Jing Wang · Baoguo Sun
Rong Tsao *Editors*

Bioactive Factors and Processing Technology for Cereal Foods

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Preface

The book summarizes the reported health benefits of bioactive factors in cereal foods and the potential mechanisms behind. It focuses on potential mechanisms that contribute to the different effects of bioactive factors on obesity, diabetes, and other metabolic diseases. It could help clarify some dilemmas and encourage further investigations in this field, aiming for promoting the consumption of cereal foods or whole-grain foods to reduce the risk of chronic diseases and improve daily dietary nutrition in the near future. The book is written for researchers and graduate students in the field of nutrition, food science, molecular biology, etc.

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The original version of this book was revised: The spelling of the author name was corrected from "RongTsao Cao" to "Rong Tsao". The correction to this book can be found at https://doi.org/10.1007/978-981-13-6167-8_15

Chapter 1
Market and Consumption of Cereal Foods

Fei Guo and Xiaochen Dong

1.1 Introduction

This chapter mainly introduces the market and consumption trend of four kinds of cereal food, namely, baked cereal foods, fermented cereal food, extruded cereal food, and premixed cereal powder. The content includes the definition, the market volume, the market sales, the consumer behavior, the consumer cognition, the future development trend, and so on. Different kinds of cereal food are different in technology, taste, product orientation, and so on.

1.2 Baked Cereal Foods

Baked cereal food is made from a variety of ingredients, including wheat flour, oil, sugar, salt, egg, milk, and so on. Generally, baked cereal goods are bread, biscuits, cakes, mooncakes, pancakes, pies, etc [1].

The global baking industry is growing steadily. According to the Euromonitor (a world authoritative market research institution), the market size surpassed $300 billion in 2016, with a compound annual growth rate of 3.54% from 2002 to 2016. The global market of packaged baked cereal products shows a trend of polarization. On the one hand, the mature Western market is growing slowly. On the other hand, the Asian market is developing rapidly, due to the low market penetration, the changes of consumers' diets, and the increase of disposable incomes [2].

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At present, the global baked cereal food market shows the following characteristics. Firstly, baked sweets in many mature Western markets are having a great boom; low-sugar products still have room for development and improvement. In the United States, for example, bread had a CAGR of 1.3% in the past 5 years, compared with 4.1% for baked sweets. In the United Kingdom, the CAGR for baked sweets was 1.9%, while bread/bread products declined to 0.8%. In Germany, baked sweets increased by 1.7%, but bread/bread products dropped to 0.5%. Low sugar/no sugar/sugar reduction claims show signs of rising in all categories, but global offerings with such claims accounted for only 2% of cakes, pastries, and sweets in 2016; there are only three parts in baking mixtures and ingredients, in bread and bread products, only four. In some regions, such as Latin America, where obesity and glucose problems have increased in recent years, low-sugar/ sugar-free/sugar-reducing products accounted for 1/10 of the bread products on the market in 2016, two times of the global average. In France, United States, and China, innovative sugar-reduced products also appeared on the market, and the product lines are similar to Latin America.

Secondly, the flavor innovation in the packaged baked sweets market is still less developed, especially when comparing to the baked foods in catering channel. For example, restaurants add spicy and salty flavors to desserts, doughnuts, and cupcakes to make colorful packaging and more diverse flavors. Chocolate and fruit flavors dominate the retail market of packaged cakes in the United States. Some new flavors have also come out to the market, such as cinnamon (spices) and salty caramel. It is worth noting that salty caramel is still a relatively new flavor applied in the retail cake products, indicating that the packaged cake market has been out of date.

Thirdly, there are more and more seasoned products of bread. In 2016, for example, the ratio of unseasoned/plain bread of all bread and bread products on the market has fallen from 67% 5 years ago to 61%. Globally, fruit and vegetable flavors (mainly garlic, tomatoes, raisins, onions, and olives) are the most common ones. Fruit and vegetable flavors are nothing new, but recently, there has been a significant change – the proportion of fruit and vegetable flavors in bread is changing to highlight the healthy characteristics of the product. Other important flavors used in bread include dairies (mainly cheese, butter, and milk), herbs, and spices (mainly herbs, rosemary, salt, and cinnamon) [3].

Baked cereal goods mainly originated from Western countries. The main contributor of consumption in global baked cereal market is from Europe and America. However, with the continuous development of the industry, the popularization of products, and the improvement of consumption level, baked cereal products have also registered significant growth in many developing countries. For example, the baking industry of China in recent years has been developing very rapidly. From 2011 to 2016, the compound growth rate was 11.93%, compared to Brazil's 11.24%, United States's 2.17%, and Japan's 0.11%. By comparison, the consumption growth rate of China's baked food market was significantly higher than the other four countries which are in the top 5 baked food market volume ranking [2].

The baking industry has a long history in China. The original bakery is characterized as the family bakery, single brand, homogeneous products and low market penetration. The modern baking industry has only developed for about 20 years in China. In 1980s, bakery companies from Hong Kong, Taiwan, and other regions entered the China market and gradually became an important branch of the food industry. With the rapid development of China's economy, people's living standards have been significantly improved, and the eating habits have gradually changed. Western food culture gradually enters people's life. There are more and more international brands appearing in the market day by day, the market saturation became higher step by step, and the market size expands unceasingly. At present, domestic well-known bakery companies have gotten rid of the traditional "store in front and factory at behind" mode of operation and generally adopted the management of central factory production, multi-network sales mode, and large-scale distribution. In general, since China's reform and opening up, China's baking industry has made great progress in product types, production volume, flavor, food safety, quality, packaging, raw and auxiliary ingredients development, scientific and technological innovation, market development, and other aspects.

The market of China's baking industry grows steadily in recent years. In 2017, according to the Euromonitor, sales value in the bakery retail market reached 194.48 billion yuan, and sales volume reached 9.527 million tons. Significantly, sales value is growing at a faster annual rate than sales volume, reflecting that the prices of baked goods are rising. Rising operating costs, premium trend, and demands for safe and healthy food of consumers are the main reasons (Charts 1.1 and 1.2.).

In Europe and America, baked goods are treated as the staple food, and almost every housewife can make cakes and snacks. In China, the popularization of baked goods is far behind the bread-eating behavior nations. In 2015, for example, in the United Kingdom, the per capita consumption of baked goods is 46.3 kg; in the United States, it is 39.8 kg; in Japan, it is 23.4 kg; and in Hong Kong, it is 15.9 kg. Per capita consumption of baked goods in China is much lower than the Western

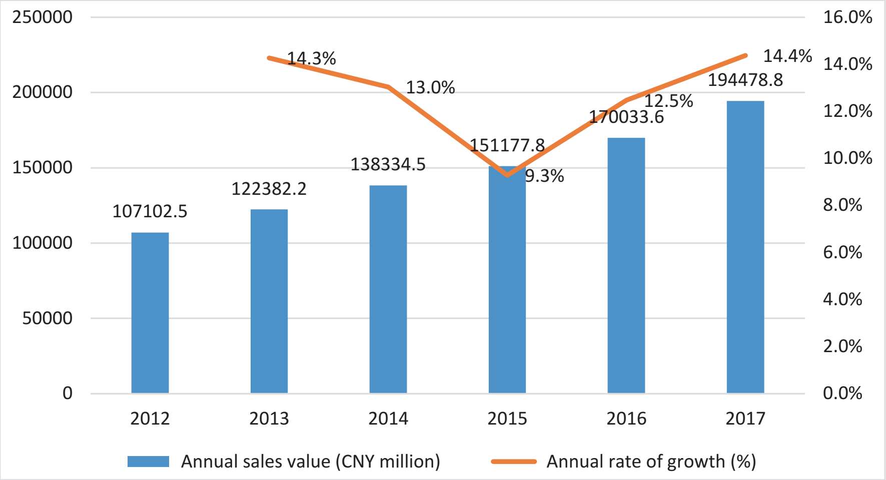

Chart 1.1 Annual sales value and rate of growth of baking industry of China from 2012 to 2017. (Source: Euromonitor)

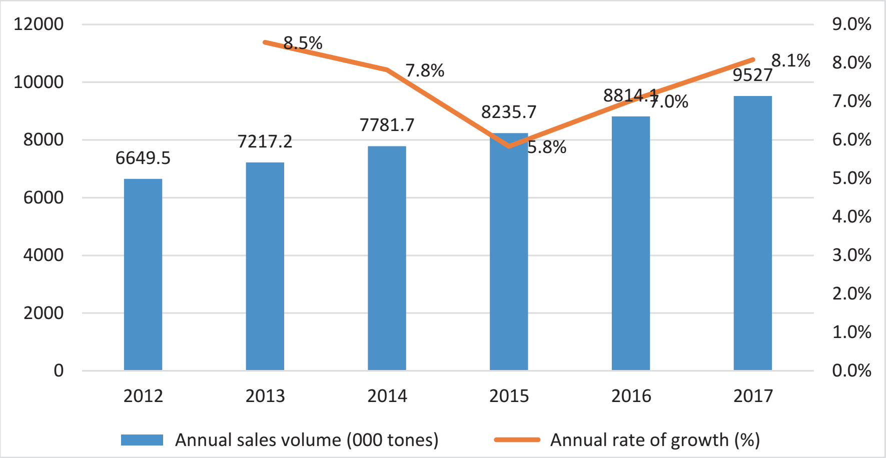

Chart 1.2. Annual sales volume and rate of growth of baking industry of China from 2012 to 2017. (Source: Euromonitor)

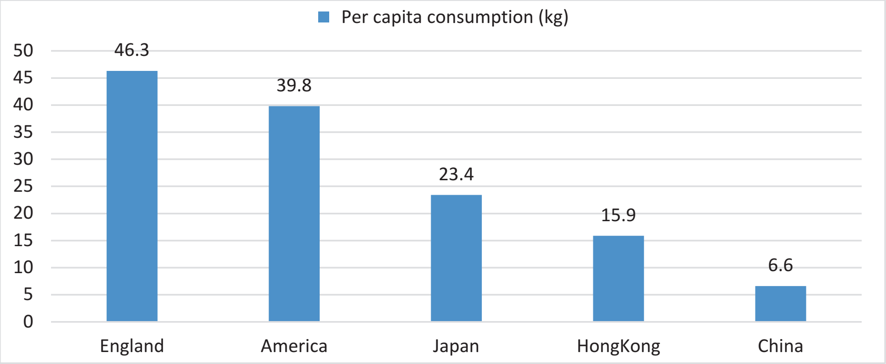

Chart 1.3 Per capita consumption of baked goods in some countries and regions. (Source: China Commercial Industry Research Institute)

countries because of the differences in eating habits. The baking food consumption per capita of China still has a large room for improvement in the future (Chart 1.3).

In terms of consumption trend, reduced-sugar/sugar-free products are getting more and more attention. Low-suger food is always welcomed by consumers, for example, about three out of ten (27%) American consumers who buy baked goods think that the low sugar/no sugar is one of the factors that influence their purchase decision. The pecentage of conumsers is only less than the pecentage of consumers who consider “stay fresh for a long time” (45%). Low sugar affects the taste of products to a certain extent. Seventy-one percent of US consumers agree that taste is more important than nutrition. How to reduce sugar while maintain the product taste will be a problem for the baking industry. Secondly, baking products need to further enhance their convenience in the future. Out of all the baked goods and ingredients/mixtures in global market in 2016, only 18% claimed to be convenient, which is much lower than that in the whole food industry: 24% claimed convenience, which is the second large claim category after natural. Thirdly, baking products will add more functional components in the future. Globally, only 5% claims for "extra benefits," while only 3% have functional healthy benefits. These percentages have risen slightly from a low base. Given that consumers are increasingly interested in the healthy feature of the products, these percentages will definitely rise in the future [3].

1.3 Fermented Cereal Foods

Fermented cereal foods mainly include the following categories: the first category is staple food products, such as steamed buns, dumplings, etc. The second category is cereal fermented beverages, including alcoholic and nonalcoholic beverages. Alcoholic beverages are made from sorghum, barley, rice, and other ingredients by fermentation or distillation, mainly referring to liquor, beer, rice wine, and so on. Non-alcoholic beverages (e.g. KbaC), fermented cereal drinks from probiotics, and so on. The third category is condiments made from fermented grains, such as rice vinegar and sweet flour paste. This part mainly introduces the current situation and trend of these three categories of products.

1.3.1 Fermented Cereal Staple

Steamed buns, dumplings, and rolls belong to the category of staple food products. These foods occupy a very important position in the Chinese market. In the past 10 years, China's staple food industry has developed very rapidly. According to the survey, about 70% of grain staples in urban areas and 40% of grain staples in rural areas depend on purchasing. At present, the need for all kinds of rice and flour-related staple food in China is very strong. All kinds of healthy staple food or balanced nutrition staple food have led the consumption trend. It is estimated that domestic staple food industry including processing, equipment manufacturing, and logistics can reach 1 trillion yuan industry volume. Thus, the time for the staple food processing industry to meet the growing needs of urban and rural residents has finally come [4].

According to statistics, the consumption of steamed buns accounted for more than 30% of the total amount of flour-related food, while the traditional noodle accounted for 75% of the total consumption of wheat in China every year. Due to the challenges of preservation, quality maintenance and transportation, steamed buns are not as easy and convenient as instant noodles and fine dried noodles, the industrialization of steamed buns is still difficult, and most of the products are still manually made.

In addition, instant frozen rice and flour-related food are also part of fermented cereal food, which developed rapidly in the last 10 years. The production of frozen rice and flour- related food in China was about 1.2897 million tons in 2005 and 5.2826 million tons in 2014. The average annual compound growth rate since 2005 was 16.96%. According to industry forecasts, in the next 5 years, the annual compound growth rate of sales of China's frozen rice and flour-related food industry will reach 13% to 17%. The momentum of increase is relatively fast [5].

The fermented cereal staple foods in China still have the following problems: firstly, the industrialization level of staple foods is not high. The average industrialized rate of staple food in developed countries is about 70%; with a high rate, it can be more than 90%. While in China, it is only 15–20%. At present, China's staple food production has not fundamentally got rid of the small workshop and the peddler mode. The industrialization degree is at a very low ratio, the number of leading enterprise is small, the product coverage is narrow, the brand popularity is low, and the product structure is unreasonable. Secondly, the problem of the key techniques in the preservation for staple food products has not been solved. For example, steamed buns have some problems such as the deterioration of quality, the deterioration of taste, the loss of flavor, the propagation, and even the decay of microorganisms. Thirdly, the industrial staple food sales mode is still relatively backward. Now, the sales mode is not diversified enough, while the randomness of consumer consumption is very obvious [5].

When focusing on consumer behavior, Chinese staple foods such as steamed buns are still popular with Chinese consumers. However, Western-style meals, such as bread, are becoming more and more popular, especially among young urban consumers. Chinese staple food is inconvenient to carry, and taste is relatively simple. In the future, manufactures need to improve traditional staples to make them more attractive to consumers (Chart 1.4).

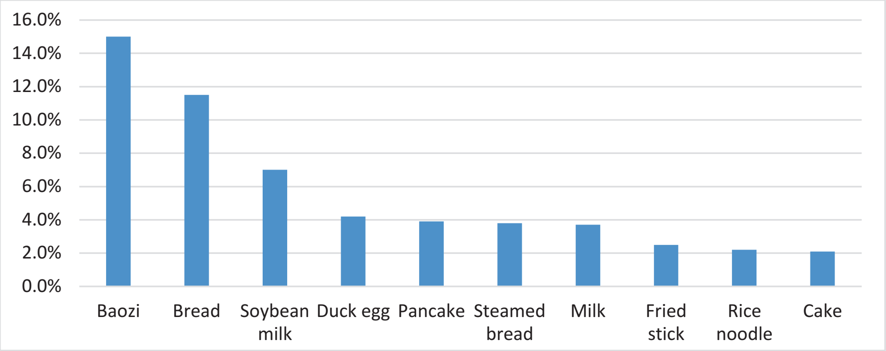

Chart 1.4 Chinese residents' preferences for breakfast. (Source: Euromonitor)

1.3.2 Fermented Cereal Beverage

Fermented cereal beverages are mainly separated into alcoholic beverages and nonalcoholic beverages. Alcoholic beverages mainly refer to liquor, beer, rice wine, whisky, vodka, and so on, with ethanol content above 0.5%. Nonalcoholic beverages are fermented by cereal and contain less than 0.5% ethanol.

The data showed that the global market value of alcoholic beverages expanded from 2010 to 2016, reaching $498.3 billion in 2016, but the growth rate slowed down after 2012. In the next few years, the global alcoholic beverages will keep growing slowly (Chart 1.5).

Alcoholic beverages such as white spirit, vodka, and whisky are strong liquor (distilled wine). In 2010, the global market value is $209.2 billion, and the industry revenue is $91.6 billion which grew steadily by 2–5% per year. The Asia-Pacific region, with the highest share of the population, accounted for 40.6%, with China and India accounting for more than a third of the population and growing at a faster rate than the world average growth rate. America accounted for 25.3%, and Europe was 24.2%. The global strong liquor industry is highly concentrated, with the top five companies accounting for more than 60% of the market, while the top two giants Diageo and Pernod Ricard together have taken about 44% shares [6].

White spirit plays a dominant role in China's liquor market. In 2016, the proportion of white spirit revenue of total liquor market was 63%, and the profit proportion is 73%. The total production volume of Chinese liquor industry reached 13.584 billion liters in 2016, an increase of 3.47% over the same period of last year (Charts 1.6 and 1.7).

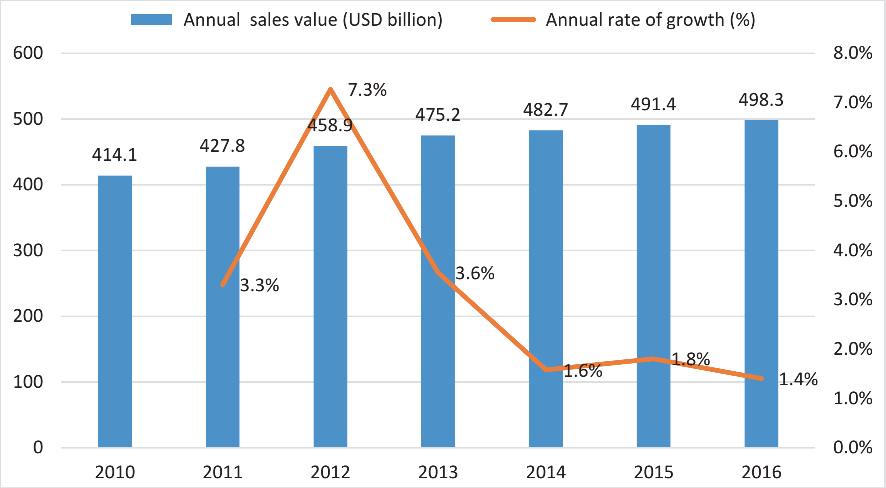

Chart 1.5 Annual market size and growth rate of global alcohol beverages from 2010 to 2016. (Source: Zhiyan consultation)

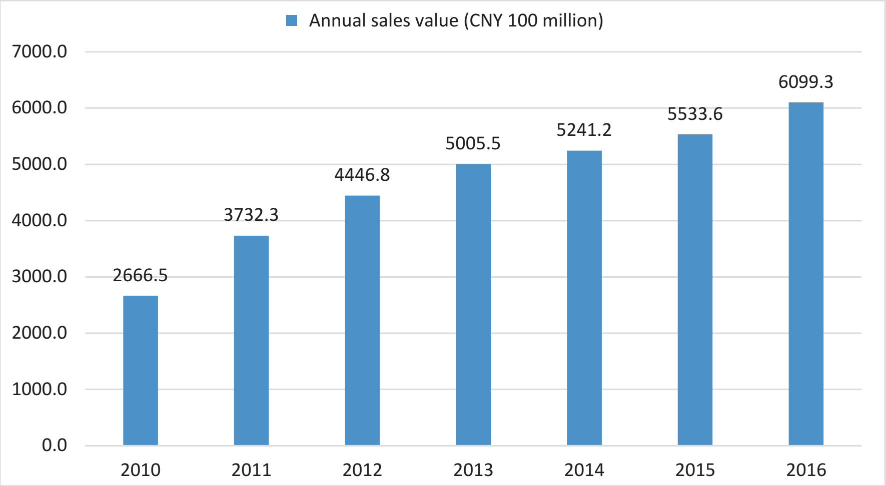

Chart 1.6 The sales value of white spirit of China from 2010 to 2016. (Source: www.chyxx.com)

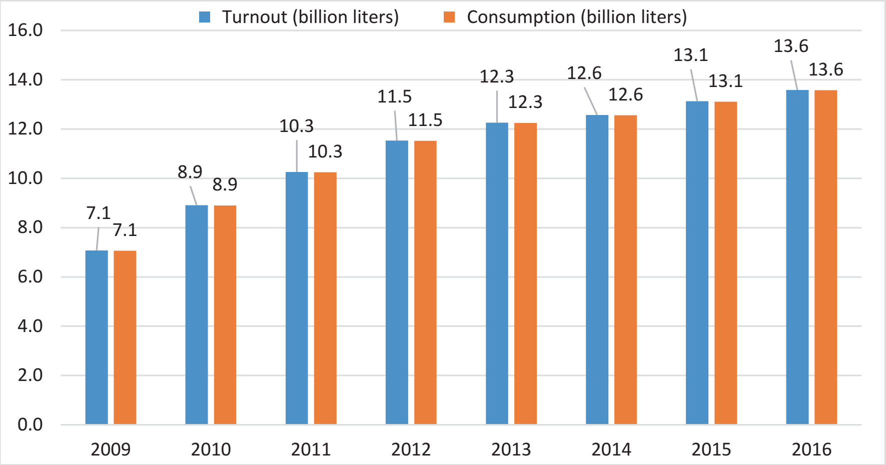

Chart 1.7 The turnout and consumption of white spirit of China from 2009 to 2016. (Source: www.chyxx.com)

In 2014, the export value of Chinese liquor accounted for about 1/1000 of the world's international wine trade. In contrast, brandy, whiskey, and other foreign distilled wines have occupied 10% of the domestic distilled liquor market, and grape wine has occupied 35% of the domestic wine market. It will take some time for Chinese liquor to go international [7].

In addition to strong liquor, there are some low-alcohol beverages which also belong to fermented cereal drinks, like beer. Beer is a fermented beverage made from wheat and malt. Beer is the oldest alcoholic beverage in the world, also the third place of world beverage consumption after water and tea. The global market of beer continues to shrink. Global beer consumption in 2016 fell 0.6% to about 1.8689 million liters, according to data released by Japan's Kirin Holdings on December 21, 2017. China, the biggest consuming country of beer, lost 3.4% of its consumption, and other markets such as Brazil and Germany also shrank. The market's reliance on global "big brands" is beginning to wane, and the market is now shifting to a personalized, pure hand-brewed beer. Some countries showed a trend of growth. The United States grew 0.6%, while in 2015, it also did not grow. The demand of pure hand-brewed beer with unique taste and expensive premium beer continues to expand. American pure hand-brewed beer accounted for more than 10% of the market, driving the growth of this mature market. The consumption needs for beer are also growing in more and more Asian countries. India grew 9.9%, Vietnam increased by 7.4%, and South Korea grew 1.0%. Consumption for beer in Asia is expected to increase in the future as the middle class expands [8].

In addition, rice wine market has caught notice in recent years. Rice wine, also known as sweet wine, is an alcoholic beverage made from rice, which can be classified into glutinous rice wine with lower alcohol content and grain wine with higher alcohol content.

As a traditional Chinese wine, rice wine has been popular in China for a very long time. Although rice wine in China has developed rapidly in the past 10 years, the rice wine industry still adopts backward management and sales models. The price of rice wine is low, the production technology still follows the old ways, and the culture of Chinese rice wine is scattered. No national rice wine brand has been formed so far. However, rice wine has a great potential. The consumer groups of rice wine are densely distributed in both urban and rural areas. Different levels of rice wine products can be developed according to different consumption levels [9].

Kbac is a cereal fermented drink. Kbac drinks were produced from black grain wheat and barley malt by fermentation with yeast and lactobacillus. It is a low-alcohol drink which is popular in Russia, Ukraine, and other Eastern European countries, brewed with dried bread, with a color similar to beer and slightly red. In the Chinese market, it is difficult to promote for its taste is not acceptable to most Chinese consumers.

1.3.3 Fermented Cereal Condiment

Fermented cereal foods also contain some flavoring foods, such as vinegar and sweet sauce, which are produced from fermentation of cereals.

Vinegar in China is mainly made from cereals, such as sorghum, barley, rice, millet, glutinous rice, corn, etc. While in foreign countries, especially in Europe and the United States, vinegar brewed with alcohol and fruit vinegar are more popular. Apple and other fruits are the most widely used for fruit vinegar. So this part focuses on the introduction of China's vinegar market.

Since vinegar has few negative features, its health benefits are well known. In the past few years, the sales volume and value of this market have been increasing year to year in China. This shows that the status of vinegar has been upgraded in the Chinese diet. The annual growth rate is maintained at more than 10%. Annual sales have also maintained steady growth, reaching 782.1 million tons in 2016, with an annual growth rate of around 10% (Charts 1.8 and 1.9).

With consumers' increasing interests to the quality of life, consumers' demand for vinegar products has gradually improved. The function of vinegar products has been transformed from a single basic flavoring function to diversified functions, like beverage vinegar and healthy vinegar. Some brands have extended the use of vinegar from cooking to the beverage ingredient.

In recent years, markets of flavoring foods are becoming increasingly premium. In the vinegar market, some enterprises have introduced the concept of vintage. They introduce vinegar in different years (indicating how long it was brewed) to distinguish the different grades of vinegar. The vintage of vinegar ranges from less than 1–10 years, and products of more than 5 years are generally considered high-end products. Five-year vinegar usually costs 1.5 times more compared to the 1-year vinegar.

At present, annual vinegar consumption per capita of China is only about 2.3 kg. In Japan, it is 7.9 kg; in the United States, the number is more than 6.5 kg. Chinese vinegar industry still has huge room for growth.

Due to the emergence of food safety problems, in recent years, consumers in China became more and more sensitive to food safety. Research shows that consumers pay much more attention to food safety and food health problems than other factors when consuming the flavoring foods (Chart 1.10).

