

UV ABSORBING COMPOUNDS IN BUCKWHEAT PROTECT PLANTS AND PROVIDE HEALTH BENEFIT FOR HUMANS

UV ABSORBIRAJOČE SNOVI V AJDI ŠČITIJO RASTLINE IN PRISPEVAJO K ZDRAVJU LJUDI

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<http://dx.doi.org/10.3986/fbg0070>

ABSTRACT

UV absorbing compounds in buckwheat protect plants and provide health benefit for humans

Buckwheat became a pan-Eurasian crop, when it expanded via Himalaya to Europe. Common buckwheat is one of the oldest domesticated crops in Asia, while Tartary buckwheat is still thriving as a wild or weedy plant. Buckwheat belongs to dicotyledonous crops that can tolerate poor soils and extreme environment conditions. Buckwheat grows on high elevation, where the intensities of UV radiation are usually high. Buckwheat is a fast-growing plant rich in flavonoids, which absorb UV radiation and have an antioxidant potential. Flavonoids have positive effect also on human health. Besides common buckwheat flour, Tartary buckwheat flour is more and more used in preparing dishes, due to its much higher content of flavonoids rutin and quercetin compared to common buckwheat. Therefore, the studies on how the technological procedures of preparing Tartary buckwheat bread affect the content, availability and efficacy of flavonoids in buckwheat bread have been made. Buckwheat is commonly used in the dishes in Japan (soba noodles), China (buckwheat noodles), Korea (buckwheat noodles), Italy (buckwheat polenta), France (galettes), Slovenia (kasha, žganci). Common buckwheat and Tartary buckwheat are plants suitable for designing foods with good functional value and healthy features. Therefore, it has been determined that different technological procedures, such as hydrothermal treatment of grain, sourdough fermentation, dough preparation and baking influences the availability and changes in the content of flavonoids, rutin and quercetin and antioxidant activity in sour bread and food products, made with buckwheat flour.

Key words: Common buckwheat, Tartary buckwheat, sourdough bread, rutin, quercetin, flavonoids, UV absorbing compounds

IZVLEČEK

UV absorbirajoče snovi v ajdi ščitijo rastline in prispevajo k zdravju ljudi

Ajda je postala vseevrazijska kultura, ko se je preko območja Himalaje razširila v Evropo. Navadna ajda je ena najstarejših gojenih rastlin v Aziji, medtem ko tatarska ajda še vedno uspeva tudi kot divja ali plevelna rastlina. Ajda spada med gojene dvokaličnice, ki lahko prenašajo slaba tla in ekstremne razmere v okolju. Ajda raste na visoki nadmorski višini, kjer je intenziteta ultravijoličnega sevanja običajno visoka. Ajda je hitro rastoča rastlina, bogata z flavonoidi, ki absorbirajo UV sevanje in imajo antioksidativni potencial. Flavonoidi pozitivno vplivajo tudi na zdravje ljudi. Poleg moke iz navadne ajde se moka iz tatarske ajde vse pogosteje uporablja pri pripravi jedi, ker ima v primerjavi z navadno ajdo veliko večjo vsebnost flavonoidov kot sta rutin in kvercetin. Zato so bile narejene študije o tem, kako tehnološki postopki priprave kruha iz tatarske ajde vplivajo na vsebnost, razpoložljivost in učinkovitost flavonoidov v ajdovem kruhu. Ajdo je zelo pogosto uporabljajo v jedeh na Japonskem, na Kitajskem, Koreji, v Italiji, v Franciji, Sloveniji. Navadna ajda in tatarska ajda, sta rastlini primerni za pripravo živil z dobro funkcijsko vrednostjo in lastnostmi ugodnimi za zdravje. Ugotovljeno je bilo, da različni tehnološki postopki, kot so hidrotermična obdelava zrnja, mlečnokislinska fermentacija, priprava testa in peka, vplivajo na dostopnost in spremembe v vsebnosti flavonoidov, rutina in kvercetina in antioksidativno aktivnost kisljih kruhov in prehranskih izdelkov pripravljenih iz ajdove moke.

Ključne besede: navadna ajda, tatarska ajda, kruhi s kisljim testom, rutin, kvercetin, flavonoidi, UV absorbirajoče snovi

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1 INTRODUCTION

Buckwheat origins in southern China, probably Yunnan province (OHNISHI 1998), from where it gradually spread to the north of China, and further on across Russia and Ukraine (KREFT 1995). It became a pan-Eurasian crop, when it expanded via the Himalaya region to Europe (HUNT et al. 2018). Common buckwheat is one of the oldest domesticated crops in Asia, while Tartary buckwheat is still thriving as a wild or weedy plant (TSUJI & OHNISHI 2009). Buckwheat is an ancient dicotyledonous crop that tolerates poor soils and extreme environments (BILAL PIRZADAH et al. 2013). Buckwheat, as a robust and undemanding plant, is becoming an important alternative staple foods crop. The residual nutrients from preceding crops are often sufficient for its adequate growth. Tartary buckwheat is grown in Luxembourg, and as a mixed crop with common buckwheat in Bosnia and Herzegovina. Tartary buckwheat has been introduced also to Slovenia, Italy and Sweden (GAO et al. 2016). Crop production of grains that are botanically not cereals, such as buckwheat (*Fagopyrum* spp.), is increasing (AČANSKI et al. 2015). It is a fast-growing plant rich in flavonoids, which contribute efficiently to its biological activity (HORBOWICZ et al. 2011). Buckwheat grows on high elevation, where the intensities of UV radiation

