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Moisture dependent textural and antioxidant properties of buckwheat

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Abstract
Pseudo cereals namely Buckwheat (*Fagopyrum esculentum Moench*.) is gluten-free grains characterized by an excellent nutrient profile. They have been used as nutritious ingredients in gluten-free formulations. They have been considered as underutilized food material in India and used mainly used in fasting days. Functional properties of buckwheat based foods are due to proteins and many rare components with healing effects. Among them, the most attractive ones are flavones, flavonoids, phytosterols, fagophyrins, and thiamine-binding proteins found in buckwheat grains. Hence, the knowledge about the textural properties and antioxidant properties of buckwheat grains is important for designing processed foods. In this regard, the study of the textural as well as antioxidant properties of buckwheat grain in the moisture content range of 9% to 17% wb. was conducted. Five different levels of moisture content in this range were selected. Textural properties particularly initial cracking force, initial cracking energy were evaluated and antioxidant properties such as total phenolic content and radical scavenging activity of buckwheat seeds, buckwheat whole kernel, broken and parboiled kernel were determined in this range. At the given moisture levels, initial cracking force varied from 4.50N to 5.69N in this moisture range, intial cracking energy varied from 26.16Nmm to 44.29Nmm and antioxidant activity such as total phenolic content and radical scavenging activity varied from 286.09 to 625.05 mg/100g and 70.94% to 87.55% of parboiled kernel and buckwheat seeds, respectively.

Keywords: buckwheat, textural property, antioxidant property, moisture content

Introduction

Buckwheat is the most important crop of the mountain regions above 1600m above sea level both for grain and greens. It occupies about 90% of cultivated lands in the higher Himalayas with a solid stand. It is a short duration crop (2-3 months) and fits well in the high Himalayas where a crop's growing season is of limited period because of early winter and snow fall. In the higher Himalayas, up to 4500m, this is the only crop grown (Joshi and Paroda, 1991) [8]. There are two species of buckwheat cultivated in the Himalayas (*F. esculentum and F. tataricum*). It is highly nutritive, unlike cereals which are deficient in lysine, one of the essential amino acids for human health (Anonymus, *1979*) [1]. In India, the crop is widely grown in Jammu and Kashmir in the west and Arunachal Pradesh in the east. Its high concentration was observed in high mountains of Jammu and Kashmir (Ladakh, Udhampur), Himachal Pradesh (Bharmaur, Pangi, Kulu, Shimla and Kinnaur), Uttar Pradesh (Uttar kashi, Chamoli, Pauri, Almora and Pithoragarh), West Bengal (Darjeeling), Sikkim (Lachan and Lachoong), Meghalaya, Arunachal Pradesh (Tawang, Bomdilla and Dirang) and Manipur. In South India, it is sporadically grown in the Nilgiris and Palni hills (Joshi, 1999) [8]. Buckwheat is widely grown in the North-eastern states and it is also cultivated in West Khasi Hills and in some areas of the Assam plains. This is the only crop, which can be grown widely in the high altitude areas of Sikkim and Arunachal Pradesh (Hore and Rathi, 2002) [6].

Buckwheat is actually a fruit seed that is related to rhubarb and sorrel making it a suitable substitute for grains for people who are sensitive to wheat or other grains that contain protein glutens. Buckwheat, unlike most cereals, is an alternative crop belonging to the polygonaceae family. The increasing attention for buckwheat cultivation and utilization of buckwheat products is due to rising number of data focused on its functional characteristics, which can provide many health benefits based on buckwheat products consummation, first of all during prevention and healing chronic diseases (Li and Zhang, 2001) [9]. Buckwheat's beneficial effects are due in part to its rich supply of flavonoids, particularly rutin. Flavonoids are phytonutrients that protect against disease by extending the action of vitamin C and acting as antioxidants.