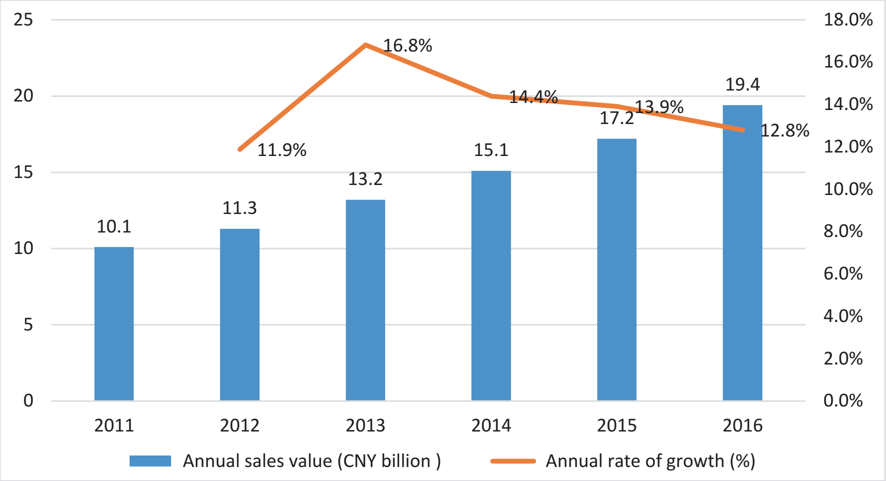

Chart 1.8 The annual sales value and rate of growth of vinegar of China from 2011 to 2016. (Source: Mintel)

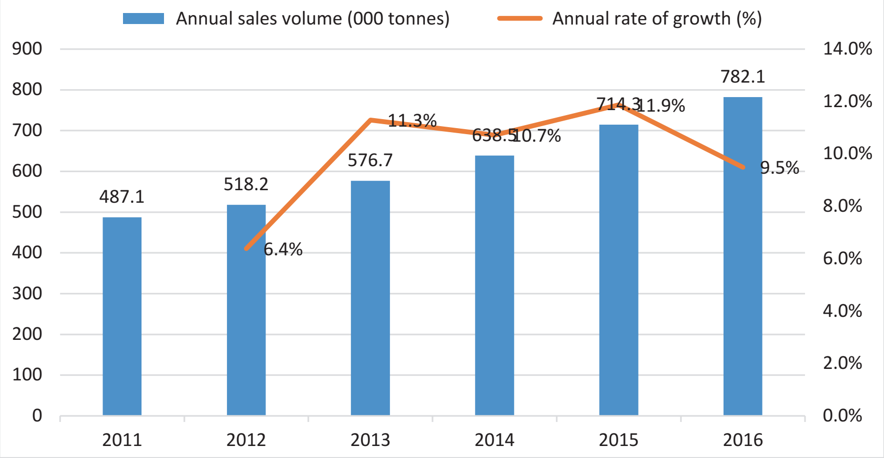

Chart 1.9 The annual sales volume and rate of growth of vinegar of China from 2011 to 2016. (Source: Mintel)

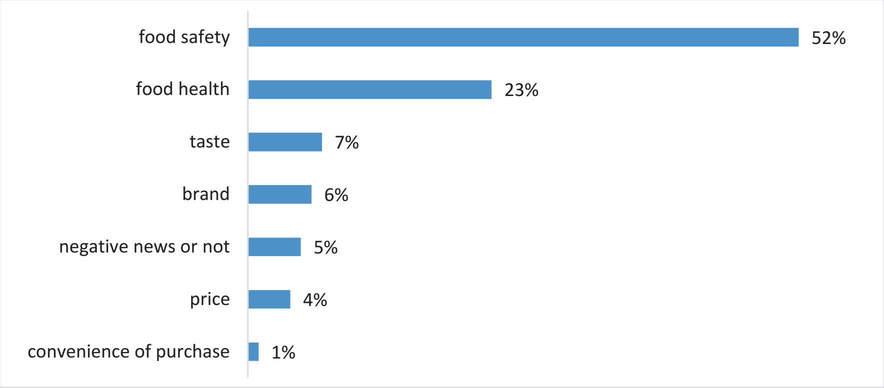

Chart 1.10 The factors that consumers pay attention to when buying condiments. (Source: Ipsos)

In terms of consumption, according to the data, 38% of consumers have consumed more vinegar in the past 6 months. The percentage of consumers who choose to eat more vinegar is the highest among the various sauce and spices. The ranking of sweet sauce, which account for 21% of all sauces, is relatively low on the list. At the same time, the consumers ate less monosodium glutamate nowadays. This shows that consumers are paying more attention to healthy diet (Chart 1.11) [10].

The condiment market has grown at a double-digit rate over the past few years, outpacing the overall retail food market growth rate reported by the National Bureau of Statistics. In the future, the status of condiments in the food market will be gradually enhanced. The increase in consumers' disposable income has driven consumption upgrading. Cereal fermented condiments such as vinegar and sweet sauce also

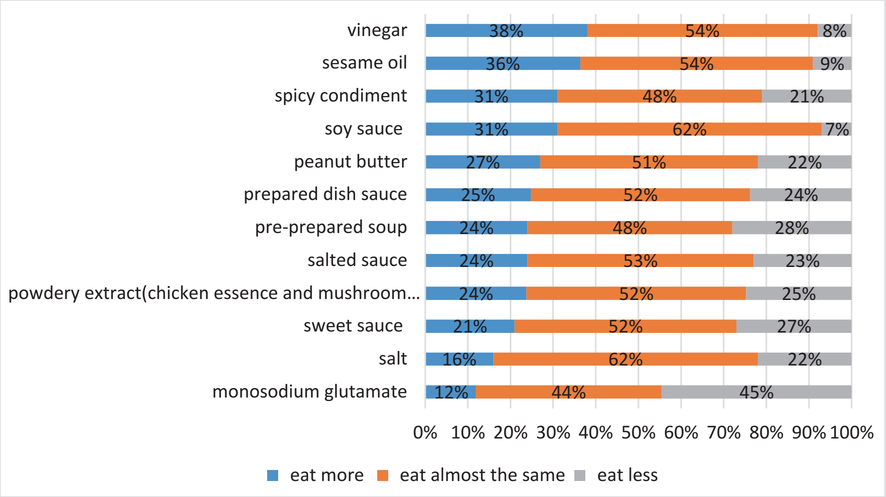

Chart 1.11 Consumption trend of sauces and condiments. (Source: Mintel)

have a room for development. At present, further market segmentation and being premium are the two most obvious trends. Innovations of vinegar, sweet sauce, and other condiments are still urgently needed.

1.4 Extruded Cereal Foods

There are two main categories of extruded cereal foods. One is extruded puffed food, which uses corn powder, potato or bean powder, and starch as the main raw materials. And by adding sugar, salt, and other auxiliary materials, after conveying, mixing, feeding, extruding, cutting, forming, seasoning, drying, and packaging, the extruded food is made. During extrusion, some natural anti-nutritional factors and toxic substances are destroyed with starch gelatinization and protein denaturation, the number of microorganisms is greatly reduced, and the palatability of the products is improved. Extruded puffed food mainly includes puffed small foods, breakfast cereals, extruded vegetarian breakfast foods, extruded tissue protein, and so on. The other one is extruded non-puffed foods, such as rice noodles, rice cakes, pasta, and so on.

1.4.1 Extruded Cereal Staple

Staple cereal foods mainly include breakfast cereals, spaghetti, and so on. Breakfast cereals include instant breakfast cereals, oatmeal and hot porridge, and other breakfast cereals. Spaghetti is also called as pasta, made of wheat with high density, high protein, and high gluten.

The sales of global breakfast cereals reached $32.5 billion in 2016.The compound annual growth rate was 6.1% over the 5 years from 2007 to 2012. Sales of breakfast cereals through the retail and catering industries account for 91% of the total. While consumers buy breakfast cereals mainly through retail channel, the sales of breakfast cereals sold through restaurants have reached $2.9 billion, and the number is still rising. The United States remains the largest consumer market in the world, followed by China, the United Kingdom, France, and Germany. In 2012, the sales of breakfast cereals in the United States were $8.1 billion, China was $6.2 billion, Britain was $4.2 billion, France was $1.7 billion, Germany was $1.5 billion, and other countries were $10.9 billion [11].

Breakfast cereals have been developed in most developed countries such as Europe and America for a long time. They have developed their own breakfast cereals according to the characteristics of raw materials and residents' eating habits. But studies have shown a decline in cereal breakfast sales in the United States, which is linked to a growing number of people not eating breakfast at home and the "millennials" (especially those born after 1990 grannies) who find it too troublesome to wash the dishes after eating [12].

At present, traditional Chinese breakfast foods are still the first choices for most Chinese consumers, but cereals and other Western breakfast have been gradually accepted. According to the data, 53% of consumers ate instant oats for breakfast and said they liked them. With the gradual cultivation of dietary habits, cereal and other Western-style cereals will have a good prospect in the Chinese market (Chart 1.12) [13].

Another staple extruded cereal food is spaghetti. In the twenty-first century, the output of spaghetti production has reached 10 million tons per year. In Italy, each person eats at least 28 kg of pasta a year. The spaghetti on the market can be divided

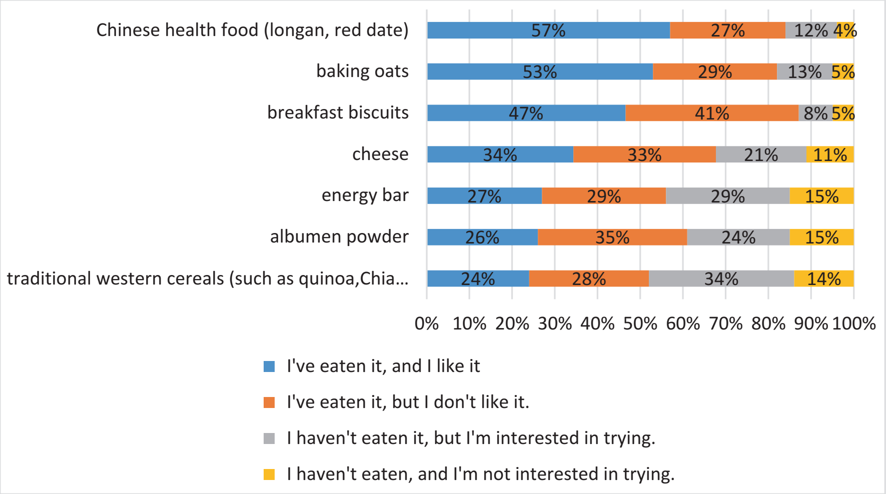

Chart 1.12 Trends of consumer choices for breakfast foods. (Source: Mintel)

into two categories, dry pasta and fresh pasta. In addition, spaghetti can be divided into different varieties according to shape, size, and texture. According to Wikipedia, there are 310 different shapes of spaghetti recorded in the world today, with 1300 different names, like capellinius, bucatin, pappardelle, penneet, and so on. The popularity of spaghetti in the world is due to its industrialization of standardized production hundreds of years ago, which greatly reduced the cost of production and dissemination. From the end of the nineteenth century to the beginning of the twentieth century, the spaghetti industry rose rapidly. Transportation has covered all over the world. Another reason of the popularity is the tolerance of spaghetti. It can be changed into different styles to get acclimatized to different customs. For example, Americans add chicken steak and steaks into spaghetti, and tea restaurants in Guangdong and Hong Kong add luncheon meat, ham, eggs, etc. [14] In terms of output and sales, spaghetti is on the rise these years (Charts 1.13 and 1.14).

1.4.2 Extruded Cereal Snack

Puffed food is an important part of extruded cereal food, which is regarded as a rising star in snack food. Puffed food is made from cereals, beans, potatoes, vegetables, and so on. Through the processing of extruding equipment, it is produced with great varieties, exquisite appearance, rich nutrition, and crispy fragrance.

At present, the global demands for puffed food continue to grow, and China has become one of the largest markets. TechNavio, a London-based market research

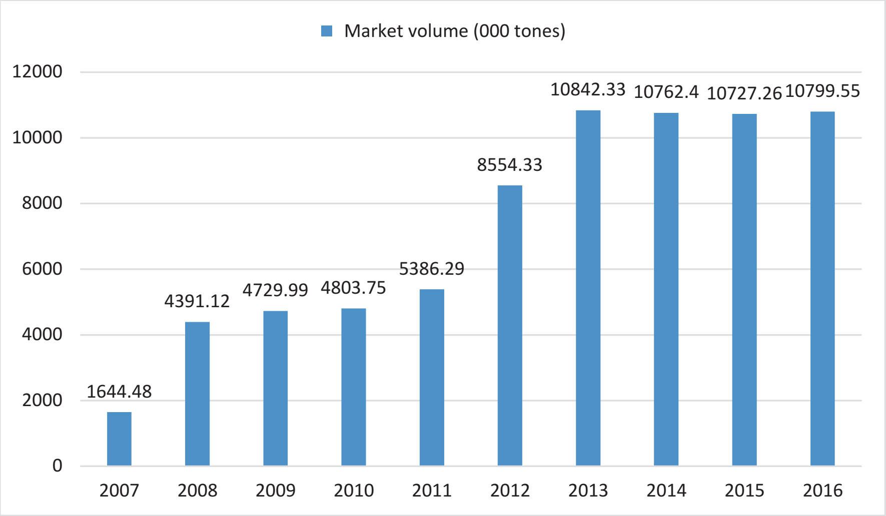

Chart 1.13 The market volume of global pasta from 2007 to 2017. (Source: Mintel)

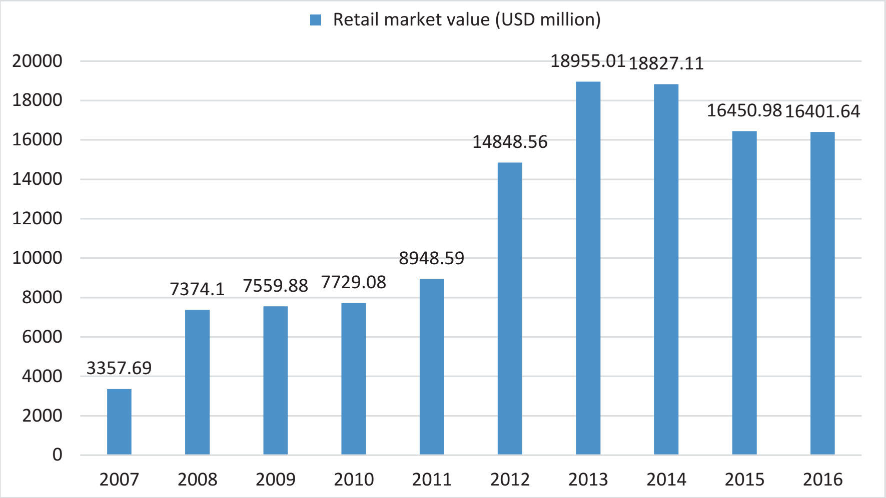

Chart 1.14 The retail market value of global pasta from 2007 to 2016. (Source: Mintel)

firm, expects this category to grow at a compound rate of 4.15% a year over the next 5 years [15].

The market growth of puffed foods benefits from the urbanization in developing countries. China and India are the two fast-growing salt-flavored snack market, according to a report by market research firm Mintel about salt-flavored snacks. The United States and China remain the top two countries in the salt-flavored snack market, followed by India, Mexico, Japan, and the United Kingdom [16].

With the improvement of people's living standard and health consciousness, puffed food will develop toward healthy products in the future. In addition, by the impact of consumer upgrading, consumers pursue high-end and high-quality products gradually. This requires the puffed food enterprises to continue to promote nutritious, high-end, and healthy food [17].

1.5 Premixed Cereal Powder

The premixed powder is a kind of functional blending powder. Its raw materials include wheat flour, sugar, soybean powder, milk powder, salt, etc. Pre-mixed powder is produced by blending equipments and packaging equipments (e.g. packaging and sealing machines). The main consumers of premixed powder are small food factories, food mills, and families.

In the bakery market of developed countries such as the United States, more and more premixed powder is used to stabilize the quality of bread, reduce the consumption for raw materials, stabilize the price, and improve the economic benefit. It is beneficial to the development of small bakeries.

Pre-mixed powder is not well known in China, because it is originated in baking industry, instead of staple food industry. The development of baking industry has greatly promoted the production and application of premixed powder in China. However, due to the limitations of technical conditions, cost, and ideas, the range and amounts of the application of premixed powder in China are far lower than that in the Western countries. At present, the clients of premixed powder in China are mainly some bakeries who have the high-quality requirements, like coffee shops, hotels, and so on.

In the next few years, with the rapid development of the baking industry, the premixed powder market will also grow fast. The trend will be more convenient, more natural and organic, more high-end, more economic, less additives, and so on. The traditional baking industry is becoming more and more popular, and at the same time, the premixed powder industry needs to introduce more innovative and distinctive products to attract young, diverse consumers [18].

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Chapter 2
Technologies for Improving the Nutritional Quality of Cereals

Rong Tsao

2.1 Introduction

Plants are the major source of human diet with over 50,000 edible plants available worldwide. Among them, rice, maize, and wheat alone provide 60% of the world's food energy intake. Cereals are the most dominant staple foods (51%) of the world average diet, followed by animal-based foods (meat, fish, milk, and egg) (13.5%), fruits and vegetables, pulses and nuts (8.2%), and roots and tubers (5.3%) [1]. Grains and pulses have traditionally been considered "poor people's foods"; however as their nutritional values continue to be revealed, whole foods and functional foods based on these are becoming increasingly popular.

Cereals and other grains not only provide substantial macronutrients, i.e., protein, lipids, and carbohydrate, but also many essential vitamins, minerals, and phytochemicals. Dietary fibers and phytochemical antioxidants, especially insoluble fibers and bound phenolics and their roles in human health, particularly intestinal health, have been an emerging area of research [2–4]. Cereals are consumed in prepared forms. Processing of cereals mainly include primary processing such as dehulling or debranning and milling followed by secondary treatments such as various cooking processes. Cereal grains are also consumed in sprout form or in fermented forms. These processes impart special characteristics to the physical and physiochemical qualities and alter nutritional and organoleptic properties of the original cereal grains.

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Impact of cereal processing technologies may be beneficial to human health as they can help remove toxins such as mycotoxins and anti-nutritive factors such as enzyme inhibitors and phytic acid and certain types of saponins, although it may also result in lowered nutritional quality as many nutrients may be lost during physical fractionation or heating. However, when used properly, many of the postprimary processing technologies can be used to improve the overall nutritional quality by minimizing the loss, enriching the nutrient content, and enhancing the digestibility and bioavailability of various nutrients, thus ultimately maximizing the health benefits. Current consumer perception on food nutritional quality is no longer limited to the conventional sense of nutritional value but has shifted to functional foods, i.e., foods that are demonstrated to have physiological benefits and/or reduce the risk of chronic disease beyond basic nutritional functions [5]. Many food bioactives, including phenolic compounds and carotenoids, play a vital role in reducing risk of chronic and degenerative diseases, especially those related to oxidative stress [4, 6, 7]. Processing method can significantly affect the retainment of composition of food bioactives and consequently the health beneficial effects such as antioxidant and anti-inflammatory activities [8]. This chapter is intended to give an overview of recent advances in cereal processing technologies that help improve nutritional quality of cereals. Conventional cooking by boiling, steaming, and roasting will not be covered in this review, and the focus will be on selected thermal (extrusion cooking, high pressure processing, microwave processing) and nonthermal processing technologies (milling, germination, fermentation, and enzymatic processing). Also mainly micronutrients and phytochemicals will be discussed.

2.2 Extrusion Cooking

All thermal processing technologies are theoretically deleterious when micronutrients are considered. Micronutrients other than the minerals go through chemical reactions thus are likely destroyed or degraded upon heating. Extrusion cooking is one of the most important and perhaps most widely used food processing technologies since the mid-1930s for a variety of foods, especially in the past two decades [9]. Although extrusion cooking have been used to produce foods with diverse textural properties, only in recent years, efforts have been made to improve the nutritional quality such as digestibility and nutrient bioavailability using this technology over conventional cooking methods [10, 11]. Effects of extrusion on food components and nutritional quality depend on different processing parameters including screw speed, die diameter, feed speed, and feed moisture content.

The overall effect on the nutritional quality and health outcome may also depend on the nutrients and bioactives in the feed, and research thus far have shown varied results. Extrusion may cause chemical and physicochemical changes of macronutrients like carbohydrates, protein, and lipids, thus affecting their digestibility and bioavailability. Extrusion changed starch components of barley and oats in solubility of dietary fiber and enhanced functional properties of cereal products [12–14]. The same may happen to micronutrients, e.g., vitamins, phytochemical antioxidants such as phenolics, carotenoids, and other food bioactives [9, 15, 16]. The effect of extrusion cooking on the bioaccessibility and bioavailability is a dichotomous thermal process which causes bioactive compounds such as phenolics and vitamins to decompose, while the heat also leads to improved release of compounds as a result of disruption of the cell wall matrices and cleavage of certain covalent bonds [17].

Extrusion generally reduces total phenolic content (TPC) of cereals and grains; however, other than the parameters of the extrusion process, a major factor that affects the bioactive compounds of cereals is the type of grain and its cultivar. For example, Alexa et al. [18] found that the degree of reduction of TPC was much significant in dark red bean compared to that in navy bean. Similar result was found in a recent study on brown rice. Extrusion cooking was found to increase the free TPC, total flavonoid content (TFC), and antioxidant activities as measured by ferric reducing antioxidant power (FRAP) and oxygen radical absorbance capacity (ORAC) assays, but not the bound phenolics and antioxidant activity [16]. However, closer examination of the profile of individual phenolic acids showed that although the seven phenolic acids (ferulic, vanillic, *p*-coumaric, chlorogenic, gallic, caffeic, and syringic acids) detected were affected differently, no significant effects were found in their composition. Vanillic acid in bound form was the only phenolic acid found to be increased significantly after extrusion cooling [16]. Other studies have shown different results. A recent study on the impact of extrusion on the phenolic profile and bioaccessibility of cereals (wheat, oat, and brown rice) showed that total free phenolic acids of brown rice and wheat were drastically decreased by 5.88% and 45.66%, respectively, whereas the total bound phenolic acids of all cereal grains were significantly increased by 6–9% [15]. The effect of extrusion also had different impact on the bioaccessibility of phenolics and antioxidant activity. Extrusion significantly decreased the bioaccessible phenolics of brown rice and oat by 31.09% and 30.95%, but it had minimal effect on those of wheat [15]. The differences observed may be due to the different matrix, especially protein structures of the cereals, as extrusion causes denaturation of grain proteins and alters or promotes tannin-protein interaction causing the formation of tannin-protein complexes which also affects the bioaccessibility and antioxidant activity [9]. Extrusion cooking of grit from different hulled barley led to a significant decrease in TPC and TFC which was dependent on both the feed moisture and extrusion temperature. However the antioxidant activity increased significantly upon extrusion, which may be caused from Maillard products, although the authors did not specifically pointed out [19].

Vitamins are even more severely affected during extrusion. Fat-soluble vitamins, such as vitamin A, including the provitamin A (e.g., β-carotene) and vitamin E, and the water-soluble vitamins such as vitamin C, B1, and folic acid have been most sensitive to extrusion cooking. Vitamins of the B group, such as B2, B6, B12, niacin, Ca-pantothenate, and biotin, are relatively stable during extrusion [20]. Oxidation occurred to the vitamins, phenolics, and carotenoids during extrusion cooking may be prevented or reduced by adding natural antioxidants such as ferulic acid and benzoin to the feed of cereal foods [21]. TPC, gamma-aminobutyric acid (GABA), and the antioxidant activity were significantly lower in extruded germinated brown rice (GBR) than those in un-extruded GBR [22].

2.3 High Pressure Processing

High pressure processing (HPP) or high hydrostatic pressure (HHP) processing is a nonthermal method that cooks food under very high pressure (5–1000 MPa) [23]. HPP inactivates certain microorganisms and enzymes and thus is mostly used as an alternative to pasteurization that leads to improved shelf life and increased microbial safety and quality of foods. The effect of HPP on the nutritional quality of cereal foods is also mainly on macronutrients, especially proteins as HPP has a limited effect on covalent bonds within foods or beverages. It has been found to affect the secondary structures which may help improve digestibility [24]. For this reason, the overwhelming majority of the literature on HPP and its effect on food nutritional quality was on perishable foods or their derivatives, and there was no reported studies on HHP and its effect on micronutrients in cereal grains before 2005 [23–25], and this situation has not changed since [26–29]. In terms of the impact of HPP treatment on food quality, more significant effect was found in color, flavor, texture, and sensory properties of fruit- and vegetable-based foods [30].

In a most recent review on using HPP to improve health and safety attributes of foods, Barba et al. [27] gave an overview of the latest findings and stated that HPP has emerged as a novel processing technology for food microbial safety and for foods with improved quality characteristics such as enhanced flavor and color. While a variety of foods including fruits, vegetables, dairy, and meat products have been studied and the effect of HPP on different micronutrients in those foods were discussed, none were related to cereals. In terms of micronutrients such as polyphenols, carotenoids, glucosinolates, and other phytonutrients, HPP is found to improve the extraction yield or recovery rate of these compounds from fruits and vegetables. Among the very limited studies on cereals, a recent study on rice showed that HPP improved grain shape, adhesiveness, cohesiveness, texture, and overall quality of rice, but its effect on nutritional quality was not studied. Moreover, despite the "encouraging potential to manipulate the functionality, extractability, allergenicity and bioavailability of micronutrients and components in a diverse variety of foods" of HPP, the authors concluded that more studies are needed to better understand the impacts of HPP on different bioactive compounds in food products with health benefits [31]. A study on HPP extract of buckwheat showed increased antioxidant activity, and the authors implied that the effect might be associated with the release of bound phenolic compounds, which was not verified [32].

2.4 Microwave Processing

Microwave processing is relatively mature thermal processing technology that is with high thermal efficiency, shorter processing time, reduced operational cost, and improved product quality [33]. It has many applications in both domestic and industrial food preparation. Microwave efficiently generates heat which is applied in drying, pasteurization, sterilization, thawing, tempering, and baking of fruits, vegetables, meat, and fish products [34, 35]. Owing to the high temperature it generates, microwave heating has been found to not only alter the texture and color of foods but also change flavor and nutritional qualities of foods in a similar manner as conventional and other novel thermal processing technologies, although to a lesser extent because of significantly shorter time of exposure [34, 36]. Microwave cooking was more efficient than conventional boiling in starch release thus higher glycemic index [37], in terms of micronutrients, like other thermal processing techniques; microwave cooking is also a dichotomous process: on one hand, it helps the release of bioactive components by effectively disrupting the cell wall, and on the other hand, the heat also causes thermal decomposition of these compounds. In terms of food micronutrients, one of the main applications of microwave processing is the microwave-assistant extraction or its variations such as combination with ultrasonication, ohmic heating, electron irradiation, infrared heating, and vacuum processing [38]. Again, applications on cereals are less studied [34, 35]. Microwave cooking was more effective in preventing the loss of flavonoids of buckwheat groats than conventional cooking (boiling) [39]. Baba et al. studied the effect of microwave roasting on antioxidant and antiproliferative activities of barley flour and found although roasting reduced significantly the TPC, the bioactivities were dose-dependent and significant [40]. Microwave cooking of barley significantly reduced TPC and TFC and antioxidant activity, greater effects on nonenzymatic browning, polyphenol oxidase (PPO) activity, compared to sand roasting [41]. The effects of domestic processing with dry heat including microwave heat were examined against wet heat on sorghum and found microwave heating significantly increased TPC and individual phenolic compounds, total vitamin E content, and individual tocopherol and tocotrienol concentrations and antioxidant activity. Lutein and zeaxanthin content was slightly reduced by microwave cooking [42].

2.5 Milling

Milling and grinding is a processing technology that renders grains into finer primary fractions for secondary processing. Milling removes the endosperm (starch components) of the seeds from the pericarp, testa, and aleurone layers. There are two types of milling, wet milling and dry milling. Dry milling separates the kernel or grain into anatomical parts or fractions (endosperm, bran, and germ), whereas wet milling separates the grain constituents into different fractions, i.e., protein, starch, fiber, and oil [43]. Milling can significantly influence the nutritional quality of cereals as the nutrients are contained in different fractions. A large amount of bran is generated during milling of cereal grains, which in most cases is considered a processing by-product with low value. However, cereal bran has been found to contain most of the nutrients of the grain and is a great source of dietary fiber and micronutrients such as vitamins, minerals, and phytochemicals, especially various phenolic compounds [44, 45]. Retainment of these nutrients is therefore largely dependent on the milling conditions. The milling process imparts unique characteristics and enhances organoleptic properties to the cereals; however it also changes the quantity and quality of nutrients and the physicochemical properties of the components, resulting in either improved or reduced nutritional quality. Optimizing milling conditions can therefore help in minimizing the loss of the nutrients and maximizing removal of antinutrients and toxins such as mycotoxins.

Milling is also a refining process which leads to reduced nutrients of cereals. Dietary fiber and micronutrients are significantly lower in refined wheat flour compared to the whole flour. Fractionation of the whole flour into different particle sizes also affects the content and digestibility, bioaccessibility, and bioavailability of both micro- and macronutrients [46]. Milling mechanically breaks down the cell wall of the cereal grains and thus improves the bioaccessibility for nutrients of the bran to the digestive enzymes, resulting in enhanced nutrient bioavailability the increased release of nutrients bound to the cell wall matrix [46, 47]. Extractable TPC and antioxidant activity were found to be increased when the insoluble dietary fiber of wheat bran was reduced to submicron size [48]. Grinding of wheat bran significantly increased TPC, TFC, and carotenoid content and antioxidant activity [49, 50]. Similar results were found in buckwheat hulls [51]. A recent study showed that both extractable and bound TPC, TFC, and antioxidant activity of superfine rice bran fiber fractions were significantly higher in finer powders [52].