are usually high. Thus, it is feasible to study the effect of UV radiation on the synthesis of UV absorbing compounds. Among grain crops, research on buckwheat is raising attention because of its content of many healthy compounds (CHRISTA & SORAL-ŠMIETANA 2008; CHITTARRINI et al. 2014). The comparative study of SOFIĆ et al. (2010) showed that out of 50 medical plant species, rue (*Ruta graveolens*) plants contained the highest amount of rutin (86.6 mg/g DM) followed by buckwheat flowers (53.5 mg/g DM) (BUDZYNSKA et al. 2018). Besides common buckwheat flour, Tartary buckwheat flour is more and more used in preparing dishes, due to its much higher content of rutin and quercetin compared to common buckwheat (FABJAN et al. 2003; JIANG et al. 2007; KREFT 2016). Therefore, the studies on how the technological procedures of preparing Tartary buckwheat bread affect the content, availability and efficacy of flavonoids in buckwheat bread have been made (VOGRINČIČ et al. 2010; ZHANG et al. 2010; KOČEVAR GLAVAČ et al. 2017; COSTANTINI et al. 2014; LUKŠIČ et al. 2016a, 2016b). Buckwheat is commonly used in the dishes in Japan (soba noodles), China (buckwheat noodles), Korea (buckwheat noodles), Italy (buckwheat polenta), France (galettes), Slovenia (kasha, žganci) (Škrabanja et al. 2018).

2 THE EFFECT OF UV RADIATION ON THE CONTENT OF UV ABSORBING COMPOUNDS

Flavonoids have great potential to scavenge reactive oxygen species (ROS), compounds, which are also produced during water shortage (HIDEG & STRID 2017). The production of UV-absorbing compounds in plants like flavonoids and related phenyl-propanoids are primary protective mechanisms protecting plants from potentially damaging solar UV radiation (ZHANG et al. 2012; BARNES et al. 2016, LIANG et al. 2006). HIDEG & STRID (2017) reported that flavonoids can scavenge reactive oxygen species (ROS) by acting as antioxidants. The production is determined by the UV dose, radiation quality and time of exposure. Since UV-B triggers the secondary metabolic pathway, it may serve as a significant stimulator for plant antioxidant activity (SEBASTIAN et al. 2018). KISHORE et al. (2010) evidenced the positive correlations between phenolic compounds and the amounts of certain antioxidants and altitude of the growing site of Tartary buckwheat. In buckwheat leaves rutin and rutin-oxidase enhance the defence against UV radiation, low temperature and water shortage (SUZUKI et al. 2015). In the study of GABERŠČIK et al. (2002)

common buckwheat plants (*Fagopyrum esculentum* Moench, variety 'Darja') were grown in outdoor experiments under reduced and ambient UV-B levels, and an UV-B level simulating 17% ozone depletion in Ljubljana (Slovenia). UV-B radiation induced synthesis of UV absorbing compounds. The flavonoid synthesis is significantly enhanced by UV radiation as shown in many studies (GABERŠČIK et al. 2002; SUZUKI et al. 2005; GOLOB et al. 2018). REGVAR et al. (2012) studied the effects of increased UV-B radiation that simulates 17% ozone depletion on fungal colonisation and concentrations of rutin, catechin and quercetin in common buckwheat and Tartary buckwheat. They found out induction of shoot quercetin concentrations in UV-B-treated common buckwheat plants, but no differences in flavonoid concentrations in Tartary buckwheat. Tartary buckwheat had higher concentrations of flavonoids comparing to common buckwheat. Authors presumed that concentrations of these secondary metabolites are the result of genetic pre-adaptation of Tartary buckwheat to higher altitudes, where they protect against UV

radiation. JOVANOVIĆ et al. (2006) studied the behaviour of the enzymatic antioxidant defense system in common buckwheat leaves and seedlings subjected to enhanced UV-B radiation (supplemented UV-B light (radiation 290-320 nm) for 90 min by use of a UV-B lamp (HPQ 100 W Phillips). Plants received 49 kJ m⁻² biologically effective UV-B radiation. UV-B applied treatment caused enhanced level of methanol-soluble flavonoids, in line with studies from GABERŠČIK et al. (2002) and SUZUKI et al. (2005). The study with fifteen populations of Tartary buckwheat from different elevations exposed to elevated UV-B radiation showed that the sensitivity of plants to UV-B radiation is not only associated with the ambient UV-B level in natural habitats but also with the relative growth rate of genotype (YAO et al. 2007). Thus, future effort to breed for more tolerant cultivars is possible. YAO et al. (2008) studied the effects of enhanced UV-B radiation on crop growth, morphology, reproduction, and physiology in three cultivars of *Fagopyrum esculentum* originating from different altitudes and revealed that enhanced UV-B radiation significantly affected plant growth, development and production, a cultivar originating from Qinghai-Tibet plateau being the most tolerant.

DEBSKI et al. (2016) studied the impact of short-term UV-B treatment on the content of flavonoids and photosynthetic pigments in cotyledons, and the growth of common buckwheat seedlings. Seedlings were subjected to different doses of UV-B, 5 W·m⁻² and 10 W·m⁻². Exposure to UV-B enhanced the amount of anthocyanins in cotyledons while inhibiting hypocotyl elongation, but had no effect on the content of photosynthetic pigments. Exposure to UV-B radiation did not affect rutin levels or cause a decrease in it with respect to different cultivars.

Anthocyanin type and their contents in Tartary buckwheat stems were investigated by EGUCHI and SATO (2009). The ratio of each anthocyanin type to total anthocyanins varied with nodal positions in an outdoor experiment. This experiment showed that UV stress influences the ratio of specific anthocyanins to total anthocyanins. This growth chamber experiment showed that the ratio of cyanidin-3-O-rutinoside to total anthocyanins was higher under UV conditions in comparison to non-UV conditions. Authors presume that Tartary buckwheat may accumulate cyanidin-3-O-glucoside and cyanidin-3-O-rutinoside systematically to protect plants against UV stress.

