

# Tartary Buckwheat (*Fagopyrum tataricum* Gaertn.) as a Source of Dietary Rutin and Quercitrin

Nina Fabjan,<sup>†</sup> Janko Rode,<sup>‡</sup> Iztok Jože Košir,<sup>‡</sup> Zhuanhua Wang,<sup>§</sup> Zheng Zhang,<sup>§</sup> and Ivan Kreft<sup>\*,†</sup>

Biotechnical Faculty, University of Ljubljana, P.O. Box 2995, SI-1001 Ljubljana, Slovenia, Slovenian Institute for Hop Research and Brewing, Žalskega tabora 2, SI-3310 Žalec, Slovenia, and Biotechnology Centre, Shanxi University, Taiyuan, Shanxi 030006, China

Two samples of tartary buckwheat (*Fagopyrum tataricum* Gaertn.) from China and one from Luxembourg were studied by high-performance liquid chromatography (HPLC) to reveal the possibilities of growing tartary buckwheat herb as a possible source of rutin, quercetin, and quercitrin. The content of rutin was determined as up to 3% dry weight (DW) in tartary buckwheat herb. Quercitrin values were in the range of 0.01–0.05% DW. Only traces of quercetin were detected in just some of the samples. Tartary buckwheat seeds contained more rutin (about 0.8–1.7% DW) than common buckwheat seeds (0.01% DW). Rutin and quercetin content in seeds depends on variety and growing conditions. Tartary buckwheat seeds contained traces of quercitrin and quercetin, which were not found in common buckwheat seeds.

#### KEYWORDS: Tartary buckwheat; antioxidants; flavonoids; rutin; quercetin; quercitrin

# INTRODUCTION

Common buckwheat (*Fagopyrum esculentum* Moench) originates from Southwest China and has gradually been spread to all continents, while tartary buckwheat (*Fagopyrum tataricum* Gaertn.) is grown and used in the mountainous regions of Southwest China (Sichuan), in northern India, Bhutan, and Nepal. About 30 years ago, tartary buckwheat could also be found as a crop in some parts of Slovenia, namely, in Gorenjska, Dolenjska, and Zgornjesavinjska dolina, but nowadays, it is replaced by common buckwheat and may be found only as a weed in common buckwheat crop (*1*). In Europe, tartary buckwheat is currently grown as a crop only in Lux (2).

Tartary buckwheat grain, as an important functional food material, contains proteins with high biological value and balanced amino acid composition (2, 3); relatively high crude fiber and vitamins B1, B2, and B6 (2); and more rutin than common buckwheat (4).

Rutin and other flavonoids are UV-B absorbing secondary plant metabolites synthesized in higher plants, mosses, and ferns in order to protect them from the harmful effects of UV-B radiation and disease (5–7). Rutin and other flavonoids from buckwheat have many beneficial effects on human health too. It was established that rutin antagonizes the increase of capillary fragility associated with hemorrhagic disease, reduces high blood pressure (8, 9), decreases the permeability of the vessels, and has an antiedema effect, reduces the risk of arteriosclerosis (10), and shows antioxidant activity (11). Quercitrin, especially in combination with other flavonoids, shows antibacterial effects and protects from naftodianthron phototoxicity (12, 13).

The interrelations of the content of the free aglycon quercetin and its glycosides, rutin (dissacharide rutinose bound to quercetin aglycon) and quercitrin (monossacharide rhamnose bound to quercetin aglycon) in buckwheat herb and seeds have not been studied. Because of their beneficial health effects, we have investigated the possibility of growing tartary buckwheat as a dietary source of rutin, quercetin, and quercitrin. Two tartary buckwheat varieties from China and one from Lux were sown in spring and summer in order to determine optimal sowing and harvesting times in different cultivars.