2.6 Germination

Cereal grains and legume seeds are known to contain a plethora of phytochemicals that can act as antioxidant and anti-inflammatory agents when consumed. These bioactive compounds are considered as reasons for the many health benefits of cereal foods. Germination is a physiological process of plants that starts with water absorption of the seeds. The germination process involves the stimulation of the endogenous enzymatic activity and acceleration of a series of biochemical reactions. These events have been shown to induce hydrolysis of storage proteins and carbohydrates and to cause reduction in anti-nutritive compounds and augmentation of the levels of vitamins, phytochemicals, and GABA [53, 54]. Depending on the germination stage, the form of geminated grains or seeds for consumption may be sprouts or malts, which not only are significantly different in shape, textural, and sensory characteristics from the original seeds but also in nutritional value. Geminated seeds are traditionally consumed fresh but can also be in various dried forms. Cereal grains are among the richest sources of micronutrients in addition to protein, carbohydrates, and lipids. The biochemical and metabolic processes during germination change the composition and quantity of essential macronutrients, as well as those of vitamins and other micronutrients [55]. Antinutrient content is significantly reduced by germination, and in most cases, sprouts of cereal and pseudocereal seeds had increased crude protein content and total soluble sugars and reducing sugars and decreased total starch content compared to those of the grains. Lipid content is generally decreased after germination [55]. In terms of micronutrients, conflicting results have been reported for vitamins; however in recent years, germination has been found to be a viable way to increase bioactives such as phenolics and GABA, which leads to enhanced nutritional quality [54, 56, 57]. Our recent study showed that TPC and antioxidant activity of amaranth sprouts were higher than that of the seeds, and the sprouts also had completely different phenolic acid, flavonoid, and betanin compositions [57]. Moongngarm and Saetung [53] found that some essential amino acids, especially leucine and lysine, and GABA were significantly increased in germinated brown and rough rice. Isoflavone and GABA contents were also significantly increased during soybean seed germination and sprouting ($P < 0.05$), and such increases also led to significantly elevated antioxidant activities. GABA is a neurotransmitter that has various beneficial functions, and germinated rice and soybean seed had a phenomenally >350-fold increase compared to ungerminated soybean [53, 54]. The effect of germination depends on the species of the cereal seeds. While decreased TPC was observed for millets and a few sorghum cultivars, other germinated cereal and pseudocereal seeds including buckwheat, amaranth, quinoa, and some sorghum showed significantly increased TPC [55]. GBR is one of the most studied cereal grain. Germination significantly improved the content of GABA, TPC, γ-oryzanol, and antioxidant activity in a time-dependent manner. Sun-drying did not significantly affect the composition of these compounds except GABA. Elevated concentrations of bioactives in GBR have been found to contribute to various health beneficial effects [58, 59]. GABA, TPC, and the antioxidant activity of GBR were also significantly lowered by extrusion cooking [22]. Alvarezjubete et al. [60] studied the polyphenolic composition and antioxidant activity of amaranth, quinoa, buckwheat, and wheat and found that TPC and antioxidant activity to be generally increased with sprouting, although the bread-making process destroys some of these bioactives. The vitamins C and E and β-carotene contents in germinated wheat also steadily increased with increasing germination time, so were the concentrations of phenolic compounds such as ferulic and vanillic acids [61]. The effect of germination on the TPC in malted and unmalted barley was found to be variable depending on the steeping and kilning processes [55].

2.7 Fermentation

Fermentation as a food processing technique dates back thousands of years. Many foods and beverages are fermentation products based on plants, e.g., beans, grain, vegetables, fruit, and tea, and animal-based raw materials (e.g., honey, dairy products, fish, and meat). Fermentation is an action by the microorganisms, i.e., yeast, fungi, and bacteria, that convert carbohydrates into alcohols and organic acids. The fermentation process creates unique texture, flavors and aromas for foods and beverages, and also enriched nutritional profiles. Fermentation is one of the most simple and economical ways of improving the nutritional value, sensory properties, and functional qualities of cereals [62]. There are basically two types of fermentation process, submerged (SmF) and solid-state fermentation (SSF) [63, 64]. These processes have been reported to increase the release of phenolic compounds and antioxidant activities of cereals. The effects of fermentation on phenolic compounds depend on types of grains, microorganism species, and fermentation conditions particularly temperature, pH, and time [17]. TPC and antioxidant activity of SSF wheat by two filamentous fungi were significantly higher than unfermented grain [65]. Similar results were found recently by Sandhu et al. [66]. The increased phenolic compounds in SSF wheat were found to be mainly hydroxybenzoic acids and hydroxycinnamic acids [67], especially the latter which are mostly in bound form in unfermented wheat but released as a result of fermentation. Increased release of originally bound phenolics after fermentation increases the bioaccessibility and bioavailability of these antioxidants, as seen in wheat bran fermented with yeast and treatment of cell wall hydrolytic enzymes and in millets [68, 69]. SSF of rice also led to increased antioxidant and other bioactivities [70]. In recent years, bond phenolics have been a focus of many studies because of their antioxidant and anti-inflammatory effects and their role in gut health [3, 71, 72].

Liberation of phenolics in fermented cereal products may be from three main routes: (1) structural breakdown of cell wall after the microorganisms are colonized in cereal-based media, (2) hydrolysis of bound phenolics by enzymes produced by microorganisms during fermentation process, and (3) newly formed soluble phenolic compounds by the microorganisms [63].

2.8 Enzymatic Processing

Enzymes are proteinaceous compounds that act as catalysts in all living organisms. Enzymes from edible organisms (plants, animal tissues, microorganisms) have long been used in food processing. The abovementioned fermentation processes are in fact actions by the enzymes by the microorganisms (bacteria, yeasts, and fungi). Although consumers are rarely using enzymes directly in day-to-day food preparation, enzymes are used in large-scale industrial production of foods and food ingredients. Commercial enzymes used in modern-day food industry are mainly isolated from microorganisms instead of plants or animals due to several advantages such as easy, cost-effective, and consistent production [73]. Enzymes are used for ingredient production, texture modification, and other applications such as production of high-fructose corn syrup, beverage clarification, brewing, baking, production of low-lactose milk, and meat tenderization [74]. Enzymes are also used for enhanced thermal and operational stability, improved specific activity, modification of pH-activity profiles, and increased product specificity [75]. The most important enzymes used in food processing include α-amylase, glucoamylase, protease, lactase, lipase, phospholipase, esterase, cellulase, xylanase, pectinase, glucose oxidase, laccase, catalase, peroxidase, α-acetolactate dehydrogenase, asparaginase, debittering enzymes, narininase, lysozyme, β-glucosidase, papain, and pepsin [73, 76].

For cereal processing, α-amylase, glucoamylase, and protease are used in baking, brewing, starch liquefaction and bread and cake making, and quality improvement. The quality of sourdough rye and wheat breads was significantly improved in texture and bread volume and in the release of phenolics and other bioactives in the presence of α-amylase, xylanase, and lipase [77]. Enzymes are used widely in the baking industry. Amylases are generally used for converting starch into sugar and dextrins, oxidases for bleaching the dough, hemicellulases for improved gluten strength, but proteases for reduced gluten elasticity. The collective action of these enzymes leads to improvement in maintenance of bread volume, crumb softness, crust crispiness, browning, and freshness [76]. Xylanases in particular can help in the redistribution of water and leave the dough softer and easier to knead, resulting in improved dough characteristics such as better dough flexibility, machinability, stability, and loaf volume and in greater bread quality such as delayed crumb formation and finer and more uniform crumbs [78]. Many of these enzymes are used instead of yeast in the brewery industry to make alcoholic beverages. α-Amylase and β-glucosidase and protease are added to unmalted barley to convert complex carbohydrates to simple sugars to reduce cost and aid the malting process and to induce fast maturation and aid filtration.

An emerging area of use of enzymes especially the carbohydrases is the so-called enzymatic polishing of grains. This is a novel processing technology that uses enzymes to modulate the grain properties such as the taste, texture, and shelf life, with minimum negative effects on nutritional value. Enzyme polishing can also liberate cell-bound nutrients such as phenolics and fibers from bran without removing the germ and bran layer. Enzymatic polishing clearly has advantages in preserving loss of nutrients compared to mechanical milling; however it still requires further research effort in scale-up and in lowering the cost [79].

To summarize, cereal grains are a major source of human food rich in macronutrients and various micronutrients. Modern society and the cereal food industry have created various processing technologies that have been applied to cereal processing. These technologies have helped in developing diverse types of cereal foods; however, because of the refining process, many nutrients are lost or reduced. Such loss or reduction in nutritional quality during primary and secondary processing of cereals can be minimized, and as discussed in the present chapter, through optimizing the different novel processing technologies, nutrients can be retained and in many cases can even be increased. This chapter focused more on the micronutrients, especially phytochemicals, e.g., phenolics, carotenoids, and other compounds that are known to contribute to the health beneficial effects of cereals. Cereal bran contains the majority of dietary fiber and phenolic content, and thermal processing technologies may give dichotomous results in that the heat increases the degradation of bioactives but also breaks the cell wall so more compounds are released. Many technologies help increase the bioaccessibility and bioavailability of bioactives. While increased processing inevitably leads to more loss of bioactive components, continued research effort on technologies for the enhancement of bioactive compounds and dietary fiber contents will ultimately lead to improved bioaccessibility, bioavailability, and health effects of cereal and cereal-based foods.

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Chapter 3
Corn

Jingwen Xu, Yonghui Li, and Weiqun Wang

3.1 Introduction

Corn, also known as maize or *Zea mays*, is a cereal crop belonging to the grass family. Variance in genotypes results in diverse corn varieties. Classification of corn can be either based on different kernel characteristics (e.g., flour corn, flint corn, dent corn, sweet corn, waxy corn) or pericarp color (white, yellow, blue, purple, red, and black) [1]. Corn has been adapted to grow worldwide but is primarily cultivated in the United States, China, Brazil, Argentina, India, France, and Indonesia. World corn production is estimated to be more than 1 billion metric tons in 2017–2018 [2]. As a staple crop, corn has been largely consumed as food in many regions, especially in Africa, South America, and some areas of Asia and Europe [3], while in the United States, corn has been mainly used for animal feed and production of biofuel, with less than 10% directly used for food and food ingredients.

Major components in corn include starch (72%), protein (9.5%), fiber (9.5%), oil (4.3%), and moisture [4]. The corn kernel is composed of endosperm (approximately 82%), germ (10–11%), pericarp (5–6%), and tip cap (1%), which are shown in Fig. 3.1. The pericarp is the outer layer protecting the corn kernel from insects and microorganisms and is rich in bioactive phytochemicals and fibers such as cellulose and hemicellulose. It is usually removed during dry milling processing, also known as dehulling or debranning. Isolated corn bran can be further refined to produce dietary fiber for food uses. Two types of endosperm are well known in corn: horny (hard) endosperm and floury (soft) endosperm. Endosperm consists of starch granules surrounded with protein matrixes and protein bodies. Fat is concentrated in

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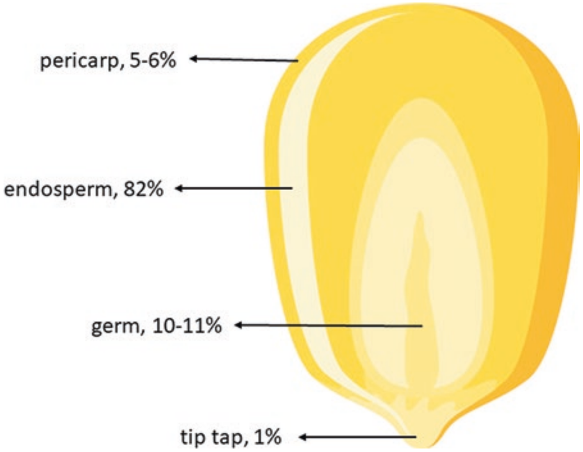
Fig. 3.1 A schematic of corn kernel with major components. (Adapted from Rausch et al. [5])



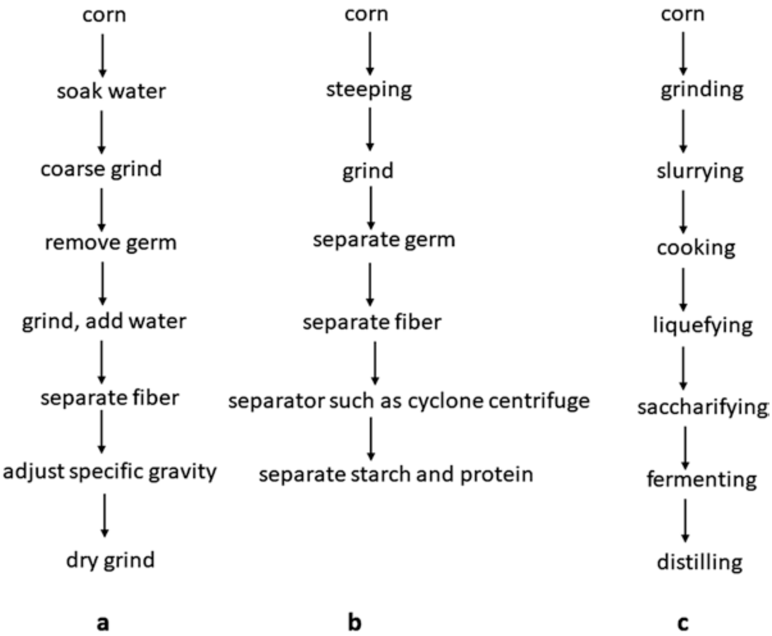


Fig. 3.2 Flow charts of corn processing, dry milling (**a**), wet milling (**b**), and corn ethanol (**c**)

the germ, which is usually used for corn oil extraction. Tip cap, the attachment point of the kernel to the cob, may be removed from the kernel during shelling. Moisture and nutrients pass through the kernel via tip cap during development and drying [6].

Industrially, corn grains are mainly processed via dry milling, wet milling, or dry grinding into different fractions and products (Fig. 3.2). During dry milling, there are several main steps including removing corn bran and germ, reducing particle size via grinding, and screening separation via sieving. Common products from dry milling include corn grits, meals, flours, and animal feed including bran and germ. Wet milling refers to the process of applying chemicals such as sulfur dioxide (SO_2) during steeping to disrupt the protein matrix surrounding starch granules, therefore separating proteins and starches in subsequent milling steps [7]. In addition to the production of purified starch, coproducts include corn gluten meal, corn gluten feed, germ meal, and oils. Dry grind processing has been widely used for production of fuel ethanol from corn. Typically, corn kernels are grounded, cooked in water, liquefied with enzymes, and then fermented in the presence of enzymes and yeast. Besides ethanol, distillers dried grains and CO_2 are the major coproducts from this process.

3.2 Bioactives in Corn

Whole grain corn is a rich source of macronutrients (i.e., carbohydrate, protein, fat, and dietary fiber), micronutrients (i.e., minerals and vitamins), and non-nutrient phytochemicals. Phytochemicals are the most important bioactive compounds unique to plants and are associated with promoting health and reducing risk of age-related chronic diseases [8, 9]. Primary classifications of phytochemicals include phenolic compounds, terpenoids, sulfur-containing compounds, and nitrogen-containing compounds. Major phytochemicals in corn include phenolic compounds primarily as phenolic acids and anthocyanins and carotenoids such as carotenes and xanthophylls. In addition, dietary fibers including resistant starch, proteins, and lipids of corn could also have beneficial bioactivities.

3.2.1 Phenolics

Phenolic compounds are defined as chemical compounds consisting of at least one aromatic ring with at least one hydroxyl group. Phenolic compounds can be further divided into subgroups of phenolic acids, flavonoids, stilbenes, coumarins, and tannins [9]. Corn is characterized by the highest total phenolic content among whole grains commonly consumed by humans (i.e., corn, wheat, rice, oat) [10]. Corn bran is an especially good source of bioactive phenolic compounds [11]. For example, corn bran was found to contain about 4% phenolic acids (dry matter), including 2.8% ferulic acid and 0.4% *p*-coumaric acid [12, 13]. The content of phenolics and their compositions in corn are dependent on genotypes and varied by environmental factors such as cultivation, fertilization, ripeness, and postharvest conditions. Phenolic acids and flavonoids are the most common phenolic compounds found in corn and other whole grains.

Phenolic acids in cereals are reported to be originally derived from benzoic and cinnamic acids [14]. Ferulic acid (4-hydroxy-3-methoxycinnamic acid) (FA) and *p*-coumaric acid are the primary phenolic acids in cereals, especially in brans [14].

FA is primarily present in the cell wall of corn, either in free form or conjugated with other biopolymers such as arabinoxylan and lignin. The chemical structure of FA is shown in Fig. 3.3a. FA contents in corn products have been reported to be 2610–3300 mg/100 g in corn bran and 313 mg/100 g in popcorn [11], 174 mg/100 g in dehulled corn kernels, and 38 mg/100 g in flour [15]. FA content in corn has been shown at least ten times higher than other cereals [16]. In Fig. 3.4, FA contents were compared within the varieties of white, yellow, red, blue, and high-carotenoid corns.

Extensive studies have demonstrated health benefits of FA such as antioxidants as lipid peroxidation inhibitors [17–19], anticarcinogens [20–23], prevention of cardiovascular diseases [24, 25], antidiabetic agents [26, 27], antimicrobial activity [28, 29], and anti-inflammation [30, 31]. The chemical structure of *p*-coumaric acid is shown in Fig. 3.3b. Main health benefits of *p*-coumaric acid include antioxidant, antimicrobial, anti-inflammatory, and anticancer effects [32–35].

Anthocyanins are the primary pigments found in colored grains, such as black, blue, and purple corns. They are a group of reddish to purple water-soluble charged pigment compounds belonged to flavonoids [36]. The typical chemical structure of anthocyanin is shown in Fig. 3.5. Depending on specific attached R groups such as –H, –OH, and $–OCH_3$, anthocyanins are further divided into six common anthocyanidins, including pelargonidin-3-glucoside, cyanidin-3-glucoside, peonidin-3-glucoside, delphinidin-3-glucoside, petunidin-3-glucoside, and malvidin-3-glucoside.

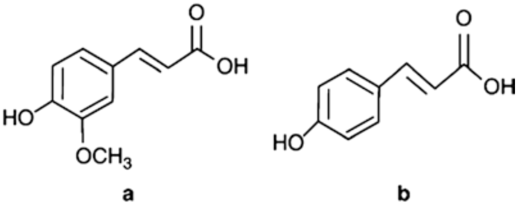


Fig. 3.3 Chemical structures of ferulic acid (**a**) and *p*-coumaric acid (**b**)

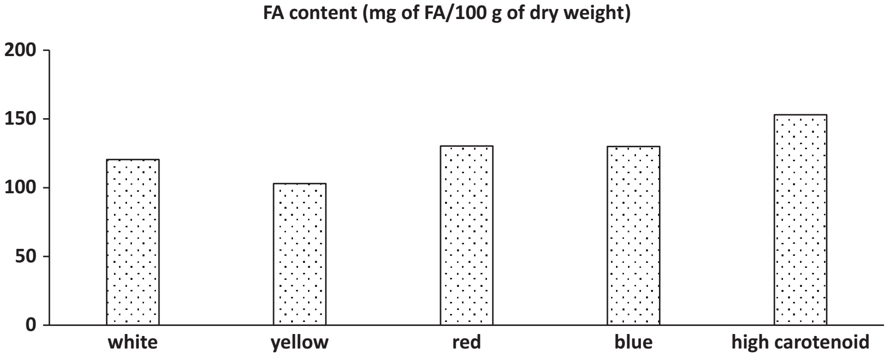
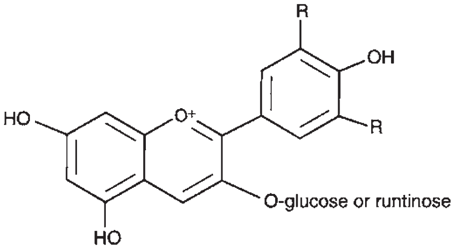


Fig. 3.4 Comparison of ferulic acid contents within the varieties of white, yellow, red, blue, and high-carotenoid corns. (Adapted from: Parra et al. [115])

Fig. 3.5 Chemical structure of anthocyanin. R groups can be attached with –H, –OH, $-OCH_3$



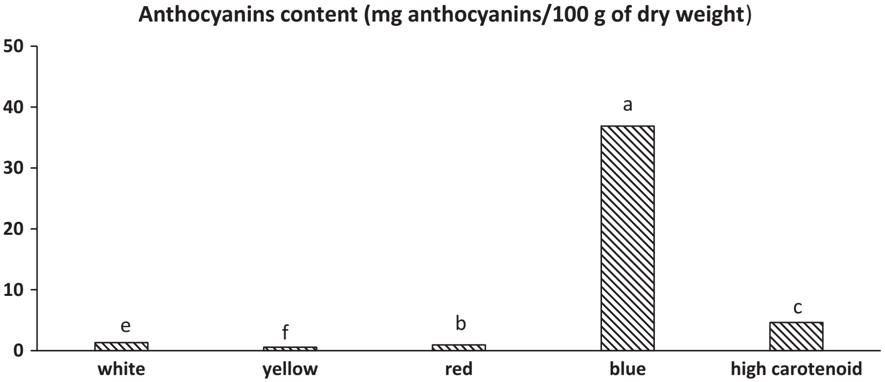


Fig. 3.6 Comparisons of anthocyanin contents within the varieties of white, yellow, red, blue, and high-carotenoid corns. (Adapted from: Parra et al. [115])

Anthocyanin derivatives have been reported to be distributed in corn pericarps [37, 38]. Colorful corns such as red, blue, and purple corns have higher amount of anthocyanins than white and yellow corns (Fig. 3.6). For example, an average of 0.43 g/kg of anthocyanin has been reported in blue corn [39]. Among different colored cereal grains, corn has the second highest anthocyanin content after rice but more than wheat or barley [36]. It has been reported that anthocyanins are effective at lowering risk of chronic diseases due to their antioxidant [40, 41], anticancer [42–45], antidiabetic [46–48], and antihypertensive functions [49].

3.2.2 Carotenoids

Carotenoids are naturally yellow, orange, and red pigments which are fat-soluble and present in plants, algae, and photosynthetic bacteria [50]. So far, more than 600 carotenoids have been identified. Carotenoids are chemically constituted of 40 units of isoprene. The carotenoids can be further classified into two groups, carotenes which lack oxygen functions (e.g., α-carotene, β-carotene) and xanthophylls which contain more than one oxygen atom (e.g., lutein, zeaxanthin) [51]. Xanthophylls are generally more polar than carotenes due to the presence of hydroxyl group. α-Carotene, β-carotene, and β-cryptoxanthin are typical representatives of carotenes, as shown in Fig. 3.7. They have provitamin A activity to metabolize to vitamin A in the human body, and β-carotene has high provitamin A activity as α-carotene and β-cryptoxanthin due to the symmetric structures. However, xanthophylls cannot metabolize to vitamin A because they contain oxygen.

Corn contains diverse carotenoids such as lutein, zeaxanthin, β-cryptoxanthin, α-carotene, and β-carotene. The predominant carotenoids found in corns are lutein and zeaxanthin [52, 53]. Yellow corn contains relatively high carotenoid content, ranging from 11 to 20 μg/g [54]. Another study reported that carotene was approximately 22 μg/g in corn [55]. Xanthophylls in corn were found to be 22.07 μg/g, consisting of 15 μg lutein and 5.7 μg zeaxanthin [56]. Carotenoid content was compared among the varieties of white, yellow, red, blue, and high-carotenoid corns and presented in Fig. 3.8.

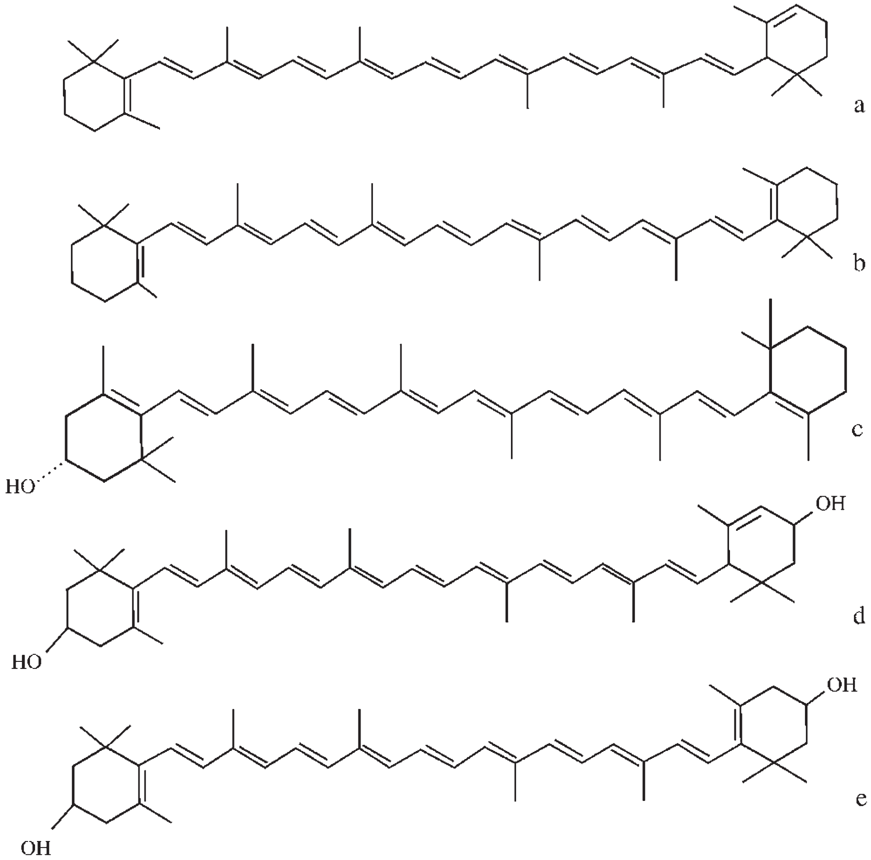


Fig. 3.7 Chemical structures of α-carotene (**a**), β-carotene (**b**), β-cryptoxanthin (**c**), lutein (**d**), and zeaxanthin (**e**)

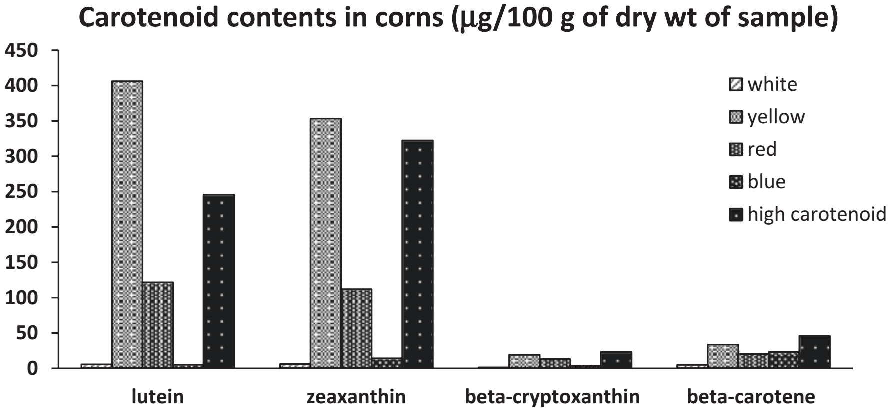


Fig. 3.8 Comparisons of carotenoid contents within the varieties of white, yellow, red, blue, and high-carotenoid corns. (Adapted from: Parra et al. [115])

Epidemiological studies suggest that a diet rich in carotenoids is associated with a variety of health benefits, such as reduced risk of multiple chronic diseases, including diabetes [57, 58], cardiovascular diseases [59, 60], cancer [61–63], and anti-inflammatory conditions [64]. Lutein and zeaxanthin absorb damaging blue light in macular region of the retina, therefore protecting vision and resulting in good eye health [65]. Besides, carotenoids have been reported to help improve visual performance, sleep quality, and adverse physical symptoms [66]. However, a diet rich in high concentration of β-carotene is not recommended for smokers due to potential induction of lung cancer [67, 68]. Sun and Yao [68] purified lutein and zeaxanthin from corn protein residues and investigated their antitumor effects [68]. They found that the hydroxyl groups were responsible for antitumor activity of lutein and zeaxanthin. In another study, lutein exhibited inhibitory actions during promotion but not initiation of hepatocarcinogenesis, which can be classified as a suppressing agent for liver cancer chemoprevention [64].

Corn contains large quantities of carotenoid pigments, which can be used as dietary supplements or as food additives. Many previous studies have focused on the extraction of carotenoids, especially lutein and zeaxanthin, from corn or corn by-products [69, 70]. Ishida and Chapman [71] found that ethyl lactate is a good replacement of ethyl acetate to extract lutein and β-carotene from corn, with the advantage of bio-origin and low flammability [71]. Some carotenoids bind to the protein in corn endosperm, which could limit its extraction and recovery. Ye et al. [70] reported that ultrasound assistance significantly improved the extraction efficiency of carotenoids from corn meal using ethanol [70]. With the pretreatment of corn gluten meal using a protease (e.g., Neutrase), the yields of crude lutein, crude zeaxanthin, and total carotenoids were increased from 74.1, 77.1, and 393.6 to 113.5, 140.1, and 599.1 μg/g, respectively [72].

