated at the Plant Production Institute named after VYa Yuriev of NAAS (Kharkiv), Plant Breeding and Genetics Institute of NAAS (Odesa), Institute of Steppe Agriculture of NAAS (Kropyvnytskyi). In Ukraine, the purpose of the breeding of barley with pigmented grain is biofortification of the grain nutritional value, as high contents of polyphenols means good antioxidant activity and inhibits α -glycosidase. As a result, pigmented barley can be a powerful antioxidative and hypoglycaemic product [7,8,13-16].

The Plant Breeding and Genetics Institute launched a large-scale program to create breeding material for winter and spring food barley cultivars. Canadian cultivars, CDC Alamo and CDC Candle, served as sources of the *waxy* gene. A naked cultivar, Akhilles, and lines with rounded hard grains were derived from crossing with Mc Gwire and BRL-6 cultivars. The protein content in the created lines amounts to 17.14–21.06%; the β -glucan content – to 8.66%; the oil content is 2.73–3.24%; the linolenic acid percentage in oil is 5.49% [4,17,18]. The Plant Production Institute named after VYa Yuriev of NAAS have bred waxy barley cultivars (Shedevr and Amil) and naked cultivars (Yavir, Orlan, Obrii, and Rondo). At Nosivka Breeding And Research Station, Kozatskyi, a naked cultivar has been bred; at the Institute of Steppe Agriculture, Gatunok has been created.

Phenolic Compounds and Anthocyanin's as Factors of Antioxidant Activity in Barley

Numerous studies have demonstrated that AOA steadily depends on genotypes, in particular, on polyphenolic compound contents [5,6,8-10,12,13,19,20]. These data are consistent with experimental results obtained by scientists of the Plant Production Institute named after VYa Yuriev of NAAS. Thus, the phenolic compound content affects the total

antioxidant activity. There is a significant positive correlation between these two features ($r = 0.668$), characterizing a close linear relationship [11]. This is in agreement with data of Xiangzhen Ge, et al. [9]. Under any conditions, the highest AOA was inherent in waxy naked genotypes (2.02 - 3.46 mg chlorogenic acid equivalents/g), and the lowest AOA - in chaffy accessions with wild-type starch (1.54 - 2.20 mg chlorogenic acid equivalents/g). It should be noted that CDC Alamo (naked cultivar) had the highest AOA (3.46 mg chlorogenic acid equivalent /g) of all the cultivars under investigation [11].

Barley has unique dietary features due to the fact that it is one of the richest sources of phenolic compounds among cereals. AOA is directly related to phenolic compound contents in barley grain, in particular pigments [9,10]. Studies during the last decades convince that barley products are functional foods, a preventive measure against the three most serious diseases - cardiovascular pathologies, diabetes and cancer. Oxidative stress and inflammation are two key factors that contribute to the development of atherosclerosis. A study of naked barley, viz. its protective function in the regulation of antioxidant protection, revealed powerful protective functions of barley upon oxidation and potential of barley in preventing chronic inflammation in cardiovascular diseases [1-5,9,12].

The Plant Production Institute named after VYa Yuriev of NAAS investigated relationships between the total content of phenols, anthocyanin content and AOA. There was a close linear relationship between these features. In particular, we have created a valuable line, Violet 18-1207 (UA 0805977), var. *nudidubium*. Its anthocyanin content is 0.260 relative units D530/g; the phenol content is also high (1.04 mg gallic acid equivalent /g). In addition, Violet 18-1207 is noticeable for high resistance to smuts and leaf diseases as well as to drought. Such data are consistent with other researchers' statements about the important agronomic value of increased contents of pigments in barley, as they also associate it with resistance to abiotic and biotic stress factors [11,21,22].

Prospects of Naked Pigmented Barley Breeding

In Italy, a breeding program was initiated to obtain germplasm of naked barley with pigmented grain, rich in biologically active substances (phenols, anthocyanin's, flavonoids, and others) and with high antioxidant activity. High heritability was observed for most biochemical compounds, and grain yield was significantly positively correlated with phenols and antioxidant activity [21].

There are numerous studies on the genetic control of barley grain colour. Violet pigmentation of grain was

discovered to be controlled by the *Ant1* gene on chromosome 7HS and *Ant2* gene on chromosome 2HL. The *Blp* gene on chromosome 1HL controls the black coloration of glumes and pericarp in barley. Black and violet colours are inherited from female forms [10,13].

Dongdong Xu, et al. [23] identified the glutathione-S-transferase (*HvGST*) gene, which is responsible for the blue coloration of the aleurone layer in Tibetan barley (qingke). Analysis of gene variability and expression revealed that *HvGST* was also involved in the transport and accumulation of anthocyanins in purple barley.

In pre-breeding programs, the content of pigments in barley is widely studied in relation to caryopsis colour. Thus, it was shown that pelargonidins confer red (orange) colour, cyanidins - dark red, delphinidins - violet (blue) [10,23]. Cornflower pigment-3-glucoside was the main anthocyanin in blue, yellow and violet barley, while delphinidin-3-glucoside - in black barley. Dark colours indicate increased contents of anthocyanins [7]. In other studies, increased concentrations of β -glucans and anthocyanins were found purple and blue barley, while black barley did not have such nutritional properties [9]. Yao X, et al. [16] reported similar data on increased contents of anthocyanins in violet barley.

Effects of various phenolic compounds on barley grain coloration are also widely studied. In particular, the contents of total phenols and flavonoids were determined in purple barley. The main phenolic acids in blue barley were benzoic acid polyphenols; chalcones and flavonones were major types of flavonoids in black and blue barley, respectively; and in yellow and purple barley, flavonol prevailed [7].

Xiangzhen Ge, et al. [8] described the phenolic compound profile in naked pigmented (white, yellow, black and blue) barley and identified 156 phenolic substances. The profile was the most diverse in black barley, and the phenol content varies depending on grain colour. It was established that markers associated with the composition and content of phenolic compounds differed in wild and domestic barley [24].

Italian scientists managed to create barley lines that are characterized by early ripeness, high yield, high test and thousand grain weights in combination with high contents of phenols, anthocyanins, flavonoids, carotenoids, β -glucans and high antioxidant activity [21].

Thus, research into features of naked pigmented barley is widespread globally, and the breeding of cultivars with such grain appears to be promising and extremely important through the lens of ensuring food security and beneficial impact on human health.

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