## MATERIALS AND METHODS

**Rutin, Quercitrin, and Quercetin Content in Herb.** Three different cultivars of tartary buckwheat (*Fagopyrum tataricum* Gaertn.) were sown in spring (June 11) and summer (July 25) 2001 all on an experimental field in Žalec (about 350 m altitude), namely, China 1 variety (light seeded Chinese tartary buckwheat), China 2 variety (dark seeded Chinese tartary buckwheat), and a tartary buckwheat from Lux. Seeds were sown about 2 cm apart, in rows with 20 cm distance between them. Plant samples were cut weekly at 10 cm above the ground and at equal time intervals; about five plants per cultivar were collected to obtain enough sample material as the method requires. Six samples from spring-sown crop of each buckwheat variety were collected and two from summer-sown crop, since the green mass of summer sown plants was, due to environmental conditions, not sufficient for harvesting and analyses in the earlier development. Plant material was dried at 50 °C, milled into dust, and homogenized.

<sup>\*</sup> To whom correspondence should be addressed. Tel: +386 1 423 1161. Fax: +386 1 517 1488. E-mail: ivan.kreft@guest.arnes.si.

University of Ljubljana.

<sup>&</sup>lt;sup>‡</sup> Slovenian Institute for Hop Research and Brewing.

<sup>§</sup> Shanxi University.



Figure 1. Rutin content (% DW  $\pm$  SE) in the herb of spring-sown tartary buckwheat varieties China 1, China 2, and Lux.

**Rutin, Quercitrin, and Quercetin Content in Seeds.** Two accessions were used for grain analyses. Samples from the Orig of tartary buckwheat were obtained from mountainous China region (grown at about 2500–3000 m altitude) and Lux (about 340 m altitude). The other set of tartary buckwheat seeds was grown in Ljubljana (about 300 m altitude), Slovenia. In Ljubljana, we also harvested the seeds of the Slovenian common buckwheat "Siva" (*Fagopyrum esculentum* Moench). Ripe dry seeds were collected, milled into dust, and homogenized.

Analyzing was carried out at the Slovenian Institute for Hop Research and Brewing in Žalec, Slovenia. Polyphenols were extracted with methanol and fractionated by high-performance liquid chromatography (HPLC). About 0.1 g of milled and dried sample was extracted for 30 min with 50 mL of methanol ( $\rho = 0.79$  g/mL) (Merck) using an ultrasound bath (Sonis). The extracts were filtered through Blue Ribbon Filter Paper ( $\phi = 125$  mm), and the filtrate was passed through a membrane filter ( $\phi = 13$  mm; 0.45  $\mu$ m). Three independent analyses were performed for each sample.

The extracts were fractionated by HPLC (HP 1050) using a Nucleosyl 100 C-18, 10  $\mu$ m column, 250 mm × 4.6 mm (Macherey-Nagel). The injection sling was 10  $\mu$ L. The system included a UV/VIS detector. The components were detected by absorbance at 360 nm.

The mobile phase was solvent A (methanol) and solvent B (methanol-water-acetic acid 100:150:5). Water was prepared according to the ISO 3696:1987, and acetic acid was 99–100%,  $\rho = 1.05$  g/mL, purchased by Merck. Solvents A and B were filtered through a membrane filter ( $\phi = 47$  mm; 0.2  $\mu$ m) before use. The program of elution was 100% solvent B for the first 4 min, followed by a linear gradient from 0 to 100% of solvent A in 15 min, holding 100% (solvent A) for an additional 10 min, and after all followed by stepwise decrease to 0% of solvent A in 0.5 min and holding 100% (solvent B) for an additional 6.5 min. The flow rate was 1.0 mL/min. The results were statistically evaluated by the Microsoft Office Excel Program.

#### **RESULTS AND DISCUSSION**

**Rutin, Quercitrin, and Quercetin Content in Herb.** The results of rutin content in spring-sown tartary buckwheat herb are given in **Figure 1**. The first sampling of herb was made on the 50th DAS, when the flowering tartary buckwheat plants began to form the first seeds. The highest content of rutin, 2.5–3% DW, was observed as sampling started. Earlier, the green mass of plants was not yet developed to give a substantial amount of harvested herb. These results were probably close to the highest possible amount of rutin in herb. The content of rutin then began to decrease to about 2% DW on 87th DAS. Trends in rutin content were rather similar in all of the buckwheat varieties, which in this case indicates more important influence of environment than genotype on the rutin content of the buckwheat herb.