Buckwheat's lipid-lowering activity is largely due to rutin and other flavonoid compounds. These compounds help maintain blood flow, keep platelets from clotting excessively (platelets are compounds in blood that, when triggered, clump together, thus preventing excessive blood loss, and protect LDL from free radical oxidation into potentially harmful cholesterol oxides. All these actions help to protect against heart disease. The nutrients in buckwheat contribute to blood sugar control. Buckwheat grains are also a rich source of magnesium, a mineral that acts as a co-factor for more than 300 enzymes, including enzymes involved in the body's use of glucose and insulin secretion. Insoluble fiber in buckwheat help women avoid gallstones. Lignans (a phytonutrient) in buckwheat are converted into mammalian lignans, including one called enterolactone that is thought to protect against breast and other hormone-dependent cancers as well as heart disease.

Buckwheat contains no gluten and can consequently be eaten by people with coeliac disease or gluten allergies. Buckwheat is a good honey plant, producing a dark, strong monofloral honey. Buckwheat has been used as a substitute for other grains in gluten-free beer. Buckwheat hulls are used as filling for a variety of upholstered goods, including pillows and zafu. On Hindu fasting days (Navaratri, Ekadashi, Janamashthami, and Maha Shivaratri), northern states of India eat items made of buckwheat flour. The preparation of buckwheat flour varies across India. The famous ones are kuttu ki puri (buckwheat pancakes) and kuttu pakoras (potato slices dipped in buckwheat flour and deep fried in oil). In most of northern and western states, buckwheat flour is called kuttu ka atta. In Punjab, it is also called okhla, and is extensively used in flour form.

An antioxidant is a molecule capable of slowing or preventing the oxidation of other molecules. Oxidation is a chemical reaction that transfers electrons from a substance to an oxidizing agent. Oxidation reactions can produce free radicals, which start chain reactions that damage cells. Antioxidants terminate these chain reactions by removing free radical intermediates, and inhibit other oxidation reactions by being oxidized themselves. As a result, antioxidants are often reducing agents such as thiols, ascorbic acid or polyphenols. Although oxidation reactions are crucial for life, they can also be damaging; hence, plants and animals maintain complex systems of multiple types of antioxidants, such as glutathione, vitamin C, and vitamin E as well as enzymes such as catalase, superoxide dismutase and various peroxidases. Low levels of antioxidants, or inhibition of the antioxidant enzymes, cause oxidative stress and may damage or kill cells. Antioxidants are widely used as ingredients in dietary supplements in the hope of maintaining health and preventing diseases such as cancer and coronary heart disease. Although initial studies suggested that antioxidant supplements might promote health, later large clinical trials did not detect any benefit and suggested instead that excess supplementation may be harmful.

Functional properties of buckwheat based foods are due to proteins and many rare components with healing effects. Among them, the most attractive ones are flavones, flavonoids, phytosterols, fagophyrins, and thiamine-binding proteins found in buckwheat grains. The biological and pharmaceutical effects of plant flavonoids, including buckwheat flavonoids, on human beings and test animals reviewed the medical effects of plant flavonoids; they are known for their effectiveness in reducing cholesterol levels in the blood, keeping capillaries and arteries strong and flexible, and assisting as a preventative measure against blood pressure, as well as many other cardiovascular diseases (Codi *et al.,* 1986) [2]. Many of the biological functions, such as antimutacigenity, ant carcinogenicity, and anti-aging, originate from antioxidant activity of antioxidative enzymes and nonenzymic antioxidants (Cook and Samman, 1996) [3]. The flavonoids in buckwheat can perform high antioxidative activity that may have the potential to show pharmaceutical effects from this characteristic (Oomah and Mazza, 1996) [11]. Six flavonoids (rutin, orientin, vitexin, quercetin, isovitexin and isoorientin) have been isolated and identified in buckwheat, but in buckwheat seed only rutin and isovitexin were found, and rutin attributed most of the flavonoids content in buckwheat seed (Dietrych-Szostak and Oleszek, 1999) [4]. Rutin and its hemisynthetic derivatives exert different medical effects like normalization of increased vascular permeability and fragility, oedema protection (Ihme *et al.,* 1996) [7]. Flavonoids isolated from buckwheat hulls showed radical scavenging activity which is important in suppressing radical damage in lipid per oxidation processes involved in food deterioration or some diseases. The phenolic compounds in buckwheat, namely 3-flavanols, rutin, phenolic acids and their derivatives, possessed antioxidative activity stronger than antioxidative components of oats and barley (Holasova *et. al.,* 2002) [5]. The antioxidative properties of the commercially accessible buckwheat flours in comparison to the wheat flour type 500 and wholegrain wheat flour by measuring DPPH radical scavenging activity, reducing power, chelating effect on Fe2+ and total phenolics content (Zhao *et. al.,* 2012) [13]. Antioxidant activities are affected by the buckwheat processing based on the changes of chemical composition. Some report investigates major anti-oxidative constituents from the seeds of buckwheat by detecting the components of the mixture of extracts and DPPH, and suggesting that rutin and quercetin were the major anti-oxidative constituents that are responsible for the quality control of buckwheat. The sources of buckwheat production had some important influence on the DPPH radical scavenging activity. DPPH radical scavenging activity of tartary buckwheat was stronger than that of common buckwheat, rutin, kaempferol, and some unknown compound might be the major effective components for quality control of tartary buckwheat (Yang *et al.,* 2008) [12].