3.2.3 Alkaloids

Alkaloids have potent pharmacological effects, such as analgesic, antimalarial, and antispasmodic, and facilitates the treatment of hypertension and mental disorders, and have antitumor results [73, 74]. Some alkaloids might be toxic, but they have been widely applied in pharmaceutical areas as medication. Alkaloids are naturally occurring water-soluble compounds containing nitrogen atoms with a positive charge. There is a blurry boundary of nitrogen-containing compounds and alkaloids. Diverse chemical structures may belong to alkaloid groups; however, there hasn't been consistent classification. Alkaloids are primarily found in fungi and plants, but some synthetic compounds of similar structure are also termed alkaloids. Little research is available about alkaloids in corn grains. However, alkaloids have been found in corn husk [75], corn silk [76], corn hair [77], and corn root and shoot extracts [78].

3.2.4 Proteins and Peptides

Seventy-five percent of corn protein is present in the endosperm [79]. The endosperm consists of zein (40%), glutelin (30%), and some amounts of globulins and albumins [80]. Zein is the primary and mostly studied corn protein. It belongs to the prolamine class and is soluble in aqueous alcohol solutions, urea, and high alkali solutions. Zein is rich in glutamic acid (26%), leucine (20%), proline (10%), and alanine (10%) [79]. However, it is deficient in basic and acidic amino acids, especially lysine and tryptophan. The primary fractions of zein include α-zein, β-zein, and γ-zein according to its sequence homology [81]. These fractions can be separated based on their differences in solubility in alcohol solutions [82]. The characteristics of zein subgroups are listed in Table 3.1.

Bioactive proteins and peptides are gaining popularity as nutraceuticals for potential health promotion and disease prevention. Many food proteins, including corn, contain bioactive peptide sequences and domains. When proteins are in their native state, bioactive peptide domains and functional side groups from some key amino acids may be buried within the protein's hydrophobic core with weak bioactivities. However, these bioactive peptide fragments may be exposed and released during in vivo gastrointestinal digestions, in vitro enzymatic hydrolysis, microbial fermentation, chemical hydrolysis, and other food processing techniques. Various bioactivities have been reported in corn protein hydrolysates, such as anti-

Table 3.1 Zein composition, solubility, and molecular weight

	Soluble in	Percentage	Molecular weight
α-Zein	95% ethanol	75–85%	21–25 kDa
β-Zein	60%, 95% ethanol	10–15%	17–18 kDa
γ-Zein	0–80% 2-propanol	5–10%	27 kDa

Source: Pomes [83], Esen [82]

oxidants [84, 85], antidiabetes [86], and anticancer [87, 88]. Antioxidant activity in corn peptides is related to the presence of amino acids such as leucine, proline, and alanine with radical scavenging activities [89]. Corn peptides have been shown to induce apoptotic activity of liver cancer cells through in vitro study [46]. Corn peptide such as Ala-Tyr sequence processed from wet milling has shown antihypertensive activity in hypertensive rats [90].

3.2.5 Resistant Starch

Resistant starch (RS) is defined as starch which is resistant to digestion in the small intestine but passes into the large intestine and produces short fatty acid chains. Because RS reaches the large intestine and alters microbial population and aids in fermentation, RS is considered a healthy dietary fiber. RS is primarily present in high-amylose starch. Corn endosperm has been reported to contain 39.4 mg RS/100 g [91]. RS can be divided into five types including RS 1 present in food matrix; RS 2 present in potato, legumes, bananas, and corn; RS 3 present in retrograded amylose starch in cooked food stuffs such as potato and cornflakes; RS 4 present in diverse structures but not found in nature; and RS 5 in amylose-lipid complex starches [91, 92]. The amount of RS could be affected in food processing by a variety of factors, such as moisture, temperature, heating, cooling, drying, and storing [93].

Previously, most research work has been concentrated on studying RS 3 due to its high thermal stability and health benefits [94–96]. Starch is one of the primary components in food diets. Starch is gelatinized during cooking when absorbing water, resulting in an increase of glycemic index (GI). GI value is measured by the postprandial glucose in the blood after carbohydrate consumption. However, retrograded starch has high thermal stability and therefore retains stable RS 3 during heat processing [95]. Besides, resistant starch is not digested by enzymes in the colon. RS therefore results in a low GI value, thus is helpful in preventing obesity, diabetes, and cardiovascular diseases (CVD) [97]. Results reported by Murphy et al. [92] suggested that RS helped weight control due to lower calorie intake, therefore reducing the risk of obesity. Other studies demonstrated health benefits of RS. For example, resistant starch could improve glycemic response in the colon [98]; promote lipid oxidation and metabolism and impact cholesterol levels [99], reducing the risk of cecal cancer [91]; and increase mineral absorption [100].

3.2.6 Vitamins and Minerals

Corn is a good source of micronutrients such as vitamins and minerals. Both lipid-soluble (vitamin A, vitamin E, and vitamin K) and water-soluble vitamins (vitamin B) are present in corn. Carotenoid content in corn is relatively high relative to other

Table 3.2 Vitamin contents in yellow corns

	Nutrient content/100 g							
Corn kernel	B_1 (mg)	B_2 (mg)	B_3 (mg)	B_5 (mg)	B_6 (mg)	B_9 (μg)	Vitamin E (mg)	Vitamin K (μg)
Dent, dry	0.39	0.20	3.63	0.42	0.62	19	0.49	0.3
Sweet, raw	0.16	0.06	1.77	0.72	0.09	42	0.07	0.3

Source: USDA Food Composition Databases

cereals. As mentioned previously, α-carotene, β-carotene, and β-cryptoxanthin are carotenoids of provitamin A. Otten et al. [101] demonstrated retinol activity equivalent (RAE) established at 12 μg β-carotene, 24 μg α-carotene, and 24 μg β-cryptoxanthin. The recommended daily allowance (RDA) of vitamin A is 700 μg RAE and 900 μg RAE, for men and women, respectively. However, it has been reported that the loss of carotenoid content during storage is dependent on environmental conditions such as temperature, light, humidity, and genotype factors such as original carotenoid content [102].

Vitamin E is a lipid-soluble antioxidant composed of four tocopherols (α, β, τ, γ) and four tocotrienols (α-T3, β-T3, τ-T3, γ-T3). The amount of vitamin E in corn is determined by genotypes but varies depending on environmental factors. α- and γ-Tocopherols have been reported as the predominant forms in corn [103]. The RDA for vitamin E for both adult men and women is 15 mg/d [101]. Vitamin K is present in corn oil and accounted for 2.9 μg/100 g [104]. The RDA for vitamin K_1 for man and woman is 120 μg/d and 90 μg/d [101].

Corn contains water-soluble B vitamins such as thiamin (B_1), riboflavin (B_2), niacin (B_3), pantothenic acid (B_5), pyridoxine (B_6), biotin (B_7), and folate (B_9), primarily present in the endosperm and germ. Overall, processing will reduce water-soluble vitamin B contents in corn [105]. A summary of vitamins in dent and sweet corns is shown in Table 3.2.

Various minerals are present in corn, such as calcium, copper, iron, magnesium, manganese, phosphorus, potassium, selenium, and sodium (Table 3.3). However, the content of most minerals is low. Processing such as nixtamalization has been reported to reduce the mineral content in corn including iron, manganese, phosphorus, and selenium but slightly increased other minerals such as calcium, magnesium, and sodium [105].

3.3 Molecular Mechanism of Bioactives in Corn

The overproduction of superoxide and reactive oxygen species (ROS) by mitochondrial electron transport chain triggers oxidative stress and results in an imbalance of oxidants and antioxidants in serums. Uncontrolled free radicals cause cell damage, lipid peroxidation, and DNA strand breaking, which further result in aging, cancer, diabetes, etc. [106]. Antioxidants from diet can react with oxygen species and

Table 3.3 Mineral contents in yellow corns

Corn kernel	Nutrient content/100 g									
	Calcium (mg)	Copper (mg)	Iron (mg)	Magnesium (mg)	Manganese (mg)	Phosphorus (mg)	Potassium (mg)	Selenium (mg)	Sodium (mg)	Zinc (mg)
Dent, dry	7	0.314	2.71	127	0.485	210	287	15.5	35	2.21
Sweet, raw	2	0.054	0.52	37	0.163	89	270	10.6	15	0.46

Source: USDA Food Composition Databases

scavenge these free radicals, thus preventing the oxidative damage and helping fight chronic diseases. As mentioned above, bioactives such as peptides, phenolic acids, anthocyanin, carotenoids, and vitamins can all function as antioxidants to help prevent aging problems caused by ROS.

Extensive studies have demonstrated the anticancer properties of phenolic compounds. Janicke et al. [20] found that the addition of ferulic acid and dietary fiber delayed cell cycle proliferation of Caco-2 cell lines. Ferulic acid especially affected the genes on S phase checkpoint, thus preventing colon cancer. In an in vivo study, anthocyanins have been reported to reduce blood pressure and heart rate of hypertensive rats, thus showing antihypertensive effect [49].

It has been demonstrated that food intake of dietary fiber is associated with controlling body weight and preventing obesity [107]. Compared with starch-rich carbohydrate diet, dietary fiber is a low-calorie but large-volume diet which helps control body weight and even lose body weight. Besides, dietary fiber can ferment in the colon, produce short-chain fatty acids which affect lipid levels, and help keep satiety [107, 108]. Dietary fiber is proposed to form a viscous solution in the stomach, which delays gastric emptying and inhibits absorption of carbohydrates in the small intestine, thus helping to regulate blood glucose [109]. For example, resistant starch (RS) can lower glycemic index (GI). However, resistant starch added in bread did not impact the glucose and insulin levels significantly [110]. Slavin [107] stated that the effect of dietary fiber on affecting glucose and insulin levels is significant within individuals who have diabetes. For healthy individuals, insulin can secret rapidly in serum to reduce the glucose levels after food intake which makes it hard to study dietary fiber effect. Dietary fiber enhances colonic microbe colonies in the gut. These dietary fibers are considered as “prebiotics” [111].

Although antioxidant, anti-inflammation, anticancer, and antihypertensive properties of phenolic acids, anthocyanins, and peptides have been reported extensively, knowledge of impact of phenolic compounds, vitamins, and peptides extracted from corn on preventing chronic diseases is limited. Similarly, the effect of individual dietary fiber such as resistant starch on weight management, gastric emptying, and gut health has been reported; however, little is known about the impact of bioactives in corn.

3.4 Effects of Processing on Bioactive Availability

Processing before consumption is necessary for food products, primarily for the purpose of reducing foodborne diseases, increasing food palatability, and enhancing food digestion. However, sometimes processing plays a negative role in nutrition due to loss of nutrients. Meanwhile, some processing may negatively change the texture and sensory attributes.

There are two types of corn milling, dry milling and wet milling, and the objectives of these two milling methods are different. The primary purpose of dry milling is to remove the bran or pericarp to release and produce endosperm which is also known as grit. The endosperm or the grit will be milled into powder and further utilized into food applications such as tortillas and extruded and baked food stuffs. In reality, the separation of germ, endosperm, and bran is not complete because a small amount of endosperm is still attached to the germ and bran; thus, oil concentration in the germ is reduced [112]. Majority of phenolic compounds are present in corn pericarps or brans in bound form. Carotenoids such as lutein and zeaxanthin content in white corn are not affected by drying and milling [113]. The primary purpose of wet milling is to recover and purify starches, maintain the purity up to 99%, and separate from fiber. With the help of steeping in a solution of sulfurous and lactic acid, corn bran is loosened and removed easily. Meanwhile, protein is partially denatured, therefore benefiting starch and protein separation.

Nixtamalization is a traditionally well-known cooking method to make tortilla including the processes of lime-cooking and steeping. With the help of steeping, the corn pericarp will be loosened from the kernel. Starches will be gelatinized via lime-cooking [114]. Nixtamalization reduced the total phenolic compound contents especially the bound forms in cereal grains. For example, lime-cooking has been reported to decrease the lutein content in different varieties of corn such as yellow, red, and high-carotenoid corns [115]. Ferulic acid is primarily present in corn bran or pericarp and associated with cell walls. However, lime-cooking results in the loss of ferulic acid. Maya-Cortés et al. [116] demonstrated that lime-cook affected anthocyanin content in corn and increase in lime-cook time resulted in increasing loss of anthocyanins.

Extrusion processing is a high-efficiency, low-cost, and versatile technique by applying high temperature and pressure and shear forces. Extensive previous studies focused on the effect of extrusion processing on starch gelatinization, protein denaturation and digestibility, molecular mechanisms of starch and protein, water absorption and water solubility, and texture characteristics of extrudates. Limited research has been conducted on the impact of extrusion processing on phytochemical contents of extrudates. Although both free and bound forms of phenolic acids are present in corn, primarily bound form of phenolic acids is found in extrudates [117]. The effect of extrusion on phytochemical availability is controversial. Primarily, extrusion processing has been reported to be associated with reduction of phytochemicals [118, 119]. However, on the other side, a few studies showed that extrusion processing increased certain types of phenolic compounds [120, 121].

3.5 Possible Approach to Enhance Health Benefit of Corn Bioactives

The content of micronutrients such as vitamin A and minerals (e.g., zinc, iron) is low in corn. Thus, consumption of corn as a primary diet staple cannot help people live a healthy life, especially for people who live in low-income rural and urban areas. For the purpose of developing micronutrient-enriched corn, fortification is necessary for increasing micronutrient content and bioavailability.

Biofortification is an effective strategy aimed to achieve micronutrient-enriched corn crops via plant breeding. For example, HarvestPlus is a global research institute working on biofortification via corn breeding to generate micronutrient-enriched corn to help reduce the micronutrient malnutrition [122]. Fortification of vitamin E such as α-tocopherol in corn was successfully achieved via breeding [103]. Besides, with the help of genetic engineering, γ-tocopherol methyltransferase gene can convert γ-tocopherol to α-tocopherol, thus enhancing α-tocopherol levels in corn [103]. Gene transfer in corn increased the content of β-carotene, ascorbate, and folate [123]. Genetic modifications could also help decrease mycotoxins in corn such as fumonisin and aflatoxin [124].

Corn flour was fortified with micronutrient powders such as iron to improve micronutrient content for the purpose of reducing iron deficiency in consumers [125]. Corn flour was fortified with iron, zinc, folic acid, vitamin A, and vitamin B_{12} with different levels in many countries such as Brazil, Mexico, and South Africa [126].

3.6 Conclusions

Corn is an economic crop and serves as a staple and primary diet for large populations in many areas. Via dry and wet millings, both corn kernel and components such as starch, protein, and fiber are separated for further corn-based food applications. Starch accounts for the largest constituent in corn, followed by protein, fiber, fat, and micronutrients such as vitamins and minerals. Zein protein is the major storage protein; however, zein is deficient in basic and acidic amino acids, especially lysine and tryptophan. Therefore, corn is not a good source of essential amino acids. In addition to providing macronutrients and micronutrients, corn is reported to contain non-nutrient phytochemicals such as phenolic acids, anthocyanins, and carotenoids. The amount of specific phytochemicals in corn varies depending on genotypes and environmental factors. Overall, colorful corn such as blue and purple corns has more anthocyanins than yellow and white corn. Phenolic acids, anthocyanins, and carotenoids have shown many health benefits associated with lowering the risk of chronic diseases such as having anticancer, antihypertension, and anti-inflammation effects and preventing obesity. Dietary fiber in corn can also bring many health benefits such as weight control and gut health. However, the amount and bioavailability of micronutrients and non-nutrient phytochemicals in corn are very low. Heat processing will result in the loss of vitamins and phytochemicals due to their low heat stability. Hence, approaches such as fortification either in breeding or food processing have been applied for the purpose of increasing certain types of nutrient in food.

Although individual components in corn have been investigated, knowledge of the effect of micronutrients and non-nutrient phytochemicals extracted from corn on anti-inflammation, anticancer, and other aging-related chronic disease is still not well known. Little is understood about the health benefits of zein protein peptides, either. In addition to researches of corn kernel, several studies demonstrated that corn husk, corn hair, and corn silk contain alkaloids and other bioactives, which could be useful in medication [77, 127, 128]. Therefore, more research needs to be conducted for the evaluation of bioactives and their nutraceutical functions from various corn resources.

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Chapter 4
Barley

Lingxiao Gong

4.1 Introduction

Barley (*Hordeum vulgare* L.) is the fourth most valuable cereal crop in the world exceeded only by rice, wheat, and corn [1]. Specifically, barley is the most widely adapted cereal grain species with production in a variety of extreme eco-agricultural areas, including regions with high latitudes, dry temperature, or severe temperature fluctuations such as Himalayan nations, Ethiopia, Tibet, and Morocco [2]. Yet 98% of barley crops is primarily used as animal feed and malting, while only 2% is used for direct food consumption.

However, barley has won the renewed interest for consumption as a human food source due to its protective effects against chronic diseases. For example, the Food and Drug Administration of the USA has approved a claim for whole grain barley (dehulled or hull-less barley, the latter also referred to as “naked” barley) and barley-containing products, which provide at least 0.75 g of soluble fiber per serving, for reducing plasma cholesterol levels and reducing the risk of heart disease [3]. In addition to soluble fibers, barley is also abundant with bioactive compounds such as vitamins, minerals, and phytochemicals including phenolic acids, flavonoids, lignans, tocols, phytosterols, and folates [4]. These bioactive components are associated with several bioactive effects, such as antioxidant, anti-inflammatory, antihyperlipidemic, and antihypertensive or antiproliferative effects. These bio activities are directly linked to the modification of etiology of chronic diseases.

There is a need to update our knowledge about barley composition and its health bioactives, taking into account the new technology developed to enhance the health benefits of barley bioactives over the last few years.

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4.2 Bioactives in Barley

Barley is one of the most genetically diverse cereal grains, consisting of either spring or winter types, two-row or six-row, colored or uncolored, hulled or hull-less, and malting or feed varieties.

The composition common to all of the whole barley varieties is shown in Table 4.1. The following discussion focuses on barley components that have been specifically targeted for their healthy properties. Dietary fiber is a significant contributor to the health benefits of barley. The dietary fiber content in barley ranges from 11 to 34%, depending on genetic and environmental factors [6]. What is special about the composition of barley with respect to other cereals is their high content of (1→3)(1→4)-*β*-D-glucan (β-glucan). The β-glucan in barley usually ranges between 2 and 10%, but some cultivars have been reported to have up to 20% β-glucan [14]. The content of arabinoxylans in barley also depends on genetic and environmental factors but appears to be less variable than that of β-glucans [7]. Two-rowed barley cultivars generally contain slightly lower levels of arabinoxylans than six-rowed cultivars.

Phytochemicals including phenolic acids, flavonoids, lignans, vitamins, sterols, and folates are other potential important substances that, although in a lesser amounts, could contribute to the beneficial effects of barley. Phytochemicals are thought to be unevenly distributed in barley with more concentration around the outer layer than around the endosperm.

Table 4.1 Composition of whole barley

Constituent	Range of concentration	References
	g/100 g	
Starch	60–75	[5]
Protein	10–20	[4]
Lipid	2–3	
Ash	~2.5	
Total fiber	11–34	[6–8]
Soluble fiber	3–20	
β-Glucan	2–10	[9]
Arabinoxylans	3.8–6.05	[9]
	μg/100 g	
Total phenolic acids	604–1346	[10, 11]
Free form	4.6–23	
Conjugated form	86–198	
Bound form	133–523	
Flavonoids	62–300.8	[12]
	μg/g	
Tocols	40–151.1	[13]
Phytosterols	820–1153	[9]

Most phenolic acids are found in bound insoluble form, followed by conjugated and free forms, respectively. Ferulic acid (149–413 μg/g) is the primary and most abundant phenolic acid, which accounts for approximately 68% of total phenolic acids in barley. *p*-Coumaric acid (15–374 μg/g) is the second most abundant phenolic acid in barley. Additionally, smaller concentrations of p-hydroxybenzoic acid, vanillic acid, syringic acid, 2,4-dihydroxybenzoic acid, sinapic acid, and *o*-coumaric acid are also present in barley [4].

In barley, color has been most commonly used as a quantity indicator of flavonoids, which is generally proportional to the degree of color depth. Blue and purple barley grains are reported to possess the most flavonoid content among barley varieties [15]. The major types of flavonoids found in barleys are flavanols, anthocyanins, and proanthocyanidins. Flavanols and anthocyanins exist mostly as glycoside derivatives, including cyanidin-3-glucoside, penidin-3-glucoside, and delphinidin-3-glucoside.

Different from other bioactives, 95% of tocols are present in the endosperm, but 63% and 10% of tocols are present in the hull and germ, respectively [16].

Barley could be one of the riches sources of tocotrienol among cereal grains. Among the tocol isomers, α-tocotrienol (~47.7%) is the most abundant, followed by α-tocopherol (17.7–33.9%), γ-tocotrienol (10.4–20.2%), γ-tocopherol (1.9–9.2%), β-tocotrienol (2.9–7.8%), and δ-tocotrienol (2.7–6.7%) [13].

Barley contains moderate levels of phytosterol compared to other cereals. Sitosterol, campesterol, brassicasterol, stigmasterol, δ5-avenasterol, stigmastanol, stigmastadienol, and δ7-avenasterol are found in barley, among which sitosterol (53–61%) and campesterol (14–20%) are the most two abundant forms [17].

Apart from the above four classes of phytochemicals, barley is also a source of folate and lignans, providing a significant contribution to dietary intake. However, there is little information in the literature about folate and lignans. The total folate content in barley ranges from 518 to 789 ng/g, which is higher than wheat (323–774 ng/g) and oat (495–604 ng/g) and close to that of rye (598–664 ng/g). The major lignans in barley are pinoresinol, medioresinol, syringaresinol, lariciresinol, cyclolariciresinol, secoisolariciresinol, secoisolariciresinol-sesquilignan, matairesinol, oxomatairesinol, and 7-hydroxymatairesinol [18].

4.3 Molecular Mechanism of Bioactives in Barley

Emerging research in animal and cell culture models provides evidence on the effects of whole barley in ameliorating obesity, hyperglycemia, hyperlipidemia, hypertension, type 2 diabetes, and oxidative stress, the well-known risk factors for cardiovascular disease [9]. Despite the evidence from *in vitro* and *in vivo* experimental models demonstrating the strong protective effects of whole barley and its bioactives, the underlying mechanisms for these effects are largely not understood. In this section we will discuss the findings of barley's protective mechanisms.

4.3.1 Antioxidant Properties

The antioxidative activity investigated in 80% methanolic extracts originating from barley whole grain had a positive correlation coefficient value of 0.96 [19]. Barley flavonoids, phenolic acids, and tocopherol (α, β, γ) are the main phytochemicals that show high antioxidant activities [4].

A recent study of Shen et al. suggested a novel mechanism by which barley activated rat defense pathways against oxidative stress that involved the polyphenol. They reported that a 300 mg/kg administration of polyphenol extract from black highland barley could significantly increase the relative gene expression levels of the transcription factor nuclear factor erythroid-2 related factor 2 (Nrf2), glutathione peroxidase (Gpx), superoxide dismutase (SOD), and hemeoxygenase 1 (HO-1) in rats' livers [20]. Therefore, the phenolic compounds are crucial for the antioxidant properties of barley involved in the activation of the Nrf2 pathway.

4.3.2 Antihyperglycemic

Barleys contain bioactives with significant potential antihyperglycemic effects by inhibiting the activity of key enzymes including α-amylase and α-glucosidase which can regulate carbohydrate metabolism. Cold water and ethanol (12%) extracts of 13 barley cultivars have moderate to high *in vitro* α-amylase inhibitory activity [21]. In terms of α-glucosidase, only black barley has moderate levels of α-glucosidase inhibitory activity. Additionally, the study of Qian et al. [22] demonstrated that barley polysaccharide exhibited a noncompetitive type of inhibition on α-glucosidase *in vitro* [22].

4.3.3 Antihyperlipidemia

Xia et al. demonstrated that whole highland hull-less barley may regulate rat's lipid metabolism by downregulating expression of heat shock protein 60 (HSP60) and phosphatidylethanolamine binding protein 1 (PEBP1) and upregulating the expression of enoyl-coenzyme A hydratase (ECH) and peroxiredoxin 6 (PRDX6) [23]. The activation of the AMP-activated protein kinase (AMPK) could be another effective strategy for reducing hepatic lipid steatosis. AMPK is a cellular sensor of energy metabolism and a regulator for cholesterol metabolism. Its activation may stimulate oxidation of fuel molecules, including stored fats, and suppresses anabolic metabolism, such as lipid and protein syntheses [24]. Lee et al. reported that barley sprout extract, containing high levels of polyphenols and flavonoids, exerted hypocholesterolemic and hypoglycemic effects by regulating AMPK activity and its signaling pathways [25]. Moreover, barley sprout extracts activate MTP, which reduces intrahepatic lipid accumulation by transferring intracellular triglycerides to secreted very-low-density lipoprotein (VLDL) particle [26].

Another mechanism behind the lowered blood cholesterol levels associated with barley is their ability to change secondary bile acid profiles. Firstly, dietary fiber in barley has the ability to bind bile acids and liberate in the colon. In the colon, the primary bile acids are dehydroxylated and transformed by the gut microbiota to the secondary bile acids, including lithocholic, deoxycholic, and hyodexycholic acids which are directly associated with host health. Both the polyphenols and the dietary fibers in the barley could lead to specific secondary bile acid profiles by regulating the microbiota composition [27].

4.3.4 Ameliorating Obesity

Barley possesses satiating properties when fed intact. It was reported that healthy volunteers are significantly less hungry before lunch after consuming barley – but not wheat- and rice-containing foods [28]. The less in satiety was also associated with a significant reduction of energy intake of the subjects. The larger satiating effect of barley-based food may ascribe to the satiating potential of soluble dietary fibers. The satiating properties of dietary fibers have been explained by mechanisms that are related to appetite regulation such as taste, gastric emptying, absorption, and fermentation [29]. For example, whole barley is known for their high fiber as well as β-glucan content, which has oft proved to prevent the development of insulin resistance, dyslipidemia, and obesity [30]. Its health benefits are associated with their fermentability and ability to form highly viscous solutions in the gut. A higher viscosity meal delays gastric emptying and reduced enzymatic activity and mucosal absorption to slow digestion and absorption of glucose, leading to early satiety sensations [31]. Additionally, the fermentation of dietary fibers in the cecum and colon produces short-chain fatty acids which may increase satiety hormone peptides YY (PYY) and glucagon-like peptide-1 (GLP-1). Both of these hormones augment fat oxidation (lower respiratory quotient), elevate energy expenditure, and inhibit body fat accretion [32]. The study of Gao et al. (2015) also found that barley reduced intestinal fat deposition, decreased insulin resistance, and improved health span or life span in the *Caenorhabditis elegans* model system by mediated *sir-2.1*, *daf-16*, and *daf-16/daf-2* pathway [33].

Besides dietary fibers, other bioactive compounds in barley also attribute to the prevention of obesity. Seo et al. highlighted that coumaric acid and ferulic acid were the primary anti-obesity mediators in the water extracts of hulled barley which could prevent lipid accumulation *in vitro* and obesity in HFD-induced obese mice and estrogen-deficient obese rats. The presence of β-glucan in barley extract was less likely to be responsible for the lipid accumulating actions [34].

4.3.5 Modulation of Gut Microbiota Community

Recently, the composition and richness of the gut microbiota are linked to several metabolic diseases. Barley β-glucan has been investigated as a potential prebiotic, selectively promoting the growth of beneficial intestinal microorganisms such as *Lactobacili* and *Bifidobacteria* according to *in vitro* and *in vivo* studies [35]. For example, daily intake of barley β-glucan (0.75 g/day) may induce an increase of *Bifidobacteria* in older healthy volunteers [36]. Our recent research found that whole Tibetan hull-less barley exhibited stronger effect on promoting growth of *Bifidobacterium* than refined barley *in vitro* [37]. Moreover, the intake of barley and bioactives provides substrates to be metabolized into functional microbiota metabolites, including short-chain fatty acids and phenolic metabolites, which may help improve host physiological status [32].

4.4 Effects of Processing on Availability

Traditional roasting process resulted in marked increases both in phenolic content and antioxidant capacity of barleys [38, 39]. Boiling barley at atmospheric pressure resulted in a significant increase in total phenolic content and antioxidant capacity [38]. The increase of phenolic compounds might be attributed to the breakdown of cellular constituents which could release bound phenolics.