In the experiments of YAO et al. (2006), Tartary buckwheat was grown in field plots under near-ambient solar UV-B (approximately 84–88% of solar UV-B), attenuated solar UV-B radiation (43–49% reduction in solar UV-B), and supplemental UV-B radiation (two lev-

els: 5.30 and 8.50 kJ m⁻² day⁻¹). The amount of photosynthetic pigments was lowered by the ambient and enhanced UV-B radiation, while the UV-B absorbing compounds and rutin concentration increased, except at the highest level of UV-B irradiance exposure. Authors concluded that Tartary buckwheat is a potentially UV-B sensitive species, and also, that the crop response to UV-B radiation is associated with UV-B intensity, environmental factors and growing season.

ORSAK et al. (2001) provided evidence about changes of total polyphenols, phenolcarboxylic acids, and ascorbic acid in three buckwheat samples (seeds, seedlings, and plants of *Fagopyrum esculentum* Moench, cv. Pyra and Emka, and Tartary buckwheat *Fagopyrum tataricum* Gaertner), induced by UV-C irradiation (lambda = 253.7 nm, P = 75 W, 0 - control, 42 and 84 h). Authors found out that *F. tataricum* contained much higher total polyphenol and rutin levels in comparison to *F. esculentum*, and that UV-C irradiation affected seeds causing an increase in the amounts of total polyphenols and rutin.

TSURUNAGA et al. (2013) studied the effects of various light compositions on the levels of anthocyanins, rutin, and 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity in common buckwheat sprouts. Sprouts were irradiated with different sources of visible and ultraviolet light. Authors examined the effect of UV-B at wavelengths of 260-320 nm, 280-320 nm, and 300-320 nm on the synthesis of flavonoid compounds. Their results showed that irradiation with UV-B > 300 nm increased the levels of anthocyanins and rutin, as well as the DPPH radical scavenging activity. When sprouts were irradiated with UV-B light at wavelengths of 260-300 nm, yellowing or withering occurred.

The effects of blue and UV-A (365 nm)/UV-C (254 nm), or their combinations, on the levels of total flavonoids, rutin, quercetin, PAL, CHI, rutin degrading enzymes (RDEs), and DPPH radical scavenging activity in Tartary buckwheat sprouts were researched (JI et al. 2016). Authors found out that blue light in combination with UV-C (BL+UV-C) enhanced the accumulation of total flavonoids, rutin, and quercetin, while this effect was not observed when blue light was combined with UV-A (BL+UV-A).

To conclude, UV radiation stimulates phenylpropanoid biosynthetic pathway leading to the accumulation of compounds that protect plants from the UV caused damage. However, these responses differ regarding the intensity of UV radiation, buckwheat species and on elevation of origin of cultivar. Some studies showed that Tartary buckwheat is more tolerant to UV radiation since it originates in high altitudes.

3 IMPORTANCE OF BUCKWHEAT AS THE STAPLE CROP

Common buckwheat and Tartary buckwheat are used in different parts of the world for making various food products. BONAFACCIA et al. (2003) evidenced that the grain of both of these cultivated buckwheat species contains up to 27% fibre. Buckwheat seeds are considered as a prebiotic food because they can increase the lactic acid bacteria in the intestine due to their content of resistant starch (ŠKRABANJA et al. 1998, 2001). Buckwheat has small starch granules and an amylose content of starch higher than cereals, but lower than those of legumes (ŠKRABANJA & KREFT 1998; SCHIRMER et al. 2013).

Buckwheat (*Fagopyrum esculentum*) herb is used for herbal medicinal products, for preparing green buckwheat tea, for producing buckwheat green leaf flour as an additive to certain food products, and the fresh green plant parts can be used as a vegetable (KREFT et al. 2006).

Buckwheat contains more rutin than the majority of other grain crops, fruits, and vegetables (LI et al. 2011). Many authors reported that seeds of Tartary buckwheat have higher contents of high quality proteins and higher

concentrations of flavonoids rutin and quercetin than those of common buckwheat seeds (FABJAN et al. 2003; GAO et al. 2016). FABJAN et al. (2003) reported that Tartary buckwheat contains about 100-fold more rutin than does common buckwheat. Buckwheat is thus an important source of anti-oxidant activity in functional foods (HOLASOVA et al. 2002) due to the presence of the flavonoids rutin and quercetin in buckwheat grain and products, because of their anti-oxidant and anti-inflammatory effects. Rutin and quercetin were also present in baked biscuits made from flour of both species of buckwheat (WIESLANDER et al. 2011). Buckwheat products decrease cholesterol levels and also improve lung capacity in humans (WIESLANDER et al. 2011; YANG et al. 2014). Extracts from common buckwheat and Tartary buckwheat can also protect DNA from damage caused by hydroxyl radicals (VOGRINČIČ et al. 2010). Experiments showed that buckwheat flour can improve diabetes, obesity, hypertension, hypercholesterolemia and constipation (LI & ZHANG 2001).

4 RUTIN AND QUERCETIN TRANSFORMATION DURING PREPARATION OF BUCKWHEAT SOURDOUGH BREAD AND THE EFFECT OF HYDROTHERMAL TREATMENT OF TARTARY BUCKWHEAT GRAIN TO THE TRANSFORMATION OF RUTIN TO QUERCETIN

Pseudocereals have received increased interest in recent years due to the growing awareness of the need for healthy diets. Tartary buckwheat (*Fagopyrum tataricum* Gaertn.) is a pseudocereal rich in dietary beneficial components. It is a popular food source, containing balanced amino-acid composition of its proteins, fiber, retrograded starch, trace elements, vitamins and antioxidants, including flavonoids (HOLASOVA et al. 2002; BONAFACCIA et al. 2003; FABJAN et al. 2003; PONGRAC et al. 2016). Buckwheat does not contain gluten proteins, so it is safe for people suffering from gluten intolerance (VOGRINČIČ et al. 2010; KOČJAN AČKO 2015). Tartary buckwheat possesses phenolic compounds, such as rutin, quercetin, kaempferol-3-rutinoside and flavanol triglycoside, and has a high antioxidant activity that helps to reduce the risk of major chronic diseases (TIAN et al. 2002). Tartary buckwheat contain more rutin (a quercetin-3-rutinoside; 10 and 40 mg/g, respectively) than most vegetables, fruits and grain crops (LI & ZHANG 2001), and more rutin (up to about 14.7 mg per g DM) than common buckwheat (up to about 0.1 mg per g DM) (FABJAN et al. 2003; KREFT 2016). Tartary buckwheat was widely grown in the territory of Slovenia