Based on these studies were undertaken to determine textural and anti-oxidant properties of different forms of buckwheat samples namely buckwheat seeds, whole kernels, brokens and kernels of parboiled seeds to understand the functionality of this important grains.

Material and Methods

Sample Preparation

Buckwheat grains used in this study was procured from the local market in Ludhiana, Punjab. The grains were cleaned manually to remove foreign matter like dust, dirt, twigs and immature grains.

Moisture content of the sample was determined by hot air oven method described by *Nimkar and Chattopadhyay (2001)* [10]. The weight of the samples was recorded on an analytical balance (Model: TB403, Denver Instrument) of accuracy 0.001g in quadruplicate, and their average value recorded. The sample was divided into lots that were conditioned for moisture content in the range of 9% – 17% (wb) either by drying or by adding predetermined amounts of distilled water calculated from the following relationship:

$$Q = W \times \frac{(Mf - Mi)}{(100 - Mf)}$$

Where,
Q= mass of water to be added (g);
W = Quantity of sample (g);
Mi = initial moisture content of the sample (% wb.);
Mf = desired moisture content of the sample (% wb.).
The moist samples were stored in plastic bags in a refrigerator at 4°C for a week to allow uniform moisture content within the grains. Prior to starting the trials, the necessary amounts of sample were removed from the refrigerator to allow them to reach equilibrium with the room temperature.
Textural and antioxidant properties of the samples were measured for five moisture contents in the range of 9% – 17% (wb). The moisture range was selected based on various operations involved in buckwheat processing.

Measurement of Properties

Textural properties of buckwheat seeds

In order to determine textural properties such as firmness, fracture ability, resilience and other parameters in terms of initial cracking force and initial cracking energy, one grain was taken at random from the overall sample. The principle of a texture measurement system is to deform the sample in a controllable manner and measure its response. Similar to material testing machines, forces created during deformation of testing sample (i.e. food), jigs are manipulated to recreate conditions that foods are exposed to when being eaten or processed. In this way, texture is measured directly and its characteristic performance and "feel" of the testing sample can be envisaged. The texture of the buckwheat seeds were determined in terms of initial cracking force and energy required for initial cracking. For each test, single grain was placed on the platform at the center and the analyzer was operated at the conditions set up as per this details: Texture analyzer settings: a) Pretest speed: 1.00mm/sec, b) Test speed: 0.25mm/sec, c) Posttest speed: 1.00mm/sec, d) Return to start, e) Data acquisition rate: 200pps, f) Load cell: 50kg, g) Probe: SMSP/25. From the force-deformation curve, the initial peak was plotted and noted as the force required for the initial crack. The area covered under the force-deformation curve up to this initial rupture point was recorded as the energy required for the initial cracking.