Extrusion cooking could reduce both total phenolic content and total flavonoid content depending on the extrusion processing parameters [40]. However, individual phenolic compounds were influenced differently by extrusion cooking due to their different structures. It had been found that free and soluble conjugated forms increased by 200–300% when barley samples were extruded. Among individual phenolic acids, ferulic acid had predominant increases, followed by vanillic, syringic, and *p*-coumaric acid [41]. Moreover, the bioaccessibility of individual bound phenolic acids was increased by 14% after extrusion cooking in growing pigs [42]. Another study of Djurle et al. revealed that extrusion also decreased the content of β-glucan in barleys but increased its extractability [43]. The extrusion parameters affect both soluble β-glucan and insoluble β-glucan content in barley extrudates. For example, extrusion at high moisture content, as in cooking extrusion, increased soluble β-glucan, whereas extrusion at low moisture content, as in collet extrusion, lowered soluble β-glucan [44].

Our recent studies investigated the effects of steam explosion on availability of phenolic compounds in barley bran and whole barley. It was found that the content of total phenolic acids and free phenolic acids including ferulic acid and *p*-coumaric acid in barley bran was 9-fold, 59-fold, and 47.6-fold higher than untreated one, respectively [45]. In whole barley extracts, steam explosion had increased free and soluble-conjugated ferulic acids by 119.8% and 193.0% as compared with those numbers in water cooking samples [46].

Lactic acid bacteria fermentation resulted in maximum increases of free phenolics from 2.55 to 69.91 μg/g dry matter in whole barley. The major contribution was from liberated ferulic acid which accounted for 81.9% of the increase in whole barley. Higher amounts of bound phenolic acids were detected after lactic acid bacteria fermentation [46]. Recent study of Pallin also demonstrated that fermentation of barley with *Lactobacillus reuteri* may develop symbiotic products with higher content of bioactive compounds such as γ-aminobutyric acid (GABA), 1,3-propanediol, and histamine [48].

Air classification is a physical separation technique based on the density differences between particles. Gómez-Caravaca et al. used air classification technology to produce functional barley flours enriched with alkylresorcinol, β-glucan, and phenolic compounds [49].

4.5 Possible Approach to Enhance Health Benefits of Barley Bioactives

As is known, amount, molecular weight distribution, structure, and conformation of dietary fiber are important for the physical properties including hydration properties, viscosity, and gelation properties, which are associated with health benefits, such as blood glucose attenuation and serum cholesterol-lowering properties. It has been demonstrated that a reduced molecular weight of the β-glucan gives a reduced cholesterol-lowering effect in humans [50]. Technologies are developed for improving physiological properties of dietary fiber for healthy cereal foods. Ahmad et al. [51] applied germination processing to obtain lower molecular weight and viscosity of β-glucan (144 kDa and 37.33 cp) but higher antioxidant potential as compared to β-glucan obtained from microwave-processed barley and unprocessed barley [51].

It is also known that thermal processing could alter the antioxidant profile and generate more antioxidants such as Maillard browning pigments that contribute in antioxidant activity [52]. For example, the antioxidant properties of barley extrudates increased significantly upon extrusion, highest (36–69%) at 150 °C and 20% feed moisture [40]. Significant increases both in antioxidant capacity and total phenolic compounds content of barley were obtained after roasting two layers of grains or 61.5 g in microwave oven at 600 W power for 8.5 minutes [38, 39]. However, a significant decrease in total phenolic compound content and antioxidant activity (16.8–108.2%) was observed after sand roasting eight barley varieties [38]. Boiling barley at atmospheric pressure resulted in an increase in total phenolic compound content and antioxidant capacity, while red sorghum and finger millet showed a significant reduction in total extractable phenolic compounds [38]. During thermal process, the bound phenolics are released from the breakdown of cellular constituents, but free phenolics are destroyed under high temperature [41]. Thus, the health benefits of barley obtained after thermal processing are dependant on the variety of barley and processing parameters.

Zhou et al. investigated that the tea catechin as an elicitor could increase the levels of phenolic compounds in barley during soaking process, thus their antidiabetic effects via inhibition of rat intestinal α-glucosidase, maltase, and sucrase [53].

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Chapter 5
Rice

Huijuan Zhang

5.1 Introduction

Rice (*Oryza sativa* L.) is counted in the list of one of the main food crops growing in the world. Nowadays the production of rice is increasing as it is being cultivated in more than 100 different countries. The annual production of milled rice is 480 million metric tons in the world [1, 2]. Approximately 50% of the total rice is produced by India and china [1]. Over half of the world population consumed rice as staple food. In Asian countries a higher portion of protein is taken by rice, as millions of people used it as staple food [1].

After harvesting paddy rice is obtained by threshing of the rice grain. It consists of outer husk layer, bran, germ, and endosperm [1]. Brown rice is obtained by passing the paddy rice through the process of milling which removes the outermost husk layer, and white rice is obtained after removing the germ and bran layer.

Rice bran is a main by-product of the rice milling and it is approximately 10% of the total weight of rough rice. Rice bran composition is lipids 15–22%, fiber 7–11.4%, carbohydrates 34.1–52.3%, moisture 8–12%, ash 6.6–9.9%, and 10–16% highly nutritional protein [3, 4].

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5.2 Bioactives in Rice

5.2.1 Proteins

Osborne classified the rice protein in four different proteins on solubility basis. According to the classification, rice contain albumin which is water soluble, globulin protein which is salt soluble, glutelin protein which is alkali/acid soluble, and prolamin which is soluble in alcohol [5]. Storage organelles, called protein bodies (PBs), are the main forms of rice proteins, and type I, also known as PB-I, and type II, which is PB-II, are observed in rice endosperm (Fig. 5.1) [6]. The structure of PB-I is lamellar with spherical shape and it contains high amount of prolamin, whereas PB-II structure is crystalline with irregular shape, which is rich in glutelin [2].

Prolamin has the minimum content of lysine, whereas glutelin and globulin have the maximum lysine content. The highest concentration of threonine and histidine is present in albumin, while the highest content of leucine, isoleucine, and phenylalanine is present in prolamin. Globulin contains the highest amount of sulfur-containing amino acids, i.e., methionine and cysteine, whereas prolamin contains the lowest content of these amino acids (Table 5.1).

Until now, a variety of methods have been utilized to extract proteins from rice.

The main method used for extraction of rice protein is alkaline treatment which is followed by isoelectric precipitation (pH 4–4.5). Compared with the α-amylase degradation, alkaline extraction made rice protein have higher digestibility and bioavailability [7, 8]. Alkaline extraction also has some limitations, such as denaturation and hydrolysis of proteins and toxic compound development like lysinoalanine,

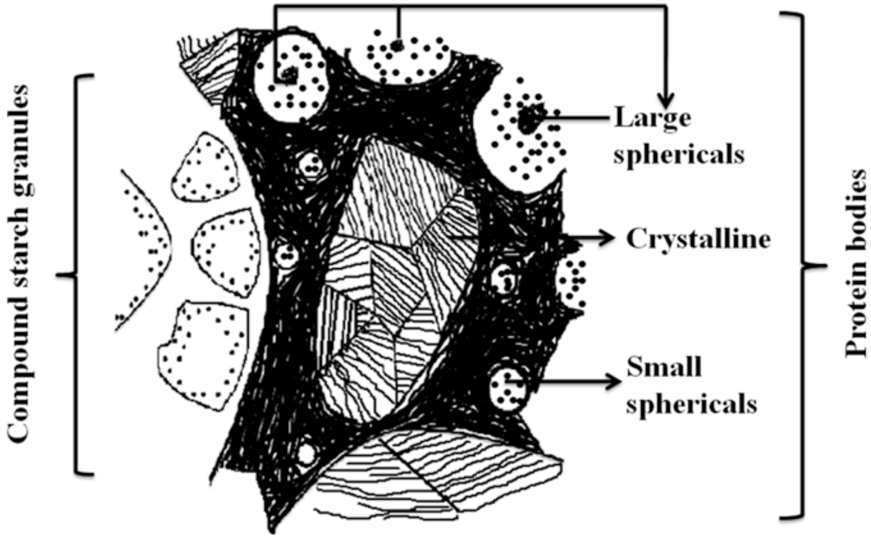


Fig. 5.1 Schematic structure of rice protein bodies and compound starch granule in the endosperm subaleurone layer. (From Coffman and Juliano 1987)

Table 5.1 Amino acid composition (g/16.8 g nitrogen) of rice protein fractions

Amino acid	Albumin	Globulin	Glutelin	Prolamin
Alanine	7.1–8.5	5.6–6.3	5.6–5.9	6.7–7.6
Arginine	7.9–10	7.2–14	9.0–11	6.1–6.9
Aspartic acid	10–11	7.1–14	10–11	8.3–8.7
Cysteine	1.9–2.3	3.3–4.0	1.2–1.8	Trace-0.8
Glutamic acid	13–18	17–19	19–21	23–33
Glycine	6.3–8.4	5.8–6.4	4.3–5.3	3.0–3.7
Histidine	2.9–3.4	1.7–2.7	2.6–2.7	1.3–2.1
Isoleucine	3.5–3.8	2.4–4.1	4.3–4.7	4.6–5.2
Leucine	6.6–8.0	6.6–6.8	7.3–9.3	13–15
Lysine	5.1–6.4	1.9–3.7	2.7–4.5	0.3–1.2
Methionine	1.9–2.1	3.0–5.4	2.0–3.1	0.5–0.9
Phenylalanine	3.7–4.6	3.3–4.8	5.4–6.0	5.8–6.7
Proline	4.5–7.1	3.8–7.5	4.9–6.2	5.0–6.7
Serine	4.2–5.4	5.5–6.5	4.5–6.2	4.2–6.1
Threonine	4.2–5.2	2.5–2.7	2.8–5.1	2.5–2.8
Tryptophan	1.5–1.8	1.4–1.5	1.0–1.6	0.5–2.6
Tyrosine	4.4–5.1	5.5–6.3	5.3–5.5	9.2–9.9
Valine	5.9–7.8	5.4–6.5	6.3–6.9	6.5–7.1

Adapted from Juliano (1985) [3]

and extraction of nonprotein components also increased which results in dark color because of increasing Maillard reactions [9, 10].

The enzymatic method is also another common technique to extract rice protein. Starch is the key component of rice endosperm. Therefore, in rice flour enzymes such as pullulanase, glucoamylase, and α-amylase are often used to separate proteins [11]. Carbohydrate-digesting enzymes, such ascellulase, hemicellulase, pectinase, and xylanase, can hydrolyze high molecular weight cell wall constituents, which have been used to extract rice bran proteins from polysaccharide-based structures [10, 12].

Protein from rice can also be extracted by using proteases, which have the ability to change the physicochemical and structural properties of integral proteins. Alkaline protease, trypsin, bromelain, and papain have all been applied to extract rice proteins [13, 14].

Cell disruption has been done by using physical processes to enhance the protein extraction, which is more economical than other techniques [15]. High-speed blending, freeze-thaw, sonication, micro-fluidization, hydrothermal cooking, colloid milling, subcritical water, and high pressure have all been applied for rice or rice bran protein extraction [2, 15].

5.2.2 Oil

Rice bran oil (RBO) is formed by the germ and is a by-product of milling of *Oryza sativa* seeds. It is pale yellow, odorless, and limpid (at 20 °C) with an acid index of <0.50 [16]. Rice bran constitutes about 10% of rough rice grain and contains 18–22% oil [16]. RBO is very popular in many countries such as India, Japan, Korea, Indonesia, and China. It is used as cooking oil because of the delicate flavor, high smoke point, and good shelf life [17]. RBO is also an excellent source of nutritionally beneficial compounds, such as tocopherols, sterols, and tocotrienols [18]. RBO is also rich in unsaponifiable fraction, containing vitamin E complexes, phytosterols, polyphenols, gamma oryzanol, and squalene [17], which may have hypolipidemic, antidiabetic, and antiatherogenic properties [19]. The typical composition of crude RBO is shown in Table 5.2 and Fig. 5.2. For phytosterols, they include β-sitosterol, campesterol, stigmasterol, squalene, and γ-oryzanol [16]. γ-Oryzanol is a blend of ferulic acid and esters of triterpene alcohols such as 24-methylene cycloartanyl and cycloartenol [20]. RBO and its main components (triterpene alcohols, unsaturated fatty acids, phytosterols, α-tocopherol, and tocotrienols) have been reported to improve the plasma lipid pattern of rabbits, nonhuman primates, rodents, and humans. It has the ability to lower the triglyceride concentration and total plasma cholesterol and also increase the level of high-density lipoprotein cholesterol [16].

5.2.3 Phenolic Compounds

Phenolic acid is another group of antioxidants found in rice bran. Caffeic acid, coumaric acid, catechins, ferulic acid, gallic acid, hydroxybenzoic acid, methoxycinnamic acid, sinapic acid, syringic acid, and vanillic acid are all found in rice bran [21]. In rice, ferulic acid and *p*-coumaric acid are the main phenolic compounds, which are present in dietary fiber as free, soluble conjugate, or insoluble bound form [22]. Chemical structures of phenolic compounds in rice are shown in

Table 5.2 Crude rice bran oil composition

Lipid type	Percent (%)
Triacylglycerol	81–84
Diacylglycerols	2–3
Monoacylglycerols	1–2
Free fatty acids	2–6
Waxs	3–4
Glycolipids	0.8
Phospholipids	1–2
Unsaponifiable lipids	4

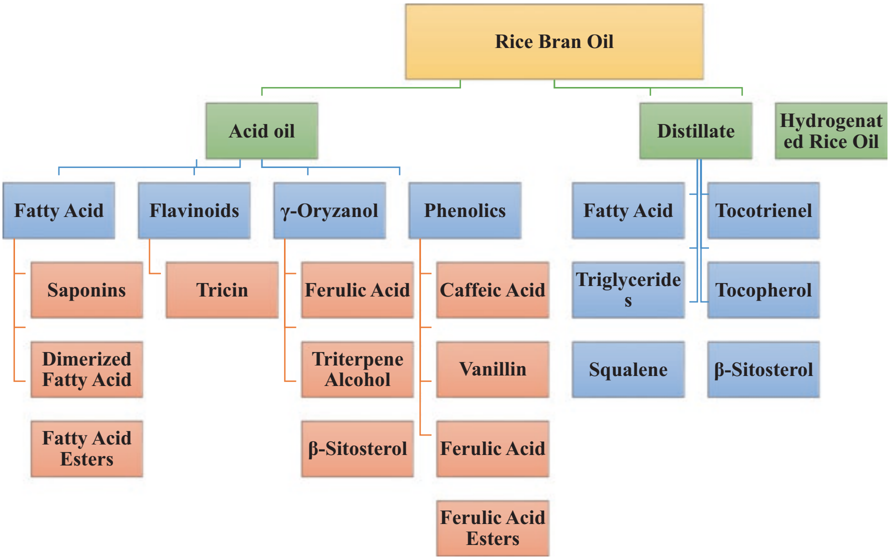
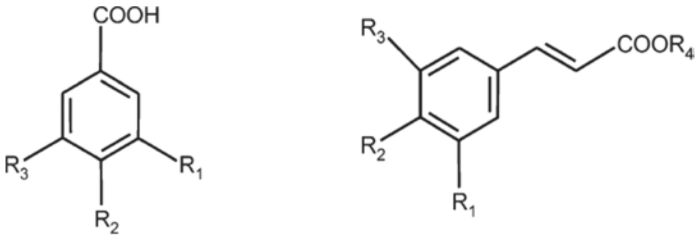


Fig. 5.2 Composition of rice bran oil [56]



Protocatechuic acid:R_1 =H,R_2=OH,R_3=OH
Hydroxybenzoic acid:R_1=H,R_2=OH,R_3=H
Vanillic acid:R_1=H,R_2=OH,R_3=OCH_3
Syringic acid:R_1=OCH_3,R_2=OH,R_3=OCH_3

Caffeic acid:R_1=OH,R_2=OH,R_3=H
p-Coumaric acid:R_1=H,R_2=OH,R_3=OH,R_4=H
Ferulic acid:R_1=OCH3,R_2=OH,R_3=H,R_4=H
Sinapinic acid:R_1=OCH_3,R_2=OH,R_3=OCH_3,R_4=H
Chlorogenic acid:R_1=OH,R_2=OH,R_3=H,R_4=quinate

Fig. 5.3 Chemical structures of phenolic compounds in rice [22]

Fig. 5.2. High concentration of ferulic acid (255–362 mg/kg grain) and *p*-coumaric acid (70–152 mg/kg grain) has been reported in brown rice, while the ferulic acid content in milled rice was just 61–84 mg/kg of grain. Meanwhile, in brown rice 80–90% of the phenolics are bound phenolic acids, and in milled rice its value ranged from 53 to 74% [23] (Fig. 5.3).

5.3 Molecular Mechanisms of Bioactives in Rice

5.3.1 Antioxidative Activities

Rice bran treated with 50% (v/v) acetone exhibited high extraction efficiency of the total phenolic content and protein, which showed the highest 1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity [24]. The antioxidant activities of rice are also correlated to the content of flavonoids, total phenolics, and anthocyanins. The antioxidant potential of tocol and anthocyanin extracts from black rice bran was analyzed by using an emulsion system which contains either fish oil (10 mg/ml) or cholesterol (1.0 mg/ml) [25]. Milled rice, brown rice, rice husk, and rice bran of a Thai variety (Khao Dawk Mali 105), collected from three different growth sites, were examined to determine γ-oryzanol, phenolic acid composition, tocopherol content, and their antioxidant capacity. The results exhibited that the bran variety had the highest tocopherols and γ-oryzanol content, while the husk variety had a higher concentration of phenolic acids, which made rice bran and husk to have higher antioxidant activities [26]. The antioxidant activities of vitamin E (α-tocotrienol, α-tocopherol, γ-tocotrienol, and γ-tocopherol) and γ-oryzanol components (24-methylene cycloartanyl ferulate, cycloartenylferulate, and campesterylferulate) extracted from rice bran were examined in a cholesterol oxidation system which is accelerated by 2,2′-azobis(2-methylpropionamidine) dihydrochloride [27]. The antioxidant activity of different rice extracts and the effects on the antioxidant enzyme activity, glutathione peroxidase and superoxide dismutase, lipid peroxidation, vitamin E, and liver enzymes in hyperlipidemia rabbits were investigated. The results demonstrated that germinated brown rice (GBR) showed the maximum antioxidant activity as compared to brown rice and white rice [28].

5.3.2 Antibiotic Activities

Rice bran extracts reduce the growth of the resulting bacteria isolated from patients suffering from diarrheal disease *Shigella* spp., *Staphylococcus aureus*, *Vibrio vulnificus*, *Salmonella* spp., *Escherichia coli*, and *Vibrio cholerae* [29]. The extracts were more active against *V. cholerae* strain O139 with the minimum inhibitory concentration (MIC) value of 0.976 mg/mL, proposing that rice bran extracts must add to the cure of diarrheal infection patient [29]. Mice were nourished with food having 10 and 20% rice bran. The food showed a decrease in *Salmonella* fecal which is used for 9 days post-infection as associated to the control feeding animals [30].

5.3.3 *Increased Immune Response*

Rice bran oil is a good source of linoleic acid which is an essential n-6 fatty acid, and it has pro-inflammatory properties which happen due to increase in eicosanoids, derived from n-6 fatty acid [31]. In male Balb/C mice, RBO modified the resistant method by increasing B-lymphocyte proliferation and TH1-type cytokines such as IL-2 or TNF-α. Furthermore, the decline established in the TH2 cytokine IL-4 and IgE levels suggested RBO might have antiallergenic properties [31]. RBO can also modify the resistant reaction by increasing B-cell growth and inducing TNF-a and IL-2 production [32]. Moreover, it has also been observed that the rice bran extract MGN-3 shows an increase in cytokine construction, DC maturation, and rise NK cell activity [33, 34].

5.3.4 *Hypolipidemic Properties*

Male Syrian golden hamsters, fed brown rice protein hydrolysate-added food, show decreased liver cholesterol, liver weight, body weight, and low-density lipoprotein cholesterol and high bile acid flow and fecal fat as compared to the control [35]. The concentrations of hepatic total cholesterol, low-density lipoprotein cholesterol, and very-low-density lipoprotein cholesterol were decreased, whereas total bile acid (TBA) and fecal total cholesterol contents were improved by the addition of fresh rice bran protein hydrolysates in mice fed the high cholesterol and fat diet [36]. One of the studies shows that rice protein of two cultivars, Koshihikari and Shunyo, reduces hepatic cholesterol discharge by isolated perfused livers of rats which are fed with cholesterol-supplemented food [37]. Meanwhile, the anthocyanin extract in black rice bran was more active at controlling cholesterol but has less effect in preventing fatty acid oxidation compared with the tocol extract [25]. Bioactive substances in RBO could decrease liver cholesterol and triacylglycerol content and increase the serum high-density lipoprotein cholesterol content of male Sprague-Dawley rats feed with food having high cholesterol [38].

5.3.5 *Anticancer Activity*

Rice bran protein hydrolysates prepared by alcalase hydrolysis were analyzed by trypan blue dye exclusion assay to test their activity in reducing the increased liver (HepG2) and human colon (Caco-2) and liver (HepG2) cancer cell lines [39].

In the azoxymethane-treated Fisher344 rats, after 45 weeks of diet, rice bran oil decreased tumor occurrence as compared with the control-fed rats [40]. Another study showed the ability of a diet high in the tocotrienol portion of rice bran oil to secure Sprague-Dawley rats against the mammary carcinogen 7,12-dimethylbenz[α] anthracene [41]. Another recent research has proved the strong correlation between eating of brown rice and cancer chemoinhibition. The results revealed that the intake of brown rice at least once in a week was related with 40% decreased chances of polyp development, which might be associated to the phytates, high fiber content, and other bioactive constituents present in brown rice which have been imagined for representing the chemoinhibition value [42].

5.4 Effects of Processing on Availability

5.4.1 Germination

Currently, GBR is one of the most remarkable grown cereal crops, and it took a lot of consideration, specifically in Asian countries, having potential of increasing health functions [43]. Germination could change the most nutritional and bioactive components of brown rice. Phenolic compounds, protein profiling, and amino acid composition of brown rice and GBR from various paddy cultivars (PB1, PB1509, PS44, PS5, and PB1121) were also examined. The results showed significant increase in γ-aminobutyric acid, arginine, histidine, methionine, proline, and acidic amino acids, and this improvement was associated to the change in increase of glutelin and prolamins with germination [43]. The content of ferulic acid of brown rice (0.32 mg/100 g of flour) improved to 0.48 mg/100 g of flour after germination and proved as the most abundant phenolic compound in GBR. Meanwhile, the total content of insoluble phenolic compounds improved from 18.47 mg/100 g of flour in brown rice to 24.78 mg/100 g of flour in GBR. The data showed that the health-related benefits of brown rice can be increased by using suitable germination conditions [22].

5.4.2 Fermentation

Fermentation is the most common technique for the production of bioactive compounds. Phenolic compound of rice bran increased by a solid-state fermentation with the *Rhizopus oryzae* fungus. Ferulic acid has shown maximum increase with fermentation, initially from 33 mg/g in rice bran up to 765 mg/g in the fermented bran [44].

Moreover, phenolic extracts derived from fermented rice bran had a greater ability to reduce DPPH, and it also showed higher polyphenol oxidase and peroxidase enzyme inhibition capacity [44]. Fermentation helps to improve the antioxidant activity of those phenols of plants which become biologically unavailable after ingestion [45]. Moreover, rice bran fermented with *Saccharomyces boulardii* showed increase in release of ferulic acid and reduction in lymphoma cell viability as compared to the non-fermented rice bran [46]. SSF also enhanced the production of many antibiotics containing oxytetracycline, bacteriocin, and cephalosporin of rice bran [47]. Brown rice fermented by *Aspergillus oryzae* have anticancer properties in male F344 rats using inhibition of phenobarbital-induced hepatocarcinogenesis and diethylnitrosoamine as a degree of preventive efficiency [48].

5.4.3 Extrusion

Extrusion cooking is a high-temperature, continuous, and short-time process which has gained popularity as it is an economical method to make new cereal products [49]. Throughout extrusion, the starch goes through physicochemical variations, such as differential scanning calorimetry (DSC) designs and gradual alterations in x-ray spreading, which may produce new functional properties [50, 51]. Increase in extrusion temperature (70–120 °C) increases the water solubility and water absorption of short-grain and long-grain rice flour. Meanwhile, increase in extrusion temperature increases the viscosity of cold paste gradually while decreases the breakdown, peak, final thicknesses, and setback viscosity [50]. Extrusion of long-grain, waxy (short-grain), and parboiled (long-grain) rice flours has been done by using five different water feed rates and at three different temperatures. Extrusion of food solubility increased and altered the thickness of rice flour. The results also confirmed that the flours extruded at 100 °C digested significantly slower than those extruded at 125 and 150 °C [51].

5.5 Possible Approach to Enhance Health Benefit of Rice Bioactives

Bioprocessing treatments, such as germination, fermentation, enzymatic hydrolysis, and so on, are the common methods to enhance health benefits of rice bioactives. Nourishing hepatoma-bearing rats a GBR diet inhibited hepatoma-induced hypercholesterolemia and increased both the activity of cholesterol 7α-hydroxylase, the rate-limiting enzyme of bile acid biosynthesis, and fecal bile acid excretion in the microsomal fraction of the liver without causing an effect on cholesterol synthesis in the host liver of hepatoma-bearing rats [52]. Glutamic acid-germinated and chitosan/glutamic acid-germinated treatment could increase the GABA content of brown rice extract, which retarded significantly the proliferation rates of L1210 and Molt4 cells [53].

Fermented bran extract of rice has also showed cancer chemopreventive action by activating specialized immune cells. According to the one study, the growth of transplanted melanoma tumor can be suppressed by an exo-biopolymer, extracted from fermented rice bran. The exo-biopolymer activates the natural killer (NK) cells which suppress the tumor. The mechanism might be in effect after oral administration of the fermented extract of rice bran; a diversity of rice bran derivative bioactive components aid in encouraging the gut-associated lymphoid tissue as a means for facilitating cancer chemoprevention in mice [54].

Bioactive peptides derived from food can be used as nutraceutical agents because they have the ability to increase the useful action against diseases. Therefore, enzymatic hydrolysis is another important technique to improve the health profits of rice bioactives. A novel pentapeptide was isolated from rice bran that contains cancer development-reducing properties on liver, colon, lung, and breast cancer cells [55].

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Chapter 6
Wheat and Wheat Hybrids

Xueling Zheng, Jiaying Shang, Qinghua Yue, and Mingfei Li

6.1 Introduction

Wheat is the most widely grown cereal crop in the world. It is the main material of major staple food in many diets, providing a large proportion of daily energy intake [1]. The demand for wheat for human consumption is also increasing globally, including in countries which are climatically unsuited for wheat production, due to the adoption of Western-style diets. After grinding, wheat flour can be used for the preparation of bread, steamed bread, biscuits, noodles, and other foods; wheat flour also can be fermented into beer, alcohol, liquor (such as vodka), or biomass fuel.

Wheat is a major staple food in many diets. Although wheat is often regarded mainly as a source of calories, it also contributes essential amino acids, minerals and vitamins, beneficial phytochemicals, and dietary fiber – all critical components to the human diet [2]. Within the context of a balanced diet, wheat represents a healthy source of multiple nutrients, dietary fiber, and bioactive compounds, especially if consumed as a whole grain. Regular whole grain consumption has been extensively associated with reduced levels of the most relevant risk factors for cardio-metabolic diseases such as total and LDL-cholesterol, triglycerides, blood glucose, blood pressure, and body mass index [3]. Recently, a meta-analysis confirmed an association between the consumption of whole grains and a substantial and significant decreased risk for cardiovascular disease, cancer, and all-cause and cause-specific mortality [4]. The mechanisms by which wheat confers protective effects on human health are attributed to the physical properties and structure of grains (granular size of semolina, amount and type of fiber, quantity and quality of phytochemicals, amylose and amylopectin content) [5]. Given the increased worldwide mortality attributable to nutrient- or diet-related chronic diseases over the last years, there is a great interest in improving wheat to ameliorate health outcomes [6].

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There is also an increasing interest in identifying wheat species with greater health potential, more specifically for improved antioxidant and anti-inflammatory properties. In the light of existing evidence derived from in vivo experiments, wheat varieties rich in bioactive substances are effective in reducing chronic disease risk [1].