since the beginning of 19th century (FABJAN et al. 2003). During the 20th century, the cultivation of Tartary buckwheat gradually decreased, due to cultivation of other crops (KREFT 1995, 2011). However, common buckwheat bread was traditionally made in the past, and its use is reviving in present times. Due to much higher content of rutin and quercetin in Tartary buckwheat flour (JIANG et al. 2007; QIN et al. 2010), the Tartary buckwheat bread has been prepared to investigate the effects of hydrothermal treatment of grain, sourdough fermentation and the baking process on rutin and quercetin content and on the antioxidant activities of common buckwheat and Tartary buckwheat bread (COSTANTINI et al. 2014; LUKŠIČ et al. 2016a, 2016b).

One of the ways to prepare bread involves sourdough fermentation, which can be accompanied by the formation of lactic acid and acetic acid that have an impact on dough processing and the preparation of sourdough bread (MICHALSKA et al. 2008). Many authors have reported that sourdough fermentation can affect the improvement of structural and sensory properties, as well as persistence of sour bread (GOBBETTI et al. 2014; RIZZELLO et al. 2016; RINALDI et al. 2017; UARAK

et al. 2017). Experiments showed that sourdough fermentation can improve the availability of proteins and minerals, total content of dietary fiber, total content of phenolic substances and antioxidant activity of sour bread (BOSKOV HANSEN et al. 2002; GANDHI & DEY 2013; COSTANTINI et al. 2014; RIZZELLO et al. 2016). It has been reported that Tartary buckwheat sour bread had a lower content of carbohydrates, lower glycemic index and a lower energy value than the same amount of Tartary buckwheat flour (NOVOTNI et al. 2012; COSTANTINI et al. 2014). In sour bread, various substances such as alcohols, aldehydes, esters, hydrocarbons, ketones, terpenes, furans and phenols are also produced during the process of lactic acid fermentation (BOSKOV HANSEN et al. 2002). Microorganisms in sourdough starter can also form some new nutritional components, such as peptides and other amino acid derivatives, and some prebiotic polysaccharides (DE VOS 2005). It has been found that proteases released by yeast and the enzymes of selected lactobacilli in sourdough starter can metabolise gluten in wheat flour (WEISER et al. 2008).

In the studies, a decrease in the content of rutin and its conversion into quercetin, which is prevented by various types of heat treatment of food products made from Tartary buckwheat and common buckwheat have been reported (VOGRINČIČ et al. 2010). Changes in the content of other substances with antioxidant activity have also been measured (VOGRINČIČ et al. 2010; ZHANG et al. 2010; SAKAČ et al. 2011). CHO AND LEE (2015) reported that changes in the content of rutin and other antioxidants have not been affected by rapid frying of the noodles, while cooking caused a significant reduction in the content of rutin in the noodles prepared from wheat flour enriched with rutin extract from Tartary buckwheat bran. JAMBREC et al. (2015) reported that in full wheat noodles with the addition of pre-autoclaved (120 °C) flour of common buckwheat, the conversion of rutin into quercetin decreased. While during the cooking of these noodles, the conversion of rutin into quercetin did not occur at all. The decrease of phenolic substances in noodles with the addition of buckwheat flour was comparable to decrease of phenolic substances in control sample (whole grain wheat noodles). In the experiments of QIN et al. (2013) it has been found that soaking of Tartary buckwheat grains (40 °C, 12-14 h) influenced the reduction of the starch and rutin content and influenced the increase in the content of quercetin, kaempferol, isoquercitrin, total flavonoids and phenolic substances. After the pre-soaked grains of Tartary buckwheat were treated with steam (100 °C, 40-60 min), the content of total flavonoids and total phenolic substances decreased, while the content of rutin in the grain samples increased. It is possible that the process of decomposition of rutin

was initiated in the process of soaking grain of Tartary buckwheat, and the steam treatment process triggered a reconnection of rutin. SENSOY et al. (2006) provided evidence that shows that the processing (roasting) of buckwheat flour had no effect on the content of total phenolic substances in buckwheat flour. The DPPH method, used for determination of antioxidant activity, however, showed a slight decrease in antioxidant activity of buckwheat flour while roasting at 200 °C for 10 min, while the roasting at 170 °C had no effect on the reduction of antioxidant activity. The significant decrease in anti-oxidant activity in Tartary buckwheat flour as a result of various thermal treatments such as roasting, steam-pressure heating, and microwaving, has been reported (ZHANG et al. 2010). A small decrease in the anti-oxidant activity in common buckwheat flour roasted for 10 min at 200 °C has also been noted (YASUDA & NAKAGAWA 1994). The results of the experiment suggests that optimization of processing is the key to maintaining healthy substances in buckwheat products.