Antioxidant Properties

Determination of antioxidant properties were buckwheat seed, whole kernel, brokens and kernels of parboiled seeds. Whole kernels and brokens were obtained by dehulling the buckwheat seeds using the lab model abrasive dehuller. Parboiled kernels were obtained by dehulling the parboiled seeds by following the unit operations namely soaking the seeds at 70 °C for 2 h and then steaming for 20 min.

a. Total phenolic content

One gram sample was ground using pestle and mortar with 10ml methane (50:50 v/v) for the extraction. This mixture was then transferred to centrifuge tubes for centrifuging at 3000 rpm for 15 min. 0.5ml of the supernatant was pippetted out for the analysis. With this, 5ml of folin ciocalteu reagent (1:10 diluted with distilled water) and 4ml aqueous sodium carbonate were added. The mixture was allowed to stand for 15 min. and the absorbance was taken at 765 nm. For the blank solution 0.5ml of 50% methanol was used in place of filtrate. The analysis was carried out with three replications in each sample.

b. Radical scavenging activity

Radical scavenging activity was determined using DPPH (2,2-Diphenyl-1-picrylhydrazyl) assay. One gram sample was taken with 10ml of 80:20 methanol: water for the extraction. This solution was centrifuged at 3000 rpm for 15 min. From the filtrate 0.1ml was taken and 3.9 ml DPPH solution was added to this. This mixture was kept in dark for 30 min and the absorbance was measured at 515nm. The reference solution was prepared by adding 0.1ml distilled water with 3.9 ml DPPH solution. 80:20 methanol: water was used as blank. The analysis was carried out with three replications in each sample.

Statistical Analysis

The experimental results were subjected to analysis of variance (ANOVA) using AGRES (version 7.01) software and least significant difference test was used to describe the means with 95% confidence.

Results and Discussion

Initial cracking force

The average values of initial cracking force (N) for buckwheat seeds were determined as 5.69, 4.50, 4.59, 4.79 and 5.52 respectively at 9, 11, 13, 15 and 17% wb moisture content. It was found that the force required for the initial cracking was the highest (5.69N) at 9% moisture content (mc) and it reduced to 4.5 N at 11% mc. After that the initial cracking force was found to increase with increase in the moisture contents (Fig 1).

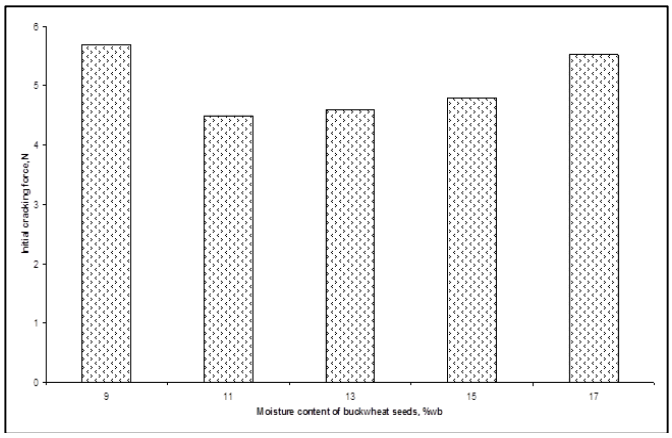

Fig 1: Initial cracking force of buckwheat seeds at different moisture content

Initial cracking energy (Nmm)

The average energy required for the initial cracking of buckwheat seeds were calculated as 39.24, 44.29, 42.71, 32.29 and 26.16 Nmm at 9, 11, 13, 15 and 17% wb moisture content respectively (Fig.2). It was found from the graph that the energy required for initial cracking was decreasing with increase in the moisture content except at moisture level of 9%. The initial cracking energy was high at the moisture content of 11% and low at the moisture content of 17%.