Whole grain is defined by AACC International as intact, ground, cracked, or flaked caryopsis (naked cereal kernel), the principal anatomical components of which starchy endosperm, germ, and bran are present in the same proportions as in the intact caryopsis [7]. The consumption of whole grain wheat products is associated with a number of health benefits which may relate in part to the contents of phytochemicals. It is well-known that the health benefits of whole grain products are mainly due to several valuable compounds of the bran. Bran is rich in natural antioxidants, phytoestrogens, and lignans, which may exert many beneficial effects on various body functions [8]. The concerns about the consumption of the refined flour have been accompanied by the promotion and increased consumption of the whole wheat flour, based on perceived health benefits. However, the growing conditions and processing technology of wheat may be different in varying regions. It is therefore necessary to consider whether bioactive phytochemicals in wheat relate to intrinsic differences between wheat species or to variation between genotypes or to the impacts of differences in cultivation and processing.

The factors affecting the content of bioactive phytochemicals in wheat and its products are planting, processing methods, and other methods. The planting conditions will affect the composition of wheat grain, which mainly contains genetic and environmental factors, such as the weather conditions, especially the temperature and water availability during grain development. For example, a comparison of a set of 26 genotypes grown in 4 or 6 environments showed positive correlations between the contents of phytochemicals and the mean temperature during grain development, with some components also showing negative correlations with total precipitation over the same period [9]. By contrast, the contents of the water-soluble arabinoxylan fiber in bran and white flour were both negatively correlated with temperature and positively correlated with precipitation [9].

The content of bioactive phytochemicals is also related to processing technology. Wheat for human food consumption is usually processed into flour. The flour extraction rate ranges from 73% to 77%, depending on the milling process, the variety of wheat, and cultivation conditions [10]. It is therefore obvious that data in the literature often shows variation in the content of bioactive compounds in wheat grain tissues, which may be due to different analytical methods, due to milling technologies, or due to the cultivar and growing location.

Addition of bioactive phytochemicals is a way to increase the content of bioactive phytochemicals of flour as well as adding wheat bran containing large amount of DF. Endosperm, germ, pericarp, testa, and aleurone layer are the main components in wheat grain enriched in nutrients. Commonly, wheat flour is a daily energy supplement in the world and has different products to satisfy people's requirements. During flour processing, wheat bran is defined as by-product and has low economic interest. However, lots of nutritional and phytochemical components existed in bran including protein, dietary fiber, phenolic compounds, and vitamins [11–14]. More and more foods and products are made by refined flour and are well welcome in the market. Due to the over processing, flour in our daily use only contains endosperm except for bran resulting in a loss of dietary fiber [15]. Considering the comprehensive nutrition of flour and human's health, it's better to keep bran (DF) in the flour.

According to the past studies, it assumed that eating whole grain foods as daily meals shows good effects on reducing the risk of metabolic disorder disease and chronic health problems involving type 2 diabetes, cardiovascular disease, and cancer [16–18]. Researchers took consideration of high-fiber content in wheat flour as the positive effects to health. However, more and more recent studies found that this beneficial phenomenon may owed to fiber as well as vitamins, phenolics, carotenoids, alkylresorcinols, and other phytochemicals [19].

The consumption of whole grain and whole grain fiber significantly improves blood glucose control, improves cholesterol levels, reduces blood pressure, and lowers the serum concentration of high sensitivity C-reactive proteins, a marker of low-grade inflammation [20–24]. These observations all indicate improvement in obesity-related metabolic dysregulation (syndrome X) and have been attributed largely to the fiber (β-glucan and arabinoxylan) and phytochemicals (phenolics, sterols, tocols, and vitamins) that are concentrated in the aleurone layer of the bran [11] as well as present in the wheat germ fraction. These compounds are thought to exert synergistic effects on specific health-related metabolic processes [25].

Although the adverse effects of wheat on some individuals should not be ignored, five major recent scientific reviews addressing the impact of cereal consumption on health and disease concluded that the consumption of whole grains, of which the most widely consumed is wheat, generally exerts positive effects on health, thus recommending increased intake of whole grain for the general public, in exchange for refined foods [25–28].

6.2 Bioactives in Wheat and Wheat Hybrids

The bioactive phytochemicals in wheat can be broadly subdivided into the following categories: dietary fiber (DF), phenolic acids, carotenoids, tocopherols, alkylresorcinols, and other miscellaneous compounds (sterols, sterylferulates, benzoxazinoids, and lignans) [29].

The structure of all the wheat cultivars was similar and was composed of bran, germ, and endosperm. In fact, the content and distribution of these bioactive phytochemicals were different when being observed. Large amounts of bioactive phytochemicals were found in germ and bran as proved in the literatures [30–32]. Other researchers [31, 33] removed the outermost layers (pearling) of grain and found phenolic compounds was existed in bran. It's mainly insoluble form (80%) instead of free-soluble form. Beyond that, a recent study also explored that 627.8–745.6 μg/g (db) bound phenolic acids were detected as compared to 66.0–97.0 μg/g (db) in refined grain [33]. As for carotenoids, it's mainly contained in germ (high level), bran, and endosperm (low level). 0.7 μg/g of carotenoids existed in durum wheat from Spain and 13.6 μg/g in einkorn accessions from Italy. Similarly, tocopherols and tocotrienols were found in the germ and the outer layers, while almost little amounts were observed in endosperm. For tocotrienols, outer layer of the grain shows 85%, such as pericarp, testa, and aleurone, and only 15% in the endosperm [19]. In a recent study, Tanwir et al. [34] investigated the levels of benzoxazinoids which were highly varied in their distribution [35]. Lignans are mostly distributed in bran and commonly stemmed from phenylalanine via dimerization of substituted cinnamic alcohols.

6.2.1 Dietary Fiber (DF)

Dietary fiber is defined as nondigestible carbohydrates and contained more than three monomeric units in foods and demonstrated its physiologic benefits, such as resistant starches [36, 37]. According to its solubility in water, dietary fiber can be defined as soluble and insoluble dietary fiber, which was involved by inulin, β-glucans, and other nonstarch polysaccharides [38, 39] and lignin, cellulose, and some hemicelluloses [40].

6.2.1.1 Distribution of Dietary Fiber in Wheat

11.5–15.5% (db) of total DF (TDF) was found in whole wheat grain; polysaccharides arabinoxylan (5.5–7.4%, db), cellulose (1.67–3.05%, db) and β-glucan (0.51–0.96%, db), and Klason lignin (0.74–2.03%, db) were main components of being cell wall as well as TDF [36]. Diverse components showed different distributions in grain tissues. In pericarp and testa, its outer layers were comprise of the cell wall materials [41], which are enrich in lignin (12%), cellulose (30%), and a complex form of arabinoxylan termed glucuronoarabinoxylan [42]. The aleurone cells which form the outer layer of the endosperm also enriched in fiber (35–40%, db) [41]. Aleurone cells are mostly consisted by 29% β-glucan, 65% arabinoxylan, and ~2% cellulose and glucomannan [43]. By comparison, the endosperm cells of starch contain only about 2–3% cell wall polysaccharides, with the major components being arabinoxylan (70%) and β-glucan (20%) with 7% glucomannan and 2% cellulose [44].

In addition to cell wall polysaccharides, there are two more carbohydrates (fructans and starch) which constitute the dietary fiber fraction of wheat. About 0.84–1.85% (db) of fructans (fructooligosaccharides) existed in the whole grain [36], and 3.4–4% (db) of starch was detected in wheat bran [45]. Besides, a small proportion of the starch is also present in the starchy endosperm cells which was considered as resistant starch and can’t be digested in the upper gastrointestinal tract and be fermented in the colon.

6.2.1.2 Official Methods to Analyze Dietary Fiber

In general, physiological aspects were considered as important indicators to established systematic methods to analyze DF. In the past years, various classifications of DF fractions were studied in published papers using analytical methods. In the year 2005, AOAC 985.29 and 991.43 have been put forward to analyze DF in food and classified as typical and official methodologies. AOAC 985.29 was the one to determine total dietary fiber in high molecular weight (high molecular weight DF, HMWDF), while AOAC 991.43 was used to distinguish soluble and insoluble fractions of fiber in forms of HMWDF [46]. However, with the in-depth study of DF, in 2008, *Codex Alimentarius* introduced a new definition of DF containing resistant starch and the option to include nondigestible oligosaccharides. The classical methods are limited and inadequate when measured DF in low molecular weight (low molecular weight dietary fiber, LMWDF), such as inulin, fructooligosaccharides, galactooligosaccharides, and polydextrose [47]. To satisfy this situation, the implementation of this measurement required a new methodology.

In recent decades, more and more studies focused on the nutritional and analytical properties of DF resulting in more focus on physiological concept instead of simple chemical concept.

It’s worthwhile to mention that several bioactive compounds (such as polyphenols) were still eager to explore appropriate methods to determination in the DF detective process. The physiological functions of DF were most likely to be studied in the digestive system. Researchers usually observed the transportation of these bioactive compounds through the gastrointestinal tract and production of fermentation metabolites in the colon. It should be studied in detail that dietary polyphenols play the role of carrier to colon, which contributes tointestinal health and has an influence on gut microbiota and antioxidant status [48].

Thus, it is essential and important to explore and use appropriate methodologies to analyze dietary fiber in foods. These should highlight the importance of dietary fiber in the promotion and maintenance of human health.

6.2.1.3 Function of Dietary Fiber

DF considered as one of significant elements for human’s good health in the diet has been established by the scientific community [49]. In the daily life, no less than 50% of functional foods were referred to DF [50]. The function of DF was commonly defined as regulation of intestinal transit, as well as risk reduction of diabetes, cardiovascular diseases, and colon cancer [49, 51]. Due to the mentioned functionality, more and more studies began using DF as a beneficial component to improve human’s health; thus more systematic achievements and further knowledge about the function of DF have been supplemented.

The dietary fiber was defined by the Food and Agriculture Organization (FAO) as a variety of indigestible plant polysaccharides including cellulose, hemicelluloses, pectins, oligosaccharides, gums, and various lignified compounds. Polysaccharides in dietary fibers may be active in their native form or after chemical/enzymatic treatments. For example, the cellulose and hemicellulose can directly stimulate bowel movements, while the inulin needs to be fermented into short-chain fatty acids by microflora so as to prevent numerous gastrointestinal disorders [52]. Among the constituents in dietary fibers, polysaccharides play an important role in disease prevention. For example, pectins, inulin, and gums are able to slow the movement of food in the digestive tract, to reduce the blood cholesterol level, and to slow the speed of sugar absorption from the food into the blood, avoiding sudden hyperglycemia after food intake. Cellulose, hemicellulose, and lignin constitute the insoluble fibers of dietary fibers which are able to stimulate movement of bowels, speeding up the passage of waste through digestive tract, preventing constipation, diverticulosis, and hemorrhoids [53, 54]. Numerous convincing epidemiological and clinical studies suggest that moderate or higher intakes of dietary fiber can effectively lower risks of developing diseases like diabetes [55], cardiovascular diseases including stroke [56], coronary heart disease and hypertension [57], hypercholesterolemia, hyperlipidemia [51, 58], obesity, and gastrointestinal (colorectal) cancer [59]. Generally, dietary fiber intake provides many benefits, including a decrease in intestinal transit time, an increase in stool bulk, and a decrease in blood total cholesterol, postprandial blood glucose, and/or insulin levels [36, 59, 60].

As “the seventh nutrient,” DF has attracted the attention of increased researchers. Considering its strong water absorption capacity, acceleration of intestinal peristalsis, DF exhibited its potential in eliminating intestinal toxins and controlling body weight [61, 62]. Dietary fiber can absorb free estrogen, reducing the risk of breast cancer [63]. It has been demonstrated that short-chain fatty acids are beneficial for our health. In the digestive system (colon), DF can be fermented by microorganisms as a substrate and produce various metabolites including the short-chain fatty acids [64–66]. In addition, increasing the intake of DF can help reduce risk of various chronic diseases embracing type 2 diabetes and cardiovascular disease [67–69], and it has been found in lots of daily diets, such as vegetables, fruits, and whole grains. Increased consumption of DF has also been shown to improve serum lipid levels thus reduce blood pressure [70]. Foods with high DF could offer important health benefits for human health sustainability.

According to the analysis above, the benefits and functionality of DF on human health have attracted more and more attention. Compared with whole grain flour, refined flour, which discarded wheat bran and aleurone layer, lacks DF and resulted in low level of nutritional value and processing performance. In order to improve its nutritional behavior, adding bran back into the flour is a popular way to obtain high DF flour. It’s also an effective and direct way to expand the utilization of by-products during wheat processing. After adding bran in the flour, poor taste is a common and urgent problem when used in foods. Further study should be focused on techniques of modifying whole wheat flour, bran, and DF by performing milling, extrusion, heat treatment, and biological treatment so as to diminish the bad effects on quality of flour and its products [71].

6.2.2 Resistant Starch

6.2.2.1 Resistant Starch and Classification

Starch is one of the main compositions of cereals such as wheat and corn. Englyst and Cummings [72] firstly assumed a concept that starch may not be fully hydrolyzed during digestion caused by the differentiation in structure and processing methods. They claimed that starch can be defined as rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) depending on its susceptibility to pancreatic amylase (in vitro) [73, 74].

RDS: RDS is a kind of starch composed by amorphous region as well as dispersed starch. When starchy foods are cooked at high moisture (bread and potatoes), RDS is produced largely. The definition of RDS is the starch can be digested in 20 min by enzymes.

SDS: SDS is regarded as a type of starch, which can be fully hydrolyzed in the small intestine with slow digestion rate. SDS can be classified into physically inaccessible amorphous starch and raw starch with the crystalline structures of type A, B, and C in original state or in cooked foods. The definition of SDS is the starch which can be digested by enzymes during 20–120 min.

RS: Englyst et al. [74] defined RS as a small fraction of starch which can't be hydrolyzed even treated by exhaustive amylase and pullulanase. Actually, starch would be fermented by gut microflora before entering the large intestine and show resistance to enzymes in the small intestine. The definition of RS is the starch cannot be digested even after 120 min by enzymes. The content of RS was calculated as followed equation: RS = TS – (RDS + SDS). TS means total starch in the starchy food.

There are numerous factors affecting hydrolysis rate of starch, such as amylose/amylopectin ratio, structure type, molecular weights (MW), particle size, amount of amylose-lipid complexes, existence of other materials in the food matrix (sugar, protein, etc.), and enzyme inhibitors [75–77]. Based on the formation and the way to resist enzyme, RS can be classified into four types:

- RS type 1 (RS1) is physically inaccessible starch founded in whole or partly milled grains or seeds.
- RS type 2 (RS2) a kind of native starched showing resistance to enzyme during digestion caused by its personal structure (such as banana, potato, and high-amylose maize starch) and can be widely applied in foods and pharmaceuticals [78].
- RS type 3 (RS3) is attributed to the retrograded starch during food processing.
- RS type 4 (RS4) is made up of modified starches by chemical reagents (such as esterification and cross bonding) [79]. The detailed information about RS4 in chemically modified ways can be found in the research by Tharanathan [80].

6.2.2.2 Methods of Analysis of Resistant Starch in Foods

A variety of methods exist to measure either total RS or specific types of RS in vitro, aiming to mimic human physiological conditions by first grinding samples (as would occur with mastication) or even self-chewing [81], removing hydrolysable starch with enzymes, and incubating at body temperature (as during digestion). These processes have been described in detail elsewhere. The Megazyme RS assay kit [82], based on the American Association of Cereal Chemists Method [83] and AOAC method [84], is widely used at present.

Different methods yield different quantitative results due to varying sample preparation, enzymes used, and length of incubation periods. For example, the RS content of cornflakes has been reported as 2.2% when using the Megazyme assay [85] and 3% and 6.5% using two other methods [74, 86]. There is evidence that the amount of RS available in the colon after food consumption varies from person to person due to individual difference in chewing habits [74]. RS can also be determined in vivo in studies of patients with ileostomies [87].

6.2.2.3 Functionality and Beneficial Physiological Effects of RS

In common, RS has low water-holding capacity with small particle size, white appearance, and bland flavor. It has desirable physicochemical properties such as swelling, viscosity increase, gel formation, and water-binding capacity, making it useful in a variety of foods [88]. These properties make it possible to use most resistant starches to replace flour on a one-for-one basis without significantly affecting dough handling or rheology. RS not only fortifies fiber but also imparts special characteristics not otherwise attainable in high-fiber foods [89]. RS2 and RS3 were commonly used as commercial sources. Its functionality and advantages are summarized as follows [90]. Compared with products with traditional fiber, foods with RS2 and RS3 have higher gelatinization temperature, better extrusion and film-forming qualities, and lower water-holding properties. In another way, improved texture, appearance, and taste (such as better organoleptic qualities) were detected in low-bulk high-fiber products in contrast to traditional high-fiber products by increasing coating crispness and bowl life of breakfast cereals. What's more, being treated as functional ingredients in foods, foods contain RS2 and RS3 exhibiting lower calorific value. Considering their medical role, products with RS2 and RS3 show its function in celiacs, such as bulk laxatives and oral rehydration therapy. Because of these effects and properties, RS2 and RS3 have been successfully used in a range of baked and extruded products.

Beneficial physiological effects of resistant starch generally contain the following aspects: prevention of colonic cancer, hypoglycemic effects, resistant starch as a prebiotic, hypocholesterolemic effects, inhibition of fat accumulation, reduction of gall stone formation, and absorption of minerals.

On account of its potential health benefits and functional properties, the increased attention has been payed to RS [91]. As one of the most abundant dietary sources of nondigestible carbohydrates [90], RS is devoted to improve colon health, prevent inflammatory bowel diseases (IBD) and colorectal cancer (CRC) [92], but show little influence on lipid and glucose metabolism [90]. So, RS was regarded as important as NSP (nonstarch polysaccharides). In addition to the mentioned influence, Sajilata et al. [91] listed other physiological effects which have also been proved to be beneficial for health, mainly depending on design approach during study and differences in the source, type, as well as dose of RS consumed [90, 93]. Due to the modern processing and food consumption practices, RS consumption turned down leading to high probability of serious colon disease occurred in developed countries. This offers opportunities for the development of new cereal cultivars and starch-based ingredients in food products as well as in clinic [92].

RS can react on short-chain fatty acids (SCFA), in adults, through its colon bacterial fermentation and increase in its prebiotic potential. Another application is using RS to reduce the energy value and available carbohydrate content of foods. Because of its special digestive behavior, its potential to accelerate the onset of satiation and to lower glycemic response, RS can be used to enhance the fiber content of foods. The potential of RS is to enhance colon health and act as a vehicle to increase the total dietary fiber content of foodstuffs, particularly those which are low in energy and/or in total carbohydrate content [90].

There are various techniques to obtain RS, involving heat treatment, enzyme, combination of both, and chemical modifications. The processing conditions such as pH, heat temperature, heat duration, number of heating and cooling cycles, freezing, and drying are the technical methods to increase RS content in foods. A number of commercially available RS preparations would make it possible for a wide range of applications with nutraceutical implications.

6.2.3 Vitamins

Vitamins are a group of organic compounds widely distributed in the plant kingdom and play important functions in human health. Generally, they can be divided into water-soluble and fat-soluble vitamins. The former mainly includes vitamin B and C, and the latter contains vitamin A, D, E, and K. Cereal grains are important sources of B vitamins. Wheat, and in particular whole grain, is an important source of B vitamins, particularly thiamine (B1), riboflavin (B2), niacin (B3), pyridoxine (B6), and folates (B9). All kinds of vitamins are mainly distributed in the embryo and aleurone layer.

6.2.3.1 Water-Soluble Vitamins

Thiamine is essential for the release of energy from carbohydrates, a healthy heart and the normal functioning of the brain and nervous system. In the United States, flour made from wheat can be enriched with thiamin at a rate of 0.44–0.55 mg thiamine 100 g flour. In the mid-1970s, a proposal for raising enrichment levels to

2.9 mg/100 g flour was made [94]. According to Kutsky [95], wheat germ is classified as a good source of thiamine, providing 1000–10,000 μg/100 g of the grain component. Toepfer et al. [96] indicated that durum wheat had a higher average thiamine content than hard red wheat. There are differences in the vitamin content of wheat components. Thiamine is the most labile of the various B vitamins found in or added to cereal grain products. It is stable under acidic conditions but largely breaks down in air (especially at higher pH), under autoclaving and during exposure to sulfites and alkali [97]. Stability at acid pH is demonstrated by the small losses noted in fermented baked products.

Like thiamine, riboflavin enrichment of wheat flour at the rate of 0.26–0.32 mg/100 g flour is allowed in the United States. Kutsky [95] and others [98, 99] classify wheat germ as moderate sources (100–1000 μg/100 g). Hard red wheat and durum wheat both contain similar amounts of this vitamin. When exposed to heat in a dry form or in an acid medium, riboflavin is stable. However, this vitamin is very sensitive to light with the rate of destruction increasing as pH and temperature rise. Ranhotra [100] found about an 8% loss in fresh baked bread made from enriched flour.

Niacin is found in cereal grains in bound and free forms, and niacin in bound form is poorly utilized by humans [101]. The niacin added during the enrichment process becomes an important contributor to dietary niacin. One half or less of the total niacin in wheat is in the free form. Niacin in the form of nicotinic acid can be added to flour at the rate of 3.56–4.45 mg/100 g flour according to enrichment standards. Kutsky [95] and others [99] indicate that barley, wheat germ, and wheat bran are moderate dietary sources (1000–10,000 μg/100 g of grain) of niacin. In general, niacin is considered to be stable in air, light, heat, acids, and alkali [97]. When wheat flour enriched with niacin baked into bread, losses of niacin are minimal (1–2% in Arabic bread) regardless of the level of enrichment [100, 102, 103].

Pyridoxine (vitamin B6) is composed of three distinctly different compounds: pyridoxine, pyridoxal, and pyridoxamine. Of the three fractions, pyridoxine is the most abundant. On average, wheat is considered to contain moderate amounts (100–1000 μg/100 g); wheat germ contains high amounts (1000–10,000 μg/100 g). With vitamin B6 enriched in flour, flour has been proposed but never implemented [94]. Vitamin B6, in the form of pyridoxine, is stable when exposed to heat, strong alkali, or acid but is sensitive to light, especially UV light, in the presence of alkali. Pyridoxal and pyridoxamine are adversely affected by exposure to air, heat, and light. All three forms of this vitamin are destroyed at neutral pH when exposed to UV light [97]. Pyridoxine deficiency appears to be an independent predictor of coronary artery disease. Pyridoxine is effective (along with folic acid and vitamin B12) in the reduction of blood plasma homocysteine levels and in the decrease of the rate of restenosis after coronary angioplasty [104].

According to Kutsky (1981) [95] and others [98, 99], wheat bran is classified as a high source (90–300 μg/100 g) of folic acid; wheat is categorized as a moderate source (30–90 μg/100 g). Large losses of folic acid are noted at autoclaving temperatures in the presence of acids and alkali. This destruction is enhanced by oxygen and light [97].

6.2.3.2 Fat-Soluble Vitamins

When considered as a whole, cereals are naturally low in lipids. Therefore, they tend to be low in fat-soluble vitamin A, which is present as the precursor carotenoids, and vitamins D, E, and K. In 1974, the enrichment of wheat flour with vitamin A at the rate of 1.3 mg/lb of flour was suggested [94]. However, at this point such enrichment is not permitted. Oil extracted from the wheat germ provides vitamin E in the form of various tocopherols. Kutsky [95] and others [99] classify wheat germ oils as high (50–300 mg/100 g) contributors and whole wheat flour as a low (0.5–5 mg/100 g) source of this vitamin. From a stability standpoint, the tocopherols are stable in acid and in the absence of oxygen and visible light. They are labile at room temperature when exposed to oxygen, alkali, and ferric salts. They are also unstable upon exposure to ultraviolet (UV) light. In general, this vitamin is stable to heat, acids, and oxygen. In foods that are alkaline and exposed to air and light, vitamin D is slowly destroyed [97]. Vitamin K sources categorized as modest contributors (10–100 μg/100 g) include whole wheat and wheat germ and bran. When processing, this vitamin is stable to heat and reducing agents. However, it is labile in the presence of alcoholic alkali, oxidizing agents, strong acids, and light [97].

6.2.3.3 Other Vitamins

Information about other vitamins found in cereals is sparse. Wheat and oats have comparable but higher amounts of pantothenic acid. Wheat is classified as moderate sources (0.5–2.0 mg/100 g) of pantothenic acid; wheat germ and bran are both considered by Kutsky [95] as high sources (2.0–10.0 mg/100 g). From a dietary source standpoint, wheat is also considered to be medium sources (10–100 μg/100 g) of biotin. This vitamin is relatively stable when exposed to air, oxygen, and UV light [97]. Mature, dry cereal grains contain no detectable ascorbic acid (vitamin C). However this vitamin can be detected in germinated cereal seeds.

6.2.4 Minerals

Minerals are inorganic elements found in small or trace amounts in various dietary constituents. Based on the amount present in the human body, minerals are classified as major (macro) and trace minerals (elements) [105]. The major minerals are those that are present in the body in amounts greater than 5 g. Trace minerals are those present in amounts less than 5 g. The average mineral content of a given grain varies significantly from one part of the world to another. This is a function of factors such as the type of grain, variety, growing conditions, and fertilizer application.

6.2.4.1 Calcium

About 95% of all mineral matter is cereal grains consists of phytates, phosphates, and sulfates of calcium, magnesium, and potassium [106]. The aleurone layer contains 53% of the calcium present in wheat. Because 87% of the phytic acid also resides in this layer, calcium probably exists as a mixed salt of calcium-magnesium phytate (Ca_5Mg phytate) [106]. Wheat germ and wheat bran are considered to be low sources of calcium (50–100 mg/100 g); wheat is classified as a moderate source (100–200 mg/100 g) [107]. One should note that certain grains can be enriched with calcium, thereby making them better sources of this mineral. Good calcium intake throughout the lifespan is thought to lower ones risk of osteoporosis [105]. This potential is one of the basis for requiring that the calcium content of a food be present on the label. Although done sporadically in the past, because of the recognition of the role of good calcium intake over time, calcium enrichment of some cereal grains is occurring more frequently.

6.2.4.2 Phosphorus

Compared to other minerals, phosphorus is found in large quantities in cereal grains. It is mostly associated with phytic acid (myoinositol hexaphosphoric acid) and its salts. In wheat, 80% or more of the total phosphorus is accounted for by the phytate [106]. Over 80% of the phytate is located in the aleurone portion of wheat. In wheat, phosphorus becomes incorporated into phytic acid during maturation [106]. From a dietary standpoint, wheat, wheat germ, wheat bran, and wild rice are classified as high sources (200–1200 mg/100 g). Quantities of phosphorus vary significantly from one wheat variety to another.

6.2.4.3 Magnesium

Eighty-seven percent of the magnesium in cereal grains is located in the aleurone layer [106]. Because magnesium binds with phytic acid, much of the magnesium is probably present as Ca_5Mg phytate or as potassium-magnesium phytate. The remainder is likely to be present in phosphates and sulfates [106]. From a dietary standpoint, wheat bran and wheat germ are considered to be high sources of this mineral (200–400 mg/100 g). In the mid-1970s the Food and Nutrition Board proposed that wheat flour be enriched with magnesium at the rate of 200 mg/lb flour. However, this proposal was never implemented. Magnesium levels vary significantly among wheat varieties. When fertilizer treatments differ, the quantity of magnesium varies significantly in spring wheat.

6.2.4.4 Iron

Iron in wheat is located in the outer endosperm and bran. Patent flour contains about 5.4 μg/g compared to 124 μg/g in the bran [106]. Morris and Ellis [108] have identified a low molecular weight compound in wheat that is believed to be monoferric phytate. This compound is thought to account for 60% of the iron in wheat bran. According to Kutsky [95], wheat germ and wheat bran are considered to be good sources of dietary iron (5–18 mg Fe/100 g). Although barley, buckwheat, and wheat are moderately good sources, enrichment of wheat flour with iron at the rate of 2.89–3.6 mg/100 g of flour has been allowed since the late 1940s. In the mid-1970s the Food and Nutrition Board suggested an increase in the allowed iron enrichment to 40 mg/lb flour. However, for various reasons related to health and safety, this proposed increase has never become official.