Later sowing had essentially no impact on rutin content in herb, as shown in **Figure 2**, which presents results for the



Figure 2. Rutin content (% DW  $\pm$  SE) in the herb of summer-sown tartary buckwheat varieties China 1, China 2, and Lux.

Table 1. Phenological State and Quercitrin Content (% DW  $\pm$  SE) in the Herb of Tartary Buckwheat Varieties China 1, China 2, and Lux Sown in Spring

		quercitrin (% DW)		
day	phenological state	China 1	China 2	Lux
50	flowering, seed formation	$0.037\pm0.008$	$0.017\pm0.008$	$0.036\pm0.004$
56 63 70 77 87	seed formation seed formation seed ripening seed ripening seed ripening	$\begin{array}{c} 0.052 \pm 0.009 \\ 0.020 \pm 0.000 \\ 0.037 \pm 0.011 \\ 0.030 \pm 0.000 \\ 0.027 \pm 0.006 \end{array}$	$\begin{array}{c} 0.027 \pm 0.004 \\ 0.020 \pm 0.000 \\ 0.010 \pm 0.003 \\ 0.025 \pm 0.004 \\ 0.022 \pm 0.000 \end{array}$	$\begin{array}{c} 0.015 \pm 0.004 \\ 0.008 \pm 0.004 \\ 0.029 \pm 0.004 \\ 0.032 \pm 0.007 \\ 0.029 \pm 0.004 \end{array}$

Table 2. Phenological State and Quercitrin Content (% DW  $\pm$  SE) in the Herb of Tartary Buckwheat Varieties China 1, China 2, and Lux Sown in Summer

		quercitrin (% DW)		
day	phenological state	China 1	China 2	Lux
68 75	seed formation seed ripening	$\begin{array}{c} 0.029 \pm 0.004 \\ 0.015 \pm 0.006 \end{array}$	$\begin{array}{c} 0.025 \pm 0.004 \\ 0.018 \pm 0.004 \end{array}$	$\begin{array}{c} 0.019 \pm 0.003 \\ 0.007 \pm 0.002 \end{array}$

summer-sown buckwheat. These samples were not harvested earlier during the crop development because there was not yet enough green mass developed. Because tartary buckwheat grows originally at higher altitudes in Nepal and Chinese mountains and is therefore evolutionary adapted to severe growth conditions (1), this could also be the reason for the relatively high rutin amount in the herb of later (summer) sown buckwheat. The highest rutin content determined in the summer-sown tartary buckwheat herb (about 2% DW) was reached when buckwheat began to form seeds, and this was probably close to the maximum possible amount characteristic of full flowering phenophase. On the 72nd DAS, the rutin content fell to 1% DW, somewhat lower than in samples of spring-sown plants.

The results for quercitrin in the herb of spring-sown tartary buckwheat are given in **Table 1**. Quercitrin values were in the range of 0.01-0.05% DW, but it needs to be emphasized that the values were close to the limit of detection and separability of the HPLC; consequently, SEs were higher, and values were less precise. The highest quercitrin content was reached later than the highest rutin content in herb. In the phenophase of green seeds (around 56th DAS), values were in the range of 0.02-0.05% DW for the spring-sown tartary buckwheat and 0.02-0.03% DW when the last sample was collected. The highest values of quercitrin were found in China 1 tartary buckwheat and the lowest in the China 2 sample.