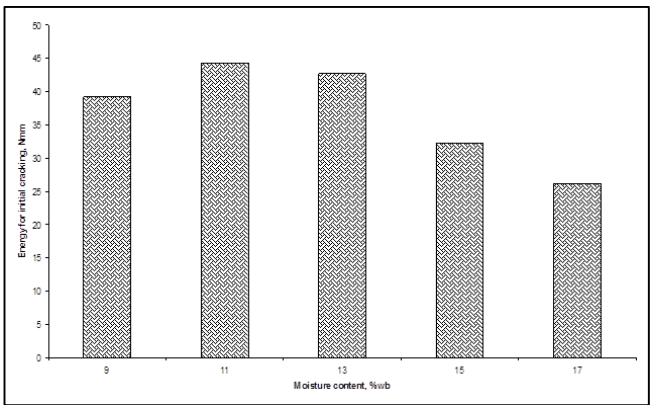

Fig 2: Initial cracking energy of buckwheat seeds at different moisture content

Total phenolic content

Total phenolic content of different buckwheat samples namely buckwheat seed, whole kernels, brokens and parboiled kernels were determined (using Folin-Ciocalteau reagent) as 625.05, 453.49, 289.23 and 286.09 mg/100g fresh sample respectively (Fig.3). The total phenolic content of buckwheat seeds were found as highest among the samples tested. It is followed by whole kernels, brokens and the parboiled kernels in decreasing order.

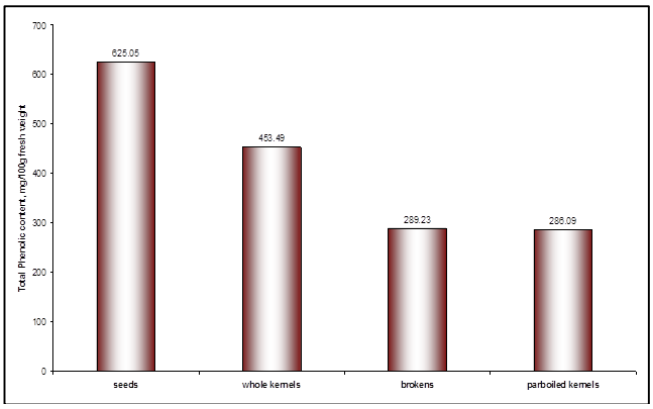

Fig 3: Total phenolic content of buckwheat samples

Radical scavenging activity

DPPH radical scavenging activity of buckwheat samples namely buckwheat seed, whole kernels, brokens and parboiled kernels were determined as 87.55%, 84.70%, 71.67% and 70.94% respectively (Fig. 4). Similar to the trend in total phenolic content, the DPPH radical scavenging activity was found high in the seeds followed by kernels, brokens and parboiled kernels.

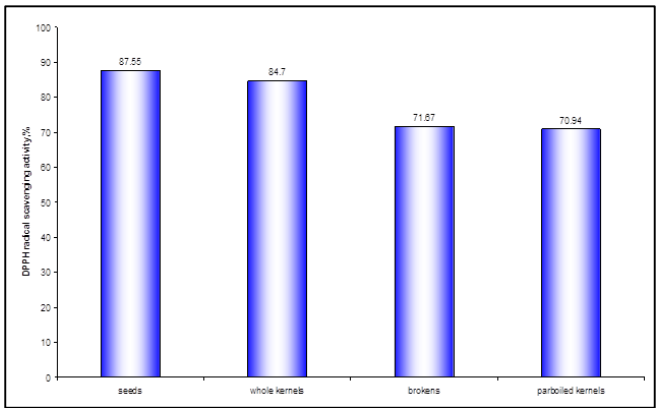

Fig 4: DPPH radical scavenging activity of buckwheat samples

Conclusions

The textural properties of buckwheat at different moisture content and the antioxidant properties of different samples of buckwheat namely seeds, whole kernels, brokens and kernels of parboiled seeds were determined. The average values of initial cracking force (N) and the average energy required for the initial cracking for buckwheat seeds were determined as 5.69, 4.50, 4.59, 4.79 & 5.52 and 39.24, 44.29, 42.71, 32.29 & 26.16 Nmm at 9, 11, 13, 15 and 17% wb moisture content respectively. Total phenolic content and the DPPH radical scavenging activity were found high in the seeds (625.05 mg/100g and 87.55%) followed by kernels, brokens and parboiled kernels.

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