Bread is a staple food for the majority of the world populations and contributes substantially to the intakes of certain nutrients. Common buckwheat and especially Tartary buckwheat flour possesses some phenolic compounds, such as rutin, quercetin and a high antioxidant activity, that is why this type of flour is suitable to obtain bread with improved nutritional value and healthy features. Therefore, the studies have been made on how the technological procedures of preparing common buckwheat and Tartary buckwheat bread affect the content, availability and efficacy of flavonoids in buckwheat bread. It has been proven that, in bread made with Tartary buckwheat flour, rutin concentration decreased, whereas the quercetin concentration increased and remained stable during processing (VOGRINČIČ et al. 2010). LUKŠIČ et al. 2016a, 2016b reported that during Tartary buckwheat bread making there was a transformation of a large portion of rutin into quercetin. Breads containing common buckwheat flour, contained several flavonoids, such as rutin and quercetin, and had higher antioxidant activity than wheat bread (LIN et al., 2009). The combined effects of sourdough fermentation and the baking process on the flavonoid concentrations and antioxidant properties of common buckwheat and Tartary buckwheat sourdough starter, bread dough and sourdough bread have also been studied. It has been established that common buckwheat and Tartary buckwheat bread making is feasible without any addition of wheat or gluten, by using the sour bread starter procedure (COSTANTINI et al. 2014; LUKŠIČ et al. 2016a, 2016b). Tartary buckwheat breads made with 100% Tartary buckwheat flour contained the highest phenol (53.3 mg GAE/g) and flavonoid (16.8 mg RE/g) contents, mean-

while Tartary buckwheat sour bread, containing 10% of chia (*Salvia hispanica* L.) flour had the highest antioxidant activity (32.0 mmol Fe²⁺ E/g and 128.6 mmol GAE/g, respectively) compared to 100% common buckwheat and wheat sour breads and common buckwheat and wheat sour breads fortified with 10% of chia flour (COSTANTINI et al. 2014). On the contrary, in another experiment a higher antioxidant activity has been measured in common buckwheat bread compared to Tartary buckwheat bread. This might be because of the synthesis of substances with antioxidant properties, including certain Maillard reaction products that occur in bread during thermal treatment (ZHANG et al. 2010; LUKŠIČ et al. 2016a). A similar result were established in a study of VOGRINČIČ et al. (2010) in which Tartary buckwheat bread and breads made of mixtures of Tartary buckwheat and wheat flour were studied. A decrease in polyphenol concentration through baking was observed in all samples. The high DPPH (2,2-diphenyl-1-picrylhydrazyl) scavenging capacity in mixed breads (32-56%) and in Tartary buckwheat bread (85-90%) decreased slightly through the bread making process, while an increase of antioxidant activity in bread made of 100% wheat flour during bread making was observed. In the experiments of Lukšič et al. (2016a) sourdough bread was prepared of flour of common buckwheat and of Tartary buckwheat to follow the transformation of rutin and quercetin during sourdough fermentation, bread making procedure and baking of bread. During Tartary buckwheat sourdough fermentation, there was conversion of rutin to quercetin. In the Tartary buckwheat sourdough bread there was no rutin, whereas there was 5.0 mg/g quercetin. In common buckwheat bread, neither rutin nor quercetin were present. VOGRINČIČ et al. (2010) reported that with the addition of water to mixtures containing Tartary buckwheat during the preparation of the Tartary buckwheat dough made with yeast, rutin concentration decreased, while quercetin concentration increased. The rutin concentration continued to decrease during the bread baking process, while the concentration of quercetin remained stable. After baking, rutin (0.47 mg/g) was present only in bread made of 100% Tartary buckwheat flour along with quercetin (4.83 mg/g). SUZUKI et al. (2015) reported that when using a version of Tartary buckwheat with traces

of rutinoidase, bread of a flour mixture of Tartary buckwheat and wheat with 0.63 mg/g rutin was prepared, representing approximately 50% of the retained rutin in bread, compared to the source material (flour).

Hydrothermal treatment is a process that involves heating with hot water or steam, followed by cooling and drying of buckwheat groats to produce husked buckwheat or kasha. It is the traditional technology known and still applied in Slovenia, Croatia, Poland, Ukraine and Russia (KREFT 2003). In a study of LUKŠIČ et al. (2016b) the impact of hydrothermal treatment on extractability of flavonoids from starchy matrix was investigated. Tartary buckwheat grain was hydrothermally treated and milled to yield hydrothermally treated flour. In control sample, not hydrothermally treated Tartary buckwheat flour, most of extractable rutin (8 mg of rutin per g DM (dry matter)) was extracted during the first 20 min of extraction. In hydrothermally treated Tartary buckwheat flour only 4 mg of rutin per g DM was extracted in 20 min, and 7 mg of rutin per g DM within 8 h, respectively. This data indicates that, during the hydrothermal treatment, rutin becomes embedded in the flour matrix. Slowly extracted rutin was protected from transformation to quercetin during bread making procedure. From an initial 7 mg of extractable rutin per g DM in hydrothermally treated buckwheat flour, Tartary buckwheat bread contained 2 mg of rutin per g DM, and 6 mg of quercetin per g DM. No other Tartary buckwheat bread making technology which would be able to conserve such an amount of rutin from flour through the process to the final bread product have been reported.

Many studies certificate that both, fermentation process and heat treatment affects changes in content and accessibility of substances with antioxidant properties in buckwheat products. However, these changes differ regarding buckwheat species and plant properties, preparation process, fermentation method and thermal treatment used. This information contributes to a better understanding of the effects of different food preparation methods on substances with antioxidant activity and information on the persistence of rutin and quercetin in sourdough bread and other food products. These findings are as well important for designing foods with high concentrations of flavonoids and good functional value.

POVZETEK

Ajda izvira iz južne Kitajske, verjetno province Yunnan, od koder se je postopoma razširila na sever Kitajske in naprej po Rusiji in Ukrajini. Postala je vseevropska ra-

stlina ko se je razširila preko Himalaje v Evropo. Navadna ajda je ena najstarejših gojenih rastlin v Aziji, medtem ko tatarska ajda še vedno uspeva tudi kot divja ra-

stlina ali plevel. Ajda je starodavna dvokaličnica, ki prenaša revno prst in ekstremna okolja. Ajda, kot robustna in nezahtevna rastlina, postaja pomemben vir za pridelavo osnovnih živil. Hranilne snovi, ki ostanejo v zemlji iz gojenih rastlin prejšnjih sezon, so pogosto zadostne za njeno ustrezno rast. Tatarsko ajdo sejejo v Luksemburgu in kot mešani pridelek z navadno ajdo v Bosni in Hercegovini. Tatarsko ajdo smo pred kratkim začeli ponovno sejati tudi v Sloveniji, Italiji in na Švedskem. Pridelava ajde (*Fagopyrum* spp.), se povečuje. Je hitro rastoča rastlina, bogata z flavonoidi, ki učinkovito prispevajo k njeni biološki aktivnosti. Ajda raste na visoki nadmorski višini, kjer so intenzitete UV sevanja običajno visoke. Zato je smiselno preučevati učinke UV sevanja na sintezo spojin, ki absorbirajo UV. Število raziskav o ajdi se povečuje ker ima visoko vsebnost snovi, ki pozitivno vplivajo na zdravje ljudi.