The content of quercitrin was lower (about 0.01-0.03% DW) if buckwheat was sown in summer time (**Table 2**). As in the

Table 3. Rutin, Quercitrin, and Quercetin Contents (% DW  $\pm$  SE) in Tartary and Common Buckwheat Seeds Grown in Slo and Orig^

variety	growth location	rutin (% DW)	quercitrin (% DW)	quercetin (% DW)
China 1	Orig	$1.22 \pm 0.039$	$0.048 \pm 0.001$	0.000
	Slo	$1.66 \pm 0.039$	$0.090 \pm 0.019$	0.000
China 2	Orig	$0.81 \pm 0.099$	$0.047 \pm 0.002$	$0.030\pm0.000$
	Slo	$1.18 \pm 0.179$	$0.050 \pm 0.007$	$0.033 \pm 0.014$
Lux	Orig	$1.23 \pm 0.085$	$0.049 \pm 0.005$	0.000
	Slo	$1.29 \pm 0.117$	$0.050 \pm 0.000$	0.000
Siva	Slo	$0.01\pm0.005$	0.000	0.000

<sup>a</sup> Tartary buckwheat varieties: China 1, China 2, and Lux. Common buckwheat: Siva.

case of rutin, there were also no statistically significant differences between the varieties studied, but all of the values decreased during further growth of the herb.

The content of quercetin was negligible. Traces were found only in the last few samples of spring and summer sowing and the range of the content was at the limit of detection of the method used. The reasons for such negligible quercetin content in the tartary buckwheat herb could be due to instant and effective drying process after the collection of samples, so the rutin could not be degraded to quercetin.

Buckwheat tea and green buckwheat flour (obtained from flowering plants, carefully dried, and milled) are the most commonly used buckwheat herb products. Tartary buckwheat has already been grown in Slovenia, and its seeds were used by the poor as a substitute for wheat, barley, or common buckwheat (1). On the basis of this study, it is clear that buckwheat herb production is feasible and that it could readily be produced as a nutritionally rich food, a rutin-rich herb tea, or food additive. According to our study, spring sowing is as appropriate as summer sowing, which could be carried out as a second crop of the season. Furthermore, it is important to harvest the herb when it contains the highest amounts of rutin, quercitrin, and quercetin, which happens simultaneously when plants are flowering or begin to form the first seeds. As regards tartary buckwheat varieties, there were no important differences in rutin content of China 1, China 2, or Lux herb samples.

Rutin, Quercitrin, and Quercetin Content in Seeds. Rutin contents in seeds grown in Slovenia and on Origs are presented in Table 3. The highest amounts of rutin in seeds were observed in China 1 sample when grown in Slovenia (about 1.66% DW), and on Orig, it was somewhat less (1.22% DW). In China, the growth conditions are quite severe since the altitude, where our experimentally studied tartary buckwheat grew, was about 2500-3000 m, in contrast to the Slo of about 300 m. Despite adaptation to the original extreme conditions, more rutin was synthesized in Slovenia probably because of the growth conditions; similar trends were shown in the China 2 variety. The China 2 sample also reached higher content of rutin in Slovenia (1.18% DW) than on Orig (0.81% DW). The rutin contents in the two Luxembourgish samples were similar at about 1.30% DW, regardless of the actual location of growing. A cultivar of common Slovenian buckwheat Siva was grown in Slovenia the same year and was analyzed in order to compare the flavonoid content in tartary and common buckwheat seeds. The rutin content was only about 0.006% DW, which was beyond the precise detection and separability of the method used.

According to the present results, higher altitude, which is often linked to higher UV radiation, did not necessarily cause the increase in rutin content in the seeds. Reasons for this could be found in the complexity of the plant growth and development in different environmental conditions (light, temperature, soil moisture, etc.).

The quercitrin and quercetin contents of tartary and common buckwheat seeds are also presented in **Table 3**. There was almost no difference in quercitrin content in seeds of tartary buckwheat varieties harvested on different locations. Generally, samples contained about 0.05% DW quercitrin; however, the China 1 variety grown in Slovenia contained almost double the amount of quercitrin (0.09% DW). The China 2 variety and Luxembourgish varieties contained amounts of quercitrin (0.05% DW) similar to those of the same samples grown on Orig. No quercitrin or quercetin was found in common buckwheat Siva seeds. Quercetin was determined only in China 2 variety seeds as about 0.03% DW, in both locations. It seems that growth location could be important for quercitrin content in the China 1 variety, which was not proven for the other two varieties.

Tartary buckwheat seeds contained more rutin than common buckwheat. Rutin content depends on variety and growth conditions. They also contained more quercitrin and more quercetin than common buckwheat seeds, where neither quercitrin nor quercetin was detected.