6.2.4.5 Zinc

Information related to zinc content of cereal grains is somewhat limited. Based on the information available, zinc content is highest in wheat [97]. According to Pekka Koivistoinen et al. [109] and Lorenz and Loewe [110], zinc levels vary significantly from one wheat variety to another; similar variation has been seen among barley varieties. From a dietary standpoint, the best source of zinc in cereals is wheat germ and bran (4–10 mg/100 g). Research coming out of the Middle East has raised some concerns about the bioavailability of zinc from plant products. When the diet is high in cereal grains of high extraction and is consumed in the form of unleavened flour products, this concern may be very significant because zinc deficiency affects growth. However, research on products that are leavened indicates that zinc becomes more physiologically available to a degree greater than can be accounted for by the action of yeast on the phytate. Therefore, the issue of bioavailability appears to be complex, including factors like the impact of yeast, the impact of pH changes, and the phytate-to-zinc ratio [111].

6.2.4.6 Copper

The refining of cereals results in significant loss of copper. However this loss is not as extensive as are losses of iron, manganese, and zinc [106]. Copper in cereal bran is soluble and released at a pH of 1 but is bound at a pH of 6.8 [106]. The copper content is reported to be lowest in corn and highest in oats, while wheat is the only grain with a significant variation in copper content among the varieties [109]. The copper content of spring wheat, barley, and rye is affected by different fertilizer treatments. From a dietary standpoint, wheat germ and wheat bran are the only cereal grains that serve as good sources of copper (1–10 mg/100 g). Barley and wheat are considered to be moderately good sources (0.1–1 mg/100 g) of this mineral.

6.2.4.7 Sodium and Potassium

Sodium and potassium are minerals of concern in health care. Therefore, the amounts of these minerals in dietary constituents are of interest. Potassium levels are high in most cereal grains. According to the work by Pekka Koivistoinen et al. [109], potassium content is relatively stable among the different varieties of wheat, rye, barley, and oats. The potassium levels found for wheat differ from those of Lorenz and Loewe [110]. Sodium levels vary significantly between the barley and oat varieties but not the wheat and rye varieties studied [112]. When comparing hard versus soft US and Canadian wheat, Lorenz and Loewe [110] did not find any significant differences in sodium content. They did note significant differences of sodium quantities in soft and hard wheat classes. From a dietary source standpoint, no cereal grain is considered to be a high or even moderate contributor of sodium to diet. Buckwheat, rye, and wheat bran are considered to be good sources (400–1000 mg/100 g) of potassium.

6.2.4.8 Other Minerals

As their name suggests, trace elements are required only in very small amounts of a few micrograms to a few milligrams per day; nevertheless, they are necessary for good health. Until 1960, nine trace elements were considered essential. These included iron, iodine, copper, manganese, zinc, cobalt, molybdenum, selenium, and chromium. Because there is more information about iron, copper, and zinc, these minerals have been discussed previously in this chapter. Since 1960, six additional trace elements have been recognized. These include tin, vanadium, fluorine, silicon, nickel, and arsenic [106]. Although the most recently recognized elements are considered to be essential, nutritional deficiency problems are unlikely to occur in humans because of the extremely small amounts needed [106].

Information about these trace elements in cereal grain is sketchy. Syvalahti [113] measured numerous elements when they were investigating the impact of different fertilizer treatments. They found that the amounts of elements like sulfur, aluminum, boron, bromine, cobalt, fluorine, manganese, molybdenum, selenium, cadmium, and lead tended to vary in the grains studied when fertilizer treatments were changed. In addition, in some of their analyses, levels of elements like arsenic and mercury were consistently below analytically detectable levels. Lag. J [114] found that the locality where wheat or barley was grown affected the selenium and molybdenum content of these grains. They even observed large variations in molybdenum level in these grains within a given area. When comparing their work to others, Lag. J [114] found some agreement with their own findings but also found variation from their study results. One should note that although buckwheat, corn oil, wheat bran, and wheat germ are considered to be high sources of cobalt, the only known need for cobalt by humans is that associated with the cobalt that comprises the center of the vitamin B12 compound, which is only supplied by animal products. Therefore, there is reason to question the value of cereal grains as a source of cobalt.

6.2.5 Phytochemicals in Wheat

As we referred in the previous, reduced incidence of chronic diseases and inflammation can be affected by the increased consumption of whole grain and its products. Except for DF, phytochemicals and antioxidants accumulated in fruits and vegetables also play an important role on human's health, as proved in whole grain and whole wheat flour, especially in germ and bran together with many other micronutrients. Systematic approaches to the phytochemical profile of wheat in recent years have shown wheat contains many health-beneficial compounds such as phenolic acids, flavonoid, lignans, carotenoids, tocopherols/tocotrienols, and phytosterol/phytostanols.

6.2.5.1 Phenolic Compounds

Phenolic compounds are a kind of plant secondary metabolite with extensive biological activity. The content in wheat is small, but the physiological impact on the human body cannot be ignored. The phenolic compounds in wheat mainly include phenolic acids, flavonoids, and lignans. Phenolic acids are the main form of total phenolic content in the bran, and 85% of the total phenolic content in wheat bran was in bound form [115]. Bound phenolic acids and other polyphenols may be more important contributed to health benefits [115, 116].

Benzoic and cinnamic acids are basic substrates of phenolic acids produced by the shikimic acid pathway in most plants and stored as hydroxybenzoates and hydroxycinnamates [117]. Due to its antioxidant activity, phenolic acids have potential to control the oxidation of LDL-cholesterol and oxidative damage to lipid membranes and DNA, which might lead to several pathological conditions, including CVD and cancer. When adding water-soluble feruloyl oligosaccharides (in bran) to a cell culture of normal human erythrocytes, oxidative damage was found to reduce erythrocytes of human beings. After intake of either bioprocessed or native rye bran samples which both contained high level of ferulic acid, little obvious differences were detected in postprandial glucose and insulin responses as reported by Lappi et al. [118]. In vitro studies on phenolic acids have shown antiproliferative activities on cancer cells and anti-inflammatory effects.

Despite the large volume of studies on the phenolic acids in wheat, information on other polyphenol content of wheat has been lacking. However, available literature indicates lignans and flavonoids are found in wheat, and they may have contributed to the many health benefits of wheat.

Flavonoids are a kind of phytoestrogen with a wide range of biological activities. Chemically, flavonoids have the general structure of a 15-carbon skeleton, which consists of two phenyl rings and a heterocyclic ring. This carbon structure can be abbreviated as C6-C3-C6. Flavonoids are divided into various classes on the basis of their molecular structure with six major subclasses, namely, anthocyanidins, flavan-3-ols, flavonols, flavanones, flavones, and isoflavones being the most widespread in the human diet. In wheat, the phytochemical profiles, particularly the flavonoid profiles, have only been thoroughly studied in recent years.

An important effect of flavonoids is the scavenging of oxygen-derived free radicals. In vitro experimental systems also showed that flavonoids possess anti-inflammatory, antiallergic, antiviral, and anticarcinogenic properties [119]. The best-described property of almost every group of flavonoids is their capacity to act as antioxidants. The flavones and catechins seem to be the most powerful flavonoids for protecting the body against reactive oxygen species. Body cells and tissues are continuously threatened by the damage caused by free radicals and reactive oxygen species, which are produced during normal oxygen metabolism or are induced by exogenous damage [120].

In addition to phenolic compounds, carotenoids, tocols, sterols, stanols, and other bioactive phytochemicals (phenolic lipids and benzoxazinoids) have also been extracted and identified in whole wheat grains.

6.3 Effects of Processing on Wheat Bioactives and the Approach to Enhance Health Benefits of Wheat Bioactives

Wheat is commonly processed prior to human consumption. Wheat producers, processors, nutritional professionals, and consumers are interested in investigating the effect of processing on bioactive phytochemicals in wheat [121]. Processing (such as milling, proofing, baking, extrusion, cooking, steaming, etc.) and its conditions (temperature, pressure, time, etc.) influenced the stability of bioactive phytochemicals. The optimal processing of wheat is important to preserve the bioactive phytochemicals in wheat-based finished products. The effects of processing on bioactive phytochemicals such as dietary fiber, phenolic acids, carotenoids, and so on are reviewed.

6.3.1 Dietary Fiber and resistant starch During Processing

Dietary fiber affects gastrointestinal function, so it has good effect on weight control, metabolic syndrome, and chronic diseases. Most of the dietary fiber in wheat is concentrated in the outer layer of wheat kernel. Wheat endosperm has less dietary fiber than outer layer. Wheat is processed into flour, bran, and germ. Wheat bran as a by-product of flour processing has a lot of dietary fiber, phenolic compounds, vitamins, and other phytochemicals. Although various types of wheat refined flour are popular by consumers, refined flour contains less dietary fiber because of removing most of wheat's outer layer. With the increase of milling refinedness, the obtained wheat flour has less dietary fiber.

Resistant starch is the sum of starch and products of starch degradation that is not absorbed in the small intestine by human individuals. In the small intestine, resistant starches can be fermented by the naturally occurring microflora [122]. Butyric acid as a main acid produced by these microorganisms is believed to play a positive role in promoting colon health [123].

Wheat and its products contain some amount of resistant starch, especially the heat-treated wheat products after cooling. Extrusion is the commonly used method in the processing of wheat-based products. The processing method is believed to influence the content of wheat-based products.

6.3.2 Phenolic Compounds During Processing

Phenolic acids are the main phytochemicals other than dietary fiber in wheat bran. Ultrafine grinding of wheat bran increased the bio-accessibility of phenolic acids (Rosa et al.) [124]. The research reported that wheat bran had 1.5-fold increased antioxidant capacity with the particle size decreased from 172 to 30 μm by ultrafine grinding, so the antioxidant activity was inversely related to the particle size of wheat bran fraction. Based on the above research result, the potential of using wheat bran ultrafine as a method to improve the bio-accessibility of *p*-coumaric acid, sinapic acid, and ferulic acid was researched by Hemery et al. [125]. The results indicated that ultrafine grinding increased the particle surface area of wheat bran, leading to the release of more p-coumaric acid, sinapic acid, and ferulic acid. Some research also got the same results. Brewer et al. [126] showed that the fine milling treatment resulted in higher levels of phenolic acids, flavonoids, anthocyanin, and carotenoids as compared to unmilled treatment.

Fermentation processes are commonly used in wheat-based food processing. Bacteria and yeasts convert carbohydrates into alcohols, CO_2, or carboxylic acids. Many metabolizing enzymes can be generated during fermentation. These enzymes can further hydrolyze the phenolic glycosides into free phenolic acids. Bhanja et al. [127] found that fermented wheat grains by two fungi had higher levels of phenolics compared with non-fermented wheat grains. Different thermal processing methods such as baking, cooking, toasting, and microwaving have varying effects on the phenolic compounds in whole wheat. Abdel-Aal and Rabalski [128] studied the effect of baking on free and bound phenolic acids in wheat bakery products and found that ferulic acid was the main phenolic acid of three whole wheat bakery products (bread, cookie, and muffin). Their results showed that baking increased the free phenolic acids in the bakery products, while bound phenolic acids decreased in bread. Lu et al. [33] investigated the influence of baking on the total phenolic acids in dough (mixed and proofed) and different bread fractions (upper crust, crumbs, and bottom crust) made from refined and whole wheat flour from three wheat varieties. The results showed that the concentration of the total phenolic acids in all whole wheat bread was 5.5- to 9.8-fold greater than the corresponding refined wheat flour. Total phenolic acids did not change significantly during the processing of bread from refined and whole wheat flour. In addition, the results indicated that the upper crust of bread had higher levels of total phenolic acids than the dough and crumb fractions [33, 129].

6.3.3 Carotenoids and Tocopherols During Processing

Carotenoids are known to be sensitive to light and heat [130]. Ranhotra et al. [102] studied the stability of β-carotene during baking and pre-baking processing steps for wheat-based products. The authors reported that baking caused significant reductions (74–85%) in the all-trans β-carotene isomer content. Similarly, Ranhotra et al. [131] found that carotene losses were observed during baking, from 4 to 15% for whole wheat bread and from 18 to 23% for crackers. Leenhardt et al. [132] reported losses of total carotenoids (~40%) during bread baking. Highest losses occurred in the crust than the crumbs because crust experienced higher temperatures during baking than crumbs. The authors also found that the most significant decreases (66%) in total carotenoids content occur during kneading, with a high correlation of these losses to the lipoxygenase activity of the wheat variety. Lu et al. [33] also observed a decrease in the concentration of tocopherols and carotenoids during baking of two bread fractions (crumbs and upper crust). Studies reported decreases in the tocopherol and carotenoid content during the processing of bread, biscuits, and pasta [133]. Recently, Kumar et al. [134] investigated the effect of temperature on fat-soluble compounds (total tocopherols and tocotrienols and carotenoids) in wheat bran and wheat germ and found that the reduction of total tocopherols and carotenoids in wheat germ started at 130 °C during heating treatment.

Nonthermal processing, such as sprouting and kneading, may also change the content of phytochemicals in wheat samples. Alvarezjubete et al. [135] reported that sprouting increased the total phenolic content in wheat. Leenhardt et al. [132] detected significant decreases (66%) in the total carotenoid content during kneading with a high correlation of these losses to the lipoxygenase activity of the wheat varieties. Furthermore, a 10–12% loss in the tocopherol content was found during dough kneading [132]. Changes in tocopherol and tocotrienol levels were also observed during dough making for bread, biscuits, and pasta [133], and the tocopherol content decreased by 21.4, 28.2, and 44.2% for bread, biscuit, and pasta, respectively.

6.3.4 Approach to Enhance Health Benefits of Wheat and Wheat Hybrid Bioactives

1. Breeding

For thousands of years, cereal modification techniques have been used to improve the nutritional content of grains. However, traditional breeding methods are mainly based on genetics and genetic principles. Modern breeding is a highly scientific process, supported by a range of modern technologies such as biochemical and molecular markers.

At the end of the last century, scientists used genetic mutagenesis to change the hardness of wheat grains, and by changing the genetic DNA to produce wheat varieties suitable for making bread, in order to achieve the release of flavor substances. In addition, by using a range of mutagens, including chemicals that cause single base changes in DNA and ionizing radiation, they can cause major structural changes in the chromosome, including deletions and rearrangements. A large number of mutations caused by single base changes are inherently recessive and result in inactivation of genes or gene products. They have been most successfully exploited in diploid species and in systems where single genes and proteins regulate important pathways or processes (e.g., starch synthesis and the hormonal control of stature). The predecessors also improved the active substances of wheat through transgenic technology and gene mutation methods. For example, this was elegantly demonstrated by Slade, et al. [136], who used TILLING to identify novel mutations at the waxy (granule-bound starch synthase 1) loci on the A and D genomes of bread wheat. Combination of these mutations with a previously identified waxy mutation on the B genome gave a full waxy phenotype. And the composition of wheat grain cell wall can be changed by genetic breeding to increase fiber content.

2. Increasing whole wheat flour and whole wheat products

Although various types of refined flour products are popular, refined flour essentially contains only the endosperm after whole grain processing, resulting in a loss of dietary fiber (Barros et al. [15]), which is largely in the wheat bran. Therefore, producing high dietary fiber flour is important for increasing dietary fiber intake in the daily diet for good health. In contrast to refined flour, which contains only the endosperm, whole wheat flour contains the bran, germ, and endosperm, resulting in dietary fiber retention. Furthermore, whole wheat flour is an important source of several vitamins, minerals, and phytochemicals with anticancer properties that could affect the risk of colorectal cancer through several potential mechanisms (Slavin et al. [137]). In addition, previous studies have indicated that consumption of whole grain foods can significantly reduce the risk of some chronic health conditions such as type 2 diabetes, cardiovascular disease, and cancer. Initially, the health-beneficial effect of whole grains was primarily attributed to its high-fiber content. However, recent research indicates that the beneficial effects of whole grain may arise from the combined action of several components such as fiber, vitamins, phenolics, carotenoids, alkylresorcinols, and other phytochemicals.

During wheat processing, the grinding intensity is negatively correlated with the dietary fiber content of wheat flour, and the bran component, such as whole wheat flour, is retained as much as possible. The dietary fiber content of wheat flour could also be enhanced by adding xylan from an external source.

3. Adding bran and germ and wheat shorts (by-products)

Wheat bran and aleurone fractions are rich in nutritional component such as protein, amino acid, vitamin E, fat, mineral, dietary fiber, and phytochemicals which are recognized as health benefits. Adding bran and dietary fiber to flour is another effective method for the preparation of high dietary fiber flour. Using high dietary fiber flour can meet human requirements for healthy foods. However, bran or dietary fiber can also affect flour quality, dough rheology, and high dietary fiber flour products. A lower shelf life appeared in whole wheat flour compared to white flour due to the release of enzymes in bran during whole wheat milling. However, it was found that the solid particle effect of bran caused insufficient formation of the gluten network in the dough and the loss of dough stability was attributed to the destabilizing effect of bran particles on the films separating gas bubbles. The growth and size of bubbles in bread dough during the fermentation and proofing was limited, which ultimately led to a reduction in the volume of the high dietary fiber bread. Bran particle size can affect the processing characteristics of flour. Studies also have shown that bran size has no significant effect on water absorption, while dough containing smaller bran particles has a decreased development time that is closer to that of native dough. Therefore, the researchers improved this phenomenon by treating the bran. Bran treatment mainly includes heat, extrusion, milling, and biological treatment.

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Chapter 7
Sorghum

Tongcheng Xu

7.1 Introduction

7.1.1 Morphological Characteristics

Sorghum is among the top cereal crops worldwide and is a key species ensuring global food security. The grain sorghum belongs to the grass family *Poaceae* (Gramineae). Within the family *Poaceae*, sorghum is classified in the genus *Sorghum* and is native to Ethiopia in the Horn of Africa [1]. The stalk of sorghum is thick, erect, 3–5 m high, and 2–5 cm in diameter, with supporting roots on the base section. The leaf sheath is glabrous or slightly whitely powdered; the ligule is hard and membranous, with a rounded apex and cilia at the margins; the leaf blade is linear to linear-lanceolate, 40–70 cm long, 3–8 cm wide, acuminate at the apex, dark green on the surface, and light green or white powder on the back, with a small sting and wider midribs.

The caryopsis is convex on both sides, pale red to reddish-brown, slightly exerted at the top, 3.5–4 mm long, and 2.5–3 mm wide at ripening. The petiolate spikelet is approximately 3–5 mm in length, linear to lanceolate, brown to copper in coloring, and fruiting occurs from June to September.

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7.1.2 Growth Habits

Sorghum is native to the tropics and has thus a characteristic resistance to high temperature and in fact requires higher temperatures than corn. A temperature of 20–30 °C is suitable for growth. Sorghum is a short-day crop, and as such shows accelerated development under short-day treatment.

In addition to its resistance against heat, sorghum is a cold-tolerant grain, which is most common in the semiarid regions of the Northern Hemisphere and West Asia [2]. It is drought-resistant, waterlog-resistant, salt-tolerant, and barren-resistant. The roots of sorghum are well developed, and the root cells have high osmotic pressure and a strong ability to absorb water from the soil. At the same time, the stem and leaf have a layer of white wax that can reduce sensitivity of drought. Sorghum can maintain stomatal openings at low levels of water potential and under a wide range of leaf turgor pressures [3]. This adaptation enables sorghum to maintain a higher rate of CO_2 exchange than corn at a high level of water stress.

7.1.3 Classification

Sorghum is classified into edible sorghum, sugar sorghum, and broom sorghum, depending on its properties and uses. Edible sorghum grain is eaten for food and used to make wine. The stalk of sugar sorghum can be used to make syrup or raw foods. Brooms or kitchen brushes can be made using the stalks of sorghum. Sorghum can be further divided into red and white sorghum, based on the color of the grain. Red sorghum (also known as wine sorghum) is mainly used for making wine. Famous Chinese wines, such as Moutai, Wuliangye, and Fenjiu, utilize red sorghum as a main ingredient; white sorghum is used mainly as food. The main edible species on the market today is white sorghum rice. Sorghum can be divided into early maturity, medium maturity, and late mature varieties according to the length of their growth period.

7.1.4 Planting Area, Distribution, and Yield

Currently, the total worldwide planting area of sorghum is basically stable at around 4400–4500 × 104 hm^2, with a total output of 59,834 × 10^4 t, and a single yield of 1.330 t/hm^2. India produces the largest amount of sorghum, with an annual planting area of 929.5 × 10^4 hm^2, accounting for 20.6% of the total area of sorghum in the world, with a total output of 745 × 10^4 t and a single yield of 0.8 t/hm^2; the second is Nigeria, with an area of sorghum of 698.3 × 10^4 hm^2, accounting for 15.5%, with a total output of 829.7 × 10^4 t and a single yield of 1.19 t/hm^2, followed by the Sudan, the United States, Niger, Mexico, Burkina Faso, Ethiopia, Tanzania, and China. China's sorghum planting area ranks 10th in the world, with a planting area of 74.3×10^4 hm^2, accounting for 1.6% of the total area. The yield per unit is 4.03 t/hm^2, which is three times higher than the average output worldwide, ranking first among the main producing countries. Total output reaches 299.5×10^4 t, ranking sixth in the world.

Sorghum is widely distributed and cultivated in China. However, the main producing areas are very concentrated, mainly based in the temperate regions of the northeast, north, northwest, and Huang Huai basins. The differences in the climate, soil, and cultivation systems of sorghum in these areas mean that there is a diversity of cultivars. Therefore, the distribution and production of sorghum have obvious regional characteristics. The country is divided into four cultivation areas: spring-sowing, early-maturing; spring-sowing, late-maturing; spring and summer-sowing; and the southern areas, as shown in Table 7.1.

7.1.5 Nutrient Components

The main parts of sorghum used are the grains, rice bran, and stalks. Nutritionally, sorghum grains contain 4.4–21.1% protein, 2.1–7.6% fat, 1.0–3.4% crude fiber, 57.0–80.6% total carbohydrates, 55.6–75.2% starch, and 1.3–3.5% total minerals (ash). Sorghum also provides 350 Kcal energy, calcium, phosphorus, potassium, carotene, and thiamin, as well as antioxidants through phenolics and various types of tannins [4].

1. Protein: The proteins of sorghum include albumin, globulin, prolamin, and glutelin. Prolamin and glutelin are all mainly present in the endosperm. Amino acid analysis of various protein fractions showed that there is a better distribution of all the essential amino acids in the globulins than in the prolamins. Sorghum protein is superior to wheat protein in terms of biological value and digestibility. The protein content of grain is generally 4.4–21.1%, which is slightly higher than that of corn. The contents of leucine and valine in the sorghum grains are slightly higher than those in corn, while the content of arginine is slightly lower than corn. The content of other amino acids is approximately equal to that of

Table 7.1 Distribution of sorghum production areas in China

Cultivation area	Cropping system	Distribution area
Spring-sowing early-maturing area	One crop per year	Heilongjiang, Jilin, Inner Mongolia, Shanxi and northern Shaanxi, Ningxia and central Gansu, and northern Xinjiang
Spring-sowing late-maturing area	Three crops every 2 years	Liaoning, Shanxi, Shaanxi, Hebei, Tianjin, Beijing, Ningxia Yellow Irrigation District, eastern and southern Gansu Province, Southern Xinjiang, and Xinjiang Basin
Spring/summer-sowing area	Two crops per year or three crops every 2 years	Some areas in Shandong, Jiangsu, Hebei, Henan, Anhui, and Hubei provinces
Southern area	Two crops per year	Sichuan, Guizhou, Hunan, and other provinces

corn. The content of crude protein in sorghum bran constitutes about 10%, with 9.3% in fresh sorghum distillers grains and 8.5% in fresh sorghum vinegar residue. The content of protein in the stalk and husk is relatively low, at 3.2% and 2.2%, respectively.

2. Fat: Grain sorghum contains higher lipid levels than most grains [5]; however, these are distributed within the kernel in different proportions. Germ is contained at the highest levels (76.2%), followed by the endosperm (13.2%), and the pericarp (10.6%). Compared with corn oil, grain oil has higher levels of oleic and stearic acids and lower levels of linoleic, myristic, and palmitoleic acid, making it less saturated oil.
3. Carbohydrates: Nitrogen-free extracts, including starch and sugar, are the main components of forage sorghum and are the main source of energy for livestock and poultry. The carbohydrate content of nitrogen-free extract in forage sorghum varies from 17.4% to 71.2%. There are more crude fibers in the sorghum stalk and husk, and their carbohydrate content is about 23.8–26.4%, respectively. Starch content in sorghum is equivalent to that of corn, but the starch granules are high in protein, so the digestibility of sorghum starch is lower than corn, and the effective energy value is 90–95% that of corn. Although the nutritional value of sorghum stalk and sorghum husk is not as good as that of concentrates, it has more sources, lower prices, and lower feed costs.
4. Minerals and vitamins: The content of calcium and phosphorus in sorghum is equivalent to that of corn, and phosphorus is phytate phosphorus, accounting for about 40%~70%. The contents of vitamins B1 and B6 are the same as those of corn, and pantothenic acid, niacin, and biotin levels are higher than those in corn; however, the absorption rates of niacin and biotin are both low. There are 1.4 mg of thiamine (vitamin B1), 0.7 mg of riboflavin (vitamin B2), and 6 mg of niacin in each kilogram of sorghum grains. There is some amount of carotene in the grains, stems, and leaves of sorghum, especially when used for green forage or silage.
5. Tannins: Tannin is a water-soluble polyphenol compound, also known as tannic acid. Most of tannins in sorghum grains are in the seed coat and pericarp. Tannin has a strong bitter taste, which prevents humans from digesting and absorbing food and can cause constipation. To eliminate the adverse effects of tannin on the human body, the cortex should be cleaned as far as possible when glutinous rice is milled. It can be soaked and boiled in water to improve the taste and reduce the impact on the human body.

7.1.6 Processing Methods

Sorghum is a raw material for wine, vinegar, starch extraction, and caramel processing. Sorghum can be eaten directly or processed. In recent years, research on sorghum deep processing in China and abroad has developed rapidly. In addition to the traditional use of sorghum as a staple food, brewing liquor, beer, and drink, a variety of uses of sorghum has been explored. For example, sweet sorghum stalks are used to make wine; forage sorghum is used for silage and green feed; sorghum is used to produce alcohol; sorghum husks are used to extract pigments; and sorghum grains are used to extract starch, produce bread, and make sorghum-based desserts.

7.2 Bioactive Materials in Sorghum

7.2.1 Resistant Starch and Slowly Digestible Starch

7.2.1.1 Content of Active Components of Starches in Sorghum

Starch is the most important component of sorghum grain, with content varying from 65.3% to 81%, with an average of 79.5%. In 1992, Englyst et al. [6] divided starch into three categories based on the speed of human body's release of glucose from starch: ready digestible starch (RDS), representing starch that is rapidly digested and absorbed in the mouth or small intestine (<20 min); slowly digestible starch (SDS), starch that can be digested slowly in the small intestine (20–120 min); and resistant starch (RS), which is not digested or absorbed by the normal human intestine. The authors pointed out that the main factors affecting starch digestibility and physiological reaction are the starches origins, particle structure, crystalline properties, the ratio of amylose to amylopectin, and other ingredients in starch (such as protein, and lipids). EURESTA (European Flair Concerted Action on Resistant Starch) defined resistant starch in 1993 as starch and its decomposable substances that cannot be absorbed by the human body's small intestine. Starch content in sorghum varies greatly among different sorghum varieties. The content, organized high to low, is as follows: slowly digestible starch (30.0–62.2%), ready digestible starch (15.3–23.6%), and resistant starch (16.7–43.2%). In general, the digestibility of starch in sorghum grain is the lowest because there is a strong correlation between starch granules, protein, and tannin.

7.2.1.2 Structure of Slowly digestible and Resistant Starch

The slow digestion of SDS reflects the natural structure of starch granules. The starch granules has a layered structure with an umbilicus in the middle, an elliptical growth ring formed by starch particles in the process of periodic photosynthesis, a double helix close arrangement of amylopectin formed in the crystalline region (5–6 nm), and amorphous starch chains and branched chains formed in the amorphous region. Enzymes bind to the surface of starches, act on irregular parts and amorphous regions of the starch's surface to destroy hydrogen bonds inside the particles used to maintain a spatial helix structure and the glucoside bonds used to hydrolyze starch, and then progressively push along the helix to the center of the particle. At the same time, the aperture of the small hole is gradually enlarged and then melts in the vicinity of the center, forming a hollow structure. However, the basic structure of the particle is maintained. With the further fragmentation of the starch granules, the internal channel expansion and conical residues with fewer layers appear. Using hydrothermal treatment to form SDS is required because the crystalline structure of A-type starch granules can increase the density of the amorphous zone and reduce the crystallinity of the crystalline region after enzyme treatment. Debranching enzymes can be used to form SDS because more short chains are produced after debranched treatment, and they are arranged and cross-linked via hydrogen bonds and hydrophobic interactions rather to forming a crystalline structure, thus leading to the slow digestion of starch.