Primerjalna študija je pokazala, da je od 50 vrst rastlinskih zdravilnih rastlin vinska rutica vsebovala največjo količino rutina (86,6 mg / g SM), sledijo ajdovi cvetovi (53,5 mg / g SM).

Poleg moke iz navadne ajde, se za pripravo jedi vedno bolj uporablja tatarska ajdova moka, zaradi veliko večje vsebnosti rutina in kvercetina. Zato so izdelane študije o tem, kako tehnološki postopki priprave tatarskega ajdovega kruha ajde vplivajo na vsebino, razpoložljivost in učinkovitost flavonoidov v ajdovem kruhu. Ajda se zelo pogosta uporablja za pripravo jedi na Japonskem (soba rezanci), na Kitajskem (ajdovi rezanci), v Koreji (ajdovi rezanci), Italiji (ajdova polenta), Franciji (gallettes), Sloveniji (kaša, žganci).

Zaradi naraščanja zavedanja o pomenu zdrave prehrane, rastline, ki botanično niso žita, med katera uvrščamo tudi tatarsko ajdo (*Fagopyrum tataricum* Gaertn.) ponovno vzbujajo zanimanje med ljudmi. Tatarsko ajdo odlikuje odlična hranilna vrednost, saj ima uravnoteženo aminokislinsko sestavo, vsebuje prehranske vlaknine, retrogradiran škrob, elemente v sledovih, vitamine in antioksidante, vključno s flavonoidi (HOLASOVA et al. 2002; BONAFACCIA et al. 2003; FABJAN et al. 2003; PONGRAC et al. 2016). Ajda ne vsebuje glutena in je varno živilo tudi za osebe z ugotovljenimi intolerancami na gluten (VOGRINČIČ et al. 2010; KOCJAN AČKO 2015). Tatarska ajda ima visoko antioksidativno aktivnost in vsebuje fenolne spojine, kot so rutin, kvercetin, kaempferol-3-rutinozid in triglikozid flavanol, ki lahko prispevajo k zmanjšanju možnosti za nastanek kroničnih bolezni (TIAN et al. 2002). Tatarska ajda vsebuje več rutina (10 in 40 mg/g), kot večina zelenjave, sadja in žit (LI & ZHANG 2001) in več rutina (do 14,7 mg/g suhe mase) kot navadna ajda (do 0,1 mg/g suhe mase) (FABJAN et al. 2003; KREFT 2016). Tatarsko ajdo so na območju Slovenije pridelovali že v začetku 19. stoletja (FABJAN et al.

2003). V obdobju 20. stoletja pa se je pridelava tatarske ajde zmanjševala, predvsem zaradi pridelave drugih žit (KREFT 1995, 2011). Kruh iz moke navadne ajde so tradicionalno pekli že v preteklosti, sedaj pa se zanimanje za ajdov kruh ponovno veča. Zaradi večje vsebnosti rutina in kvercetina v moki tatarske ajde (JIANG et al. 2007; QIN et al. 2010), so bili izdelani kruhi iz tatarske ajde, z namenom, da bi preučevali učinke hidrotermične obdelave zrnja, mlečnokislinske fermentacije testa in vpliv peke na vsebnost rutina in kvercetina ter na antioksidativno aktivnost kruhov pripravljenih iz moke tatarske ajde in navadne ajde (COSTANTINI et al. 2014; LUKŠIČ et al. 2016a, 2016b).

Eden od načinov priprave kruha vključuje mlečno-kislinsko fermentacijo, pri kateri se tvori mlečna in očetna kislina, ki vplivata na postopek priprave kislega kruha (MICHALSKA et al. 2008). Raziskovalci so poročali, da mlečnokislinska fermentacija lahko vpliva na izboljšanje strukturnih in senzoričnih lastnosti kislega kruha in lahko podaljša obstojnost takega kruha (GOBETTI et al. 2014; RIZZELLO et al. 2016; RINALDI et al. 2017; UA ARAK et al. 2017). V poskusih je bilo ugotovljeno, da mlečnokislinska fermentacija lahko izboljša dostopnost beljakovin, mineralov, skupno vsebnost prehranskih vlaknin, skupno vsebnost fenolnih snovi in antioksidativno aktivnost kislih kruhov (BOSKOV HANSEN et al. 2002; GANDHI & DEY 2013; COSTANTINI et al. 2014; RIZZELLO et al. 2016). Raziskovalci so poročali tudi, da je imel kisel kruh iz tatarske ajde manjšo vsebnost ogljikovih hidratov, nižji glikemični indeks in manjšo energijsko vrednost, kot enaka količina moke tatarske ajde (NOVOTNI et al. 2012; COSTANTINI et al. 2014). V kislih kruhkih so med procesom mlečnokislinske fermentacije nastajale tudi snovi, kot so alkoholi, aldehidi, estri, hidrokarboni, ketoni, terpeni, furani, in fenoli (BOSKOV HANSEN et al. 2002). Mikroorganizmi v osnovi za kisloto testo prav tako lahko tvorijo nekatere nove prehranske komponente, kot so peptidi in drugi derivati aminokislin, in nekatere prebiotične polisaharide (DE Vos 2005). Ugotovljeno je bilo, da lahko proteaze, ki jih v osnovi za kisloto testo sproščajo kvasovke in encimi selekcioniranih laktobacilov, presnavljajo gluten v pšenični moki (WEISER et al. 2008).