The bitter taste of tartary buckwheat seeds is ascribed to rutin, quercitrin, and quercetin, and because common buckwheat contains much less or none, it has become the more popular food for its better taste. It is possible that this explains the widespread distribution of common buckwheat as compared with tartary buckwheat.

## **ABBREVIATIONS USED**

DAS, days after sowing; DW, dry weight; Lux, Luxembourg; SE, standard error; Slo, Slovenian location; Orig, Original location.

## ACKNOWLEDGMENT

We acknowledge Ivica Zapušek-Skubic and Suzana Košenina for skillful technical assistance.

# LITERATURE CITED

- (1) Kreft, I. Ajda. CZD, Kmečki Glas; Slovenia, 1995; 112 p.
- (2) Bonafaccia, G.; Marocchini, M.; Kreft, I. Composition and technological properties of the flour and bran from common and tartary buckwheat. *Food Chem.* **2003**, *80*, 9–15.
- (3) Javornik, B.; Eggum, B. O.; Kreft, I. Studies on protein fractions and protein quality of buckwheat. *Genetika* 1981, 13, 115–121.
- (4) Kitabayashi, H.; Ujihara, A.; Hirose, T.; Minami, M. On the genotypic differences for rutin content in tatary buckwheat, *Fagopyrum tataricum* Gaertn. *Breeding Sci.* **1995**, *45*, 189–194.
- (5) Kreft, S.; Štrukelj, B.; Gaberščik, A.; Kreft, I. Rutin in buckwheat herbs grown at different UV-B radiation levels: comparison of two UV spectrophotometric and an HPLC method. *J. Exp. Bot.* 2002, 53, 1801–1804.
- (6) Gaberščik, A.; Vončina, M.; Trošt, T.; Germ, M.; Björn, L. O. Growth and production of buckwheat (*Fagopyrum esculentum* Moench) treated with reduced, ambient, and enhanced UV-B radiation. *J. Photochem. Photobiol.* **2002**, *66*, 30–36.
- (7) Dixon, R. A.; Achnine, L.; Kota, P.; Liu, C.-J.; Reddy, M. S. S.; Wang, L. The Phenylpropanoid pathway and plant defence a genomics perspective. *Mol. Plant Genomy* **2002**, *3* (5), 371–390.
- (8) Griffith, J. Q.; Couch, J. F.; Lindauer, A. Effect of rutin on increased capillary fragility in man. *Proc. Soc. Exp. Biol. Med.* 1944, 55, 228–229.
- (9) Schilcher, H.; Patz, B.; Schimmel, K. Ch. Klinische Studie mit einem Phytopharmakon zur Behandlung von Mikrozirkulationsstörungen. Ärztezeitschrift Naturheilverfahren 1990, 31, 819– 826.

Rutin in Tartary Buckwheat

- (10) Wojcicki, J.; Barcew-Wiszniewska, B.; Samochowiec, L.; Rozewicka, L. Extractum Fagopyri reduces artheriosclerosis in high-fat diet fed rabbits. *Die Pharm.* **1995**, *50*, 560–562.
- (11) Watanabe, M. Catechins as antioxidants from buckwheat (*Fagopyrum esculentum* Moench) groats. J. Agric. Food Chem. 1998, 46, 839–845.
- (12) Wilhelm, K.-P.; Biel, S.; Siegers, C.-P. Role of flavonoids in controlling the phototoxicity of *Hypericum perforatum* extract. *Phytomedizine* **2001**, *8*, 306–309.
- (13) Arima, H.; Ashida, H.; Danno, G. Rutin-enhanced antibacterial activities of flavonoids against *Bacillus cereus* and Salmonella enteritidis. *Biosci., Biotechnol., Biochem.* 2002, 66, 1009–1014.

Received for review May 24, 2003. Revised manuscript received August 22, 2003. Accepted August 22, 2003. The research was partly supported by the Ministry of Education, Science and Sports of Slovenia and by the Ministry of Agriculture, Forestry and Food of Slovenia.

JF034543E