V raziskavah poročajo, da je, kot posledica različnih načinov toplotne obdelave v živilih, pripravljenih iz tatarske ajde in navadne ajde, prihajalo do zmanjšanja vsebnosti rutina in pretvorbe tega v kvercetin. Izmerili so tudi spremembe v vsebnosti drugih snovi z antioksidativnim učinkom (VOGRINČIČ et al. 2010; ZHANG et al. 2010; SAKAČ et al. 2011). CHO & LEE (2015) sta poročala o tem, da na spremembe vsebnosti rutina in drugih antioksidantov hitro cvrtje rezancev ni vplivalo, med tem, ko je kuhanje povzročilo znatno zmanjšanje vsebnosti

rutina v rezancih, pripravljenih iz pšenične moke in iz z rutinom obogatenega izvečka otrobov tatarske ajde. JAMBREC in sod. (2015) so ugotovili, da se je v polnozrnatih pšeničnih rezancih z dodatkom predhodno avtoklavirane (120 °C) moke navadne ajde, pretvorba rutina v kvercetin zmanjšala. Med kuho teh rezancev pa do pretvorbe rutina v kvercetin sploh ni prišlo. Izguba fenolnih snovi v rezancih z dodatkom ajdove moke je bila v območju kontrolnega vzorca (polnozrnatih pšeničnih rezancev). V poskusih, ki so jih opravili QIN in sod. (2013) so ugotovili, da je namakanje zrn tatarske ajde (40 °C, 12-14 h) vplivalo na zmanjšanje v zrnju prisotnega deleža škroba in rutina in vplivalo na povečanje vsebnosti kvercetina, kaempferola, izokvercitrina, skupnih flavonoidov in fenolnih snovi. Po tem, ko so predhodno namočeno zrnje tatarske ajde obdelali še s paro (100 °C, 40-60 min), se je vsebnost skupnih flavonoidov in skupnih fenolnih snovi še naprej zmanjševala, med tem, ko se je vsebnost rutina v vzorcu zrnja povečala. Mogoče je, da je bil proces razgradnje rutina sprožen v procesu namakanja zrnja tatarske ajde, proces obdelave s paro pa je sprožil ponovno spajanje rutina. SENSOY in sod. (2006) so predložili rezultate, ki nakazujejo da procesiranje (praženje) ajdove moke ni imelo vpliva na vsebnost skupnih fenolnih snovi v ajdovi moki. DPPH metoda določanja antioksidativne aktivnosti je sicer pokazala, da je prišlo po praženju ajdove moke (200°C, 10 min) do rahlega zmanjšanja antioksidativne aktivnosti moke ajde, praženje pri 170°C pa ni imelo vpliva na zmanjšanje antioksidativne aktivnosti. Do značilnega zmanjšanja antioksidativne aktivnosti v moki tatarske ajde je prišlo, kot posledica različnih načinov toplotne obdelave moke, kot so praženje, segrevanja s paro in mikrovalovno segrevanje (ZHANG in sod. 2010). Izmerili so tudi manjše zmanjšanje antioksidativne aktivnosti v moki navadne ajde, ki so jo pražili 10 min na 200 °C (YASUDA & NAKAGAWA 1994). Rezultati poskusov nakazujejo, da je optimizacija procesiranja ključna za ohranitev zdravju koristnih snovi v ajdovih izdelkih.

Kruh je osnovno živilo za velik del svetovnega prebivalstva in lahko znatno prispeva k vnosu nekaterih hranil. Moka navadne ajde in posebno moka tatarske ajde vsebujeta nekatere fenolne snovi, kot sta rutin in kvercetin ter imata visoko antioksidativno aktivnost, zato sta primerni za pripravo kruhov z izboljšano prehransko vrednostjo in zdravju koristnimi lastnostmi. Poznavanje teh lastnosti moke je privedlo do raziskav v katerih so preučevali, kako tehnološki postopki priprave kruha iz navadne in tatarske ajde vplivajo na vsebnost, dostopnost in učinkovitost flavonoidov v ajdovih kruhah. Preučevali so tudi razmerje med flavonoidoma, rutinom in kvercetinom v ajdi, in do kakšne mere se rutin pretvarja v kvercetin, kot posledica izpostavljenosti raz-

ličnim tehnološkim postopkom priprave ajdovih kruhov. Ugotovljeno je bilo, da se je v kruhu, pripravljenem iz moke tatarske ajde, vsebnost rutina zmanjševala, vsebnost kvercetina pa je naraščala in ostala stabilna med procesom priprave kruha (VOGRINČIČ et al. 2010). Kruhi, ki so vsebovali moko navadne ajde so vsebovali flavonoide, kot sta rutin in kvercetin in so imeli večjo antioksidativno aktivnost od pšeničnega kruha (LIN et al. 2009).

Preučevani so bili tudi skupni učinki mlečnokislinske fermentacije in peke na vsebnost flavonoidov in antioksidativne lastnosti testa in kruhov iz moke navadne in tatarske ajde. Ugotovljeno je bilo, da je priprava kruha s postopkom mlečnokislinske fermentacije, iz moke navadne ajde in tatarske ajde možna brez dodatka pšenične moke ali glutena (COSTANTINI et al. 2014; LUKŠIČ et al. 2016a, 2016b). Kruhi pripravljeni iz 100 % moke tatarske ajde so imeli največjo vsebnost fenolov (53,3 mg GAE/g) in flavonoidov (16,8 mg RE/g), v kruhah pripravljenih iz moke tatarske ajde z dodatkom 10% moke oljne kadulje (*Salvia hispanica* L.) pa so izmerili največjo antioksidativno aktivnost (32,0 mmol Fe²⁺ E/g and 128,6 mmol GAE/g) v primerjavi s kruhi izdelanimi iz 100% moke navadne ajde in pšenice in kruhi izdelanimi iz moke navadne ajde in pšenice z dodatkom 10% moke oljne kadulje (COSTANTINI et al. 2014). V nasprotju s temi ugotovitvami, je bila v drugem poskusu, največja antioksidativna aktivnost izmerjena v kruhu iz moke navadne ajde v primerjavi s kruhom tatarske ajde. To je lahko posledica spajanja snovi z antioksidativnim učinkom, vključno snovi, ki lahko nastajajo med Maillardovo reakcijo, pod vplivom toplotne obdelave (ZHANG et al. 2010; LUKŠIČ et al. 2016a). O podobnih ugotovitvah so poročali tudi VOGRINČIČ in sod. (2010), ki so preučevali kruhe iz moke tatarske ajde in kruhe iz mešanice moke tatarske ajde in pšenice. V vseh vzorcih kruhov je med peko prišlo do zmanjšanja vsebnosti polifenolov. V mešanih kruhah iz moke tatarske ajde in pšenice in v kruhah iz moke tatarske ajde je med postopkom peke prišlo do zmanjšanja antioksidativne aktivnosti, ugotovljene z metodo DPPH (2,2-difenil-1-pikrilhidrazil), med tem ko je do povečanja antioksidativne aktivnosti, med postopkom peke, prišlo v kruhah iz 100 % pšenične moke. LUKŠIČ in sod (2016a) so pripravili kisle kruhe iz moke navadne ajde in tatarske ajde, z namenom, da bi spremljali pretvorbe rutina in kvercetina med postopkom mlečnokislinske fermentacije, priprave in peke kruha. Med mlečnokislinsko fermentacijo je prišlo do pretvorbe rutina v kvercetin. V kruhu pripravljenem iz moke tatarske ajde ni bilo rutina, bilo pa je 5,0 mg/g kvercetina. V kruhu iz moke navadne ajde niso izmerili ne vsebnosti rutina in ne kvercetina. VOGRINČIČ in sod. (2010) so poročali, da se je ob dodat-

ku vode testu iz moke tatarske ajde in kvasa, vsebnost rutina zmanjševala, vsebnost kvercetina pa je naraščala. Vsebnost rutina se je še naprej zmanjševala med postopkom peke kruha, medtem ko je vsebnost kvercetina ostala stabilna. Po peki se je v kruhu iz 100% moke tatarske ajde ohranilo 0,47 mg/g rutina in 4,83 mg/g kvercetina. SUZUKI in sod. (2015) so pripravili kruh iz mešanice moke tatarske ajde s sledovi rutinozidaze in pšenice z 0,63 mg/g rutina, kar je približno 50 % delež ohranjenega rutina v kruhu, v primerjavi z izvorno surovino (moko).

Hidrotermična obdelava je postopek, ki vključuje segrevanje z vročo vodo ali paro, ki mu sledi ohlajanje in sušenje ajdovega zrnja z namenom, da bi pripravili osušeno ajdovo zrnje oziroma kašo. Gre za tradicionalen postopek, ki ga še vedno uporabljamo v Sloveniji, na Hrvaškem, Poljskem, v Ukrajini in Rusiji (KREFT 2003). V raziskavi, ki so jo opravili LUKŠIČ in sod. (2016b) smo preučevali učinek hidrotermične obdelave na dostopnost in izločanje flavonoidov iz škrobnih struktur. Zrnje tatarske ajde je bilo hidrotermično obdelano in zmleto v hidrotermično obdelano moko. V kontrolnem vzorcu, hidrotermično neobdelani moki, je bila večina kvercetina izločena že po 20 minutah ekstrakcije (8 mg/g DM (suhe mase)). V hidrotermično obdelani moki

tatarske ajde je bilo po 20 min ekstrakcije, izločenega le 4 mg/g DM rutina, in 7 mg/g DM rutina po 8 h ekstrakcije. Ti podatki nakazujejo, da je med postopkom hidrotermične obdelave, rutin postal vključen v druge strukture v moki in tako postal zaščiten pred pretvorbo v kvercetin med postopkom priprave kruha. Iz začetnih 7 mg/g DM v hidrotermično obdelani moki tatarske ajde, je kruh pripravljen iz te moke vseboval 2 mg/g DM rutina in 6 mg/g kvercetina. Za nobeno drugo metodo priprave kruha iz moke tatarske ajde ni bilo ugotovljeno, da bi se med postopkom priprave kruha ohranilo toliko rutina.

Mnoge raziskave potrjujejo, da postopek mlečnikislinske fermentacije in toplotne obdelave vplivata na spremembe v vsebnosti in dostopnosti snovi z antioksidativnimi lastnostmi v izdelkih iz ajde. Te spremembe se razlikujejo glede na vrsto ajde in lastnosti rastline, postopek priprave, metodo fermentacije in potopek toplotne obdelave. Te informacije prispevajo k boljšemu razumevanju vpliva različnih metod priprave živil z antioksidativno aktivnostjo in obstojnosti rutina in kvercetina v kisljih kruhkih in drugih prehranskih izdelkih. Te ugotovitve so pomembne tudi za pripravo živil z večjo vsebnostjo flavonoidov in izboljšano funkcijsko vrednostjo.

ZAHVALA

Raziskovalna programa (št. P1-0212 »Biologija rastlin« in P3-0395 »Prehrana in javno zdravje») ter projekte L4-7552, J4-5524 in L4-9305, slednjega s sofinansiranjem Ministrstva za kmetijstvo, gozdarstvo in prehrano, je sofinancirala Javna agencija za raziskovalno dejavnost Republike Slovenije iz državnega proračuna. Raziskavo

je podpiral EUFORINNO 7 program EU za infrastrukturo EU (RegPot št. 315982). Raziskave, ki smo jih opravili so prejele sredstva iz Evropske skupnosti v okviru projekta ITEM 26220220180: Building Research Centre »AgroBioTech«.

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