According to the different sources of starch and the characteristics of enzymolysis, RS can be divided into four categories: RS1: Physically inaccessible starch. Starches in this category are embedded in a dense cell structure that cannot contact enzymes. The starch particles are embedded in other food substrates, and therefore they cannot expand and disperse in water. The rate of degradation in the small intestine is slow, and only part of it is digested and absorbed. Its structure is shown in Fig. 7.1a. RS2 (resistant granules) is a starch that is naturally digestibility-resistant because of its material structure, such as a crystalline structure. Its structure is shown in Fig 7.1b. Many studies [7] have shown that RS3 is a linear molecule of alpha-1,4-d-glucan, essentially derived from the retrograded amylose fraction, and has a relatively low molecular weight (1.2 × 105 Da) [8]. When RS3 (retrograded starch) is completely gelatinized, the starch polymer will coagulate after cooling, amylose and amylopectin coagulating to varying degrees. Starch, after coagulation and crystallization, can prevent access by amylase resulting in the anti-enzymatic properties of RS3. RS3 is heat-stable and highly resistant to enzymatic hydrolysis. Therefore, it is the key to the research of resistant starch. Eerlingen et al. [9] proposed two reasonable RS structural models: the fascicular model and the layered model. Their structures are shown in Fig. 7.1c, d. RS4 (chemically modified starch) starch is transformed from natural starch according to human needs, usually using chemical methods to introduce chemical functional groups or to change the molecular structure of starch by genetic modification to increase its anti-enzymolysis properties.

7.2.1.3 Detection of Slow Digestion Starch

The detection techniques for the SDS content are mostly based on in vitro enzymatic hydrolysis:

1. The Englyst method [6]

The principle of the method is to determine the amount of starch digested by enzymes in 20–120 min under the in vitro conditions. The basic process is 1–2 g comminuted samples in 10 mL of 5% mixed enzymes (the ratio of amylase/glucoamylase/invertase is 40:10:3), using a colorimetric method to determine the difference in starch content (i.e., the amount digested) after 20 and 120 min,

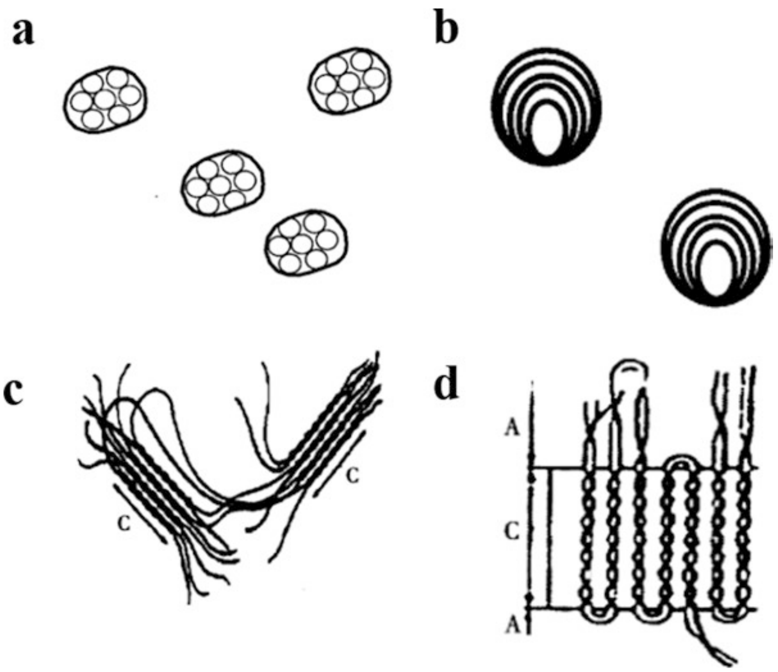

Fig. 7.1 (**a**) The structure of RS1; (**b**) the structure of RS2; (**c**) the fascicular model of RS3; (**d**) the layered model of RS3

respectively, at pH 5.2 and 37 °C. The specific calculation formula is as follows: SDS = (G120 − G20) × 0.9, where G is the starch content determined in the sample using a colorimetric method.

2. The Guraya method [10]

The principle of this method is to use pig pancreas amylase for 60 min at 37 °C. When the maltose content is hydrolyzed for certain time, 3, 5- two nitro salicylic acid (DNS) method can be used to determine SDS content at 540 nm by colorimetry. The specific calculation formula is SDS = (G − H)/I*100%, where H is the amount of maltose produced by the digestion of starch for 1 h (mg), G is the maximum amount of maltose produced by digestion of starch for 10 h (mg), and I is the total amount of starch (as the amount of maltose (mg)).

Sang et al. [11] improved the Guraya method. After adding the alpha-amylase in the freeze-dried sample, the reaction was incubated for 10 h at 37 °C [12]. The concentration of sugar produced by hydrolysis was determined by the standard curve method for maltose, namely, SDS = (B-A)/C × 100%, in which A was the amount of maltose produced by the 1 h of starch digestion (mg), B was the maximum amount of maltose produced by the 10 h of starch digestion (mg), and C is the total starch content.

The Englyst method can mimic the gastrointestinal environment of starch digestion. Therefore, it has certain advantages for the determination of different types of starch and starch degradation products. However, this method has a long operation time, uses digestion by mixed enzymes, has complex process, and the testers need special training. In addition, it has poor repeatability. Compared with the Englyst method, the Guraya method only uses a single pancreatic amylase, and the procedure is simpler and more convenient.

7.2.1.4 Detection of Resistant Starch

Most methods focus on the determination of total RS; however, specific methods have been developed to quantify RS1, RS2, and RS3. In the analysis of RS1, part of the sample (A) is chopped once, while the other part (B) is ground or homogenized to produce particles with a diameter of 0.2 mm. The released glucose G (120) is determined according to the method of determining resistant starch, as RS1 = [G120(B) − G120(A)] × 0.9. In the analysis of RS2, one portion (C) of a raw food sample is heated in 0.1 M sodium acetate buffer, at pH 5.2, in a boiling water bath for 30 min, while another portion (D) is used directly without heat treatment. The samples are hydrolyzed with amylase, and the amount of glucose in each component is determined. RS2 is then calculated as RS2 = [G120(C) − G120(D)] × 0.9. This is the most commonly used method to detect resistant starch. There are many methods to determine resistant starch in vitro. However, their basic principles are similar. They all use anti-enzymatic properties of RS, which can be dissolved in KOH or two methyl sulfoxide solution, thus making accessible to amylase. The current AOAC standard for the measurement of RS content in food comprises incubation at pH 6.0 and 37 °C with pancreatic alpha-amylase and glucoamylase for 16 h, to hydrolyze nonresistant starch in the sample into glucose [13]. Ethanol and centrifugation are then used to recover RS solids. The RS is then dissolved in 2 mol/L KOH. The glucose content is then determined after glucoamylase digestion. This method is based on a detailed study of various parameters and is simple, reliable, and reproducible.

7.2.2 *Dietary Fiber in Sorghum*

Dietary fiber in sorghum accounts for 3–8% of sorghum grain and is divided into two types: soluble dietary fiber (SDF) and insoluble dietary fiber (IDF). The AOAC method is commonly used to determine the SDF and IDF [13]. IDF accounts for 95% of total dietary fiber in sorghum and is distributed mainly in the sorghum bran but rarely in the decorticated sorghum flour. The SDF content in sorghum is very low, representing about a 5% share of the total dietary fiber. Similar to the IDF, the content of SDF in the sorghum bran and whole sorghum powder is similar and is very low in the decorticated sorghum flour [14]. With the extension of sorghum milling time, the peeling efficiency gradually increases, and the content of SDF in the decorticated sorghum flour is further reduced. The IDF in sorghum has low solubility and poor applicability to the processing of various foods. IDF also faces competition from other forms of insoluble dietary fiber, e.g., wheat bran, vegetables, and pectin. There are several disadvantages in the process of producing sorghum dietary fiber, such as high cost, poorly developed preparation techniques, and lack of application. These disadvantages have inhibited research not only on the preparation of sorghum dietary fiber but also its evaluation. The total dietary fiber, IDF or SDF, and β-glucan are significantly negatively correlated with the digestibility of sorghum flour and result in lower estimated glycemic index (EGI) values [14].

In the process of food preparation, the two most important characteristics of dietary fiber are water retention and swelling. Sorghum dietary fiber has a water-holding capacity of 7–8 ml/g, an expansion force of 7–8 g/g, an unsaturated fatty acid absorption capacity of about 2–3 g/g, a saturated fatty acid absorption capacity of 5–6 g/g, and a cholesterol absorption capacity of 6–7 g/g. These characteristics of dietary fiber are affected by many factors. With increasing temperature, the binding force between IDF and water increases, resulting in a significant increase in its water-holding capacity and expansibility. However, when the temperature exceeds 80 °C, the water-holding capacity and expansion capacity increase gradually. Under neutral conditions, the IDF shows a certain water-holding capacity and expansibility. Under a weak acid or weak base environment, hydrogen ions or hydroxide ions open hydrogen bonds inside the dietary fiber, which in turn combine with water, resulting in increased water retention and expansibility. However, in strong acid and alkali environments, the water-holding capacity and expansibility of dietary fiber decrease significantly, especially in strong alkali environments. The ionic concentration in the solution also affects the characteristics of the dietary fiber. Chloride ions, sodium ions, or potassium ions in the solution affect the expansion of the molecular structure of fiber and hydrate the electrolyte layer, resulting in a significant decrease in the binding force with water molecules. Large molecules such as sucrose in the solution can compete with the fibers for binding to water molecules, which in turn leads to a decrease in the water-holding capacity and expansibility of dietary fiber [15].

7.2.3 Sorghum Polyphenols

Polyphenols refer to a group of chemical substances in plants that are named after multiple phenol groups. In some plants, they are responsible for the plant's color, such as brown/red autumn leaves. In addition, polyphenols are strong natural antioxidants and have a variety of health functions and pharmacological effects [16, 17].

7.2.3.1 Content, Type, and Structure

Polyphenols are important secondary metabolites in sorghum kernels. They are present as many types with different structures, leading to significant differences in their bioavailability, antioxidation, and effects on the human body [18]. The effects of genes and the environment mean that the types and content of polyphenols in sorghum differ greatly depending on the species and region. Among cereals, sorghum has the highest polyphenol content, reaching 6% (w/w) in some varieties [19], and almost all plant phenolics can be found in sorghum; however the most important are phenolic acids, tannins (proanthocyanidins), and flavonoids [18].

The phenolic acids in sorghum are mainly in the form of formic acid derivatives or cinnamic acid derivatives, generally present in the free or bound form (Fig. 7.2), and are mainly distributed on the outer seed coat of sorghum grains [20]. Their content is generally between 135.50 and 479.40 μg/g [21]. The content of protocatechuate and ferulic acid is relatively high, and the content of p-coumaric acid, syringic acid, vanillic acid, gallic acid, caffeic acid, cinnamic acid, and p-hydroxybenzoic acid is relatively low [22, 23].

Tannins, also known as procyanidins, are mainly formed by the polymerization of catechins, and their structure is shown in Fig. 7.3. Cereals such as rice, wheat, and corn do not contain tannins, but they are present in sorghum and are found mainly in the seed coats [24, 25]. Tannin content in sorghum is generally between 0.2–48.0 mg/g. The darker the seed coat, the higher the tannin content, which changes with the seasons [22, 26]. The tannins in sorghum have different degrees of polymerization, and their content, distribution, and type also vary. According to the degree of polymerization (DP), they can be classified into Type I (monomer, DP = 1), Type II (low DP, $2 \leq DP \leq 10$), and Type III (high DP, $DP > 10$) [27].

The flavonoids in sorghum mainly exist in the outer seed coat of the sorghum grain. Differences in the color and thickness of seed coat therefore reflect the differences in flavonoid content among different sorghum varieties [28]. There are three major classes of flavonoids in sorghum: anthocyanins, flavones, and flavanones. Sorghum anthocyanins belong to 3-dehydroanthocyanidins and account for about 79% of the flavonoids [29]. The anthocyanin content in sorghum grains with a black seed coat (5.4–6.1 mg/g) is about 3–4 times higher than that of sorghum grains with a red and brown seed coat [30]. In addition, sorghum anthocyanins are more stable than other anthocyanins because of a lack of hydroxyl groups at the C-3 position

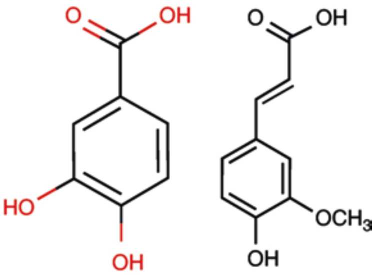

Fig. 7.2 The structure of protocatechuate and ferulic acid

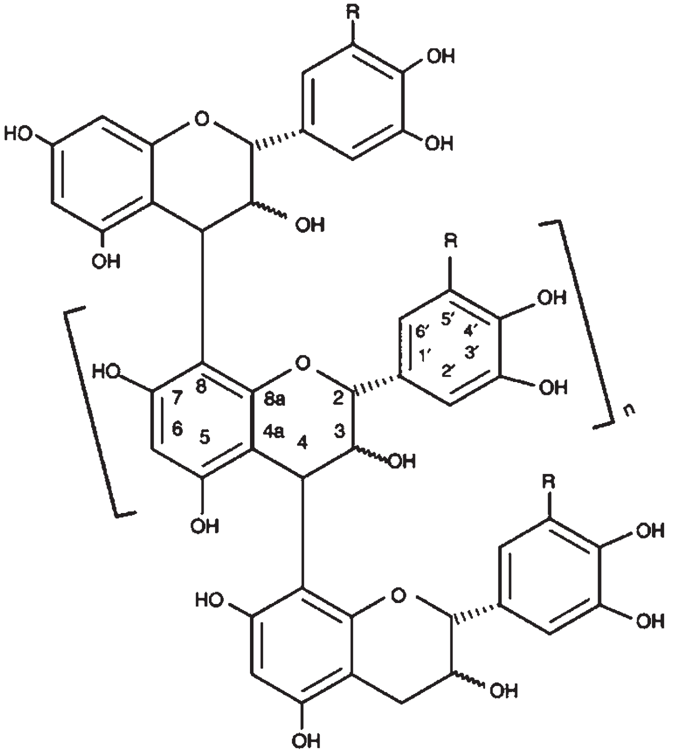

Fig. 7.3 The structure of tannins

(Fig. 7.4) [31]. The content of total flavones in sorghum is in the range of 0–386 μg/g, and they are present as the aglycone forms of luteolin and apigenin [32], the structure of which is shown in Fig. 7.5. The flavanones in sorghum are mainly present as the aglycone form of eriodictyol and naringenin (as presented in Fig. 7.6), and the highest content of flavanones is found in sorghum with lemon yellow grains (474–1780 μg/g) [28, 32].

7.2.3.2 Extraction, Separation, and Detection

There are many methods to extract polyphenols. Commonly used methods include organic solvent, ultrasonic-assisted, microwave-assisted, enzyme-assisted, and supercritical fluid extraction. The organic solvent extraction method is based on the principle of similar miscibility. Ethanol, methanol, and acetone are used as extraction solvents. This method is simple; however, it has a long extraction time and low production rate [33]. Ultrasonic and microwave-assisted extraction can destroy the cell structure to a greater extent, effectively shortening the extraction time and increasing the extraction efficiency [34]. Enzyme-assisted extraction is beneficial to

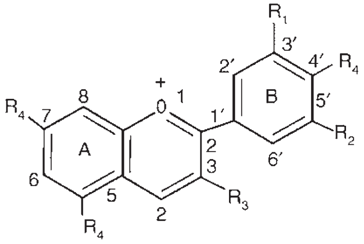

Fig. 7.4 The structure of anthocyanins (R$_1$ and R$_2$ are H, OH, or OCH$_3$, R$_3$ is a sugar group or H, and R$_4$ is a sugar group or OH)

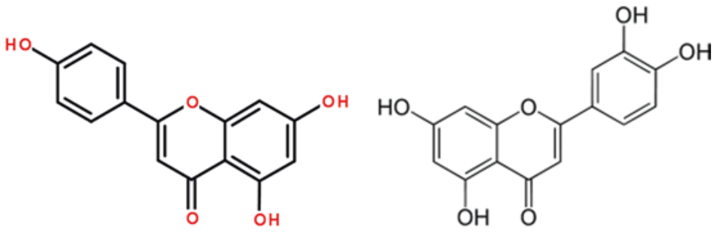

Fig. 7.5 The structure of luteolin and apigenin

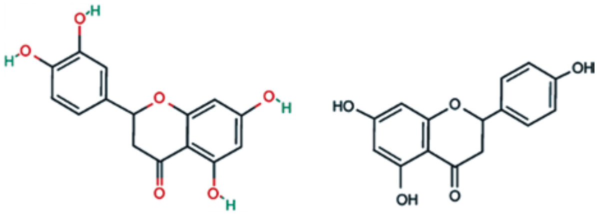

Fig. 7.6 The structure of eriodictyol and naringenin

maintain the original characteristics of the sorghum polyphenols, conditions are relatively mild, and it can maintain the conformation of natural products [35]. Supercritical fluids are nontoxic and nonpolluting and leave no residue in the extracts; however, the investment cost is high [36].

Separation and purification of extracted polyphenols is required for deep research in sorghum polyphenols. The methods used include metal ion precipitation, gel column chromatography, macroporous resin adsorption, membrane separation technology, high-performance liquid chromatography, and other methods. Metal ion precipitation technology has the advantages of simple equipment, cheap raw materials, and easy access; however, the operation is complex and the product purity is low [37]. Gel column chromatography separation can be used to process a large number of samples; however, its main drawback is that it takes a long time and consumes a large amount of solvent [38]. Macroporous resin adsorption is a separation and purification technology suitable for industrial production. Although it takes a long time and consumes a large amount of solvent, the required equipment is simple and easy to operate and has a large adsorption capacity; therefore, the resulting product is highly pure. Membrane separation is a physical change process without a phase change and is an energy-saving technology. It is generally driven by a pressure difference and has low temperature requirements. It is suitable for the separation and purification of heat-sensitive substances and can achieve separation at the molecular level. The scope of its application is extremely wide. High-performance liquid chromatography has the advantages of high speed, high efficiency, high sensitivity, and high automation; however, it requires a lot of solvents and results in a dilute product [39].

The processes for the detection of polyphenols can be divided into three categories: chemical analysis, protein binding, and physical assays. Among them, chemical analysis is the most commonly used and mainly includes colorimetry, chromatography, and spectroscopy. The colorimetric methods include the Folin-phenol method, the Prussian blue method, the Folin-Denis method, the vanillin method, and the n-butanol hydrochloric acid method [40–44]. Although colorimetric methods are cheap and easy to operate, the total relative amount of polyphenols determined by the colorimetric method cannot be used to determine certain types of polyphenols. Chromatography mainly includes gas chromatography, high-performance liquid chromatography, and liquid chromatography–mass spectrometry (LC/MS) [45, 46]. Chromatography has the advantages of simple operation, rapidity, low impurity interference, and low cost. Chromatography is a common method to determine phenolic acid compounds. Among the chromatographic methods, high-performance liquid chromatography is widely used to detect polyphenols because of its high efficiency, rapidity, small injection volume, and low degree of contamination. Common spectral detection methods include ultraviolet spectrophotometry, atomic absorption spectrometry, chemiluminescence, and near-infrared reflectance spectroscopy. Atomic absorption spectrometry is an indirect method that is more suitable to determine polyphenols with higher molecular weights and less interference. Chemiluminescence has high sensitivity, wide linear range, and simple instrumentation but suffers from poor stability [47]. Near-infrared reflectance spectroscopy has the advantages of simplicity, rapidity, low cost, and nonpolluting and does not destroy the samples. It can quickly detect the content of polyphenols in sorghum and can be used for a large number of samples [48].

7.3 Molecular Mechanism of Bioactive Compounds in Sorghum

7.3.1 Resistant Starch and Slowly Digestible Starch

SDS is easily digested in the intestines. This can improve intestinal motility, promote the excretion of excrement and intestinal toxins, and reduce the incidence of intestinal dysfunction and colon cancer. Although resistant starch is not absorbed in the small intestine, it can be fermented in the colon, producing some gases and short chain fatty acids (SCFAs). The gas produced by fermentation can increase the amount of excretion and loosen the stool. It can relieve constipation and prevent intestinal diseases, such as appendicitis and hemorrhoids. SCFAs also reduce the pH in the intestines which inhibits the growth and reproduction of tumor cells and change the expression of some oncogenes or products. Therefore, RS can be effective in preventing colon cancer. It can also improve the absorption and utilization of minerals in the intestine by reducing the intestinal pH. Natural resistant starch (RS2) in food can promote the solubility of magnesium and calcium, making them easier to absorb by human cells. However, RS3 does not have this function. RS can also help to excrete lead out of the body, stopping toxic lead from persisting in human body for too long. For patients with diabetes, the concentration of glucose in their blood increases dramatically after eating, and SDS and RS stay in the gastrointestinal tract for a long time and release glucose slowly. When glucose enters the blood, its peak value is low and the rate of decline is slow. The glucose produced can regulate the secretion of insulin. Compared with common starch, SDS stimulates postprandial insulin secretion to a lesser extent (reducing the content of the urinary C2 peptide), which regulates the blood sugar level of the body, maintaining insulin function, improving insulin sensitivity, and avoiding hyperinsulinemia and insulin resistance and other metabolic syndrome. Therefore, SDS and RS can effectively improve the postprandial blood glucose load and control the condition of patients with diabetes, especially those with non-insulin-dependent diabetes. Thus sorghum could represent a new food treatment for patients with diabetes.

With the improvement of living standards, more and more “illnesses of affluence” have appeared among modern people, such as obesity, high total blood cholesterol, and fatty liver disease. An improper diet for a long time is the main cause of simple obesity. Obesity not only has a higher mortality rate but also is associated with hypertension, heart disease, diabetes, and atherosclerosis. SDS and RS have good effects preventing and treating these symptoms. SDS is slowly digested and allows energy to be absorbed in the gastrointestinal tract. RS is not absorbed and releases energy into the gastrointestinal tract; however, it can produce a longer-lasting feeling of satiety. It is beneficial to control obesity and maintain a proper weight [49]. Eating SDS and RS every day could not only reduce the level of total cholesterol (TC) in human blood but also could reduce the content of triacylglycerol (TG). SDS reduces cholesterol mainly by increasing the level of low-density lipoprotein (LDL) receptors in the liver. The decrease in the number of TGs in LDL particles reduces the concentration of LDL cholesterol and apolipoprotein B. However, there are no obvious changes in very-low-density lipoprotein (VLDL) and high-density lipoprotein (HDL). Rat experiments showed that the effect of RS on lipid lowering is achieved by increasing the excretion of fecal sterols. Moreover, RS also plays an important role in preventing fatty liver disease, because RS can effectively reduce the level of lipids in the liver; therefore, adding dietary RS to the diet has health benefits [50].

7.3.2 Effects of Sorghum Fiber and Related Mechanisms

Few studies have evaluated the efficacy of sorghum dietary fiber. Yin [51] systematically evaluated the effects of sorghum dietary fiber on diabetes and related diseases, as well as explored the related mechanisms. The study showed that a diet containing 5% (by weight) dietary fiber reduced the body weight and reduced the liver, heart, spleen, and kidney weights significantly in insulin-resistant model rats. Sorghum dietary fiber intake also reduced glucose metabolic parameters, such as fasting blood glucose, insulin, insulin resistance, and glycated hemoglobin significantly in diabetic model rats, and significantly reduced the activity of α-glucosidase in the small intestine. The intake of sorghum dietary fiber also significantly improved blood lipid metabolism by reducing the fasting serum concentration of TC, TG, LDL-c, and free fatty acids (FFAs) significantly. Meanwhile, the serum concentration of ADP, leptin, and resistin increased significantly. Dietary sorghum fiber could significantly improve the body's antioxidant capacity. Serum malondialdehyde (MDA) levels significantly decreased, while the superoxide dismutase (SOD), catalase (CAT) activities, and total antioxidant capacity T-AOC were significantly increased after supplementation of sorghum fiber. The changes in the above four parameters in liver and heart homogenates were the same as those in the blood. Lopes et al. [52] also found that sorghum dietary fiber combined with probiotic milk could significantly reduce the serum MDA, T-AOC, and SOD activity in patients with kidney disease. Dietary sorghum fiber intake could also significantly reduce the concentrations of high-sensitivity C-reactive protein, tumor necrosis factor (TNF), and interleukin (IL)-6 in the serum, liver, and small intestine of diabetic model mice, and these effects were comparable to those of *Ginkgo biloba* extract [51]. Evaluation of the effects of sorghum whole grain on patients with nephropathy also found that serum C-reactive protein levels in the experimental group decreased significantly [52]. Sorghum dietary fiber intake could significantly inhibit a series of pathological changes caused by high glucose and high fat, such as significantly inhibiting the degree of steatosis in the liver, reducing the numbers of intracellular lipid droplets, reducing cell infiltration, inhibiting hepatocyte fibrosis, and inhibiting the degeneration of granules, steatosis, and inflammatory cell infiltration in heart tissue and the small intestine.

Sorghum dietary fiber could also effectively inhibit the proliferation of vascular endothelial cells and protect the integrity of the intima and inhibited atrophy, fibrosis, and inflammatory cell infiltration in islet cells. A mechanism study showed that compared with the high-fat model group, sorghum dietary fiber could significantly reduce the expression of genes encoding α-glycosidase, glucose transporter (GLUT-2), sodium/glucose cotransporter 1 (SGLT-1) and leptin and significantly increase the expression of the genes encoding AMP-activated kinase alpha (AMPK-α) 1 subunit, phosphatidylinositol-4,5-bisphosphate 3-kinase (PI3K) catalytic subunit delta, insulin receptor substrate 1 (IRS-1), and GLUT-4.

7.3.3 Molecular Mechanism of Polyphenols in Sorghum

7.3.3.1 Antioxidant Activity

Polyphenol compounds possess one or more aromatic rings containing phenolic hydroxyl groups, which can provide electrons, hydrogen atoms, or chelate metal ions to scavenge free radicals and exert antioxidant activity in the body. Most sorghum varieties, except for white sorghum, contain high concentrations of phenolic compounds and exhibit high antioxidant activity [53, 54]. The bran of some sorghum grain varieties has the highest antioxidant activity in all cereal crops, even higher than many fruits and vegetables [30]. The antioxidant activity of sorghum is related to the content and structure of polyphenols in bran, which is affected by the genotype and environment. Sorghum grain varieties that have a pigmented testa and thick pericarps have the highest levels of polyphenols [55].

Phenolic compounds from sorghum can upregulate the expression of phase II enzymes [56–58]. These enzymes regulate the defense system against oxidative stress by converting highly reactive electrophilic species (RES) into nontoxic and excretable metabolites [57]. The main phase II enzyme regulated by sorghum phenolic compounds is NADH-quinone oxidoreductase (NQO), and the increased activity is closely related to compounds' structure. Studies demonstrated that 3-deoxyanthocyanidins possess significant NQO-inducing activity [56, 58–60]. Meanwhile, apigenin and luteolin have no obvious efficacy; however, their 7-methoxylated forms are strong NQO inducers [56, 58]. Sorghum tannins have a poor ability to induce NQO and indeed could inhibit the increase in NQO activity caused by other phenolic compounds [56]. An in vivo study confirmed that feeding with whole red sorghum could inhibit RES in the liver of normal blood lipid animals [61].

7.3.3.2 Antitumor and Anti-metastatic Activities

Most cancers originate from DNA damage induced by carcinogens (toxic, mutagenic, and carcinogenic), which transform into reactive intermediates such as reactive oxygen species (ROS), reactive nitrogen species (RNS), and other active electrophilic metabolites, through active metabolic activation processes in vivo [31, 62]. Therefore, phenolic compounds from sorghum exert anticancer effects by scavenging active intermediates. In addition, the carcinogenesis rate is strongly dependent on the activity of the phase I (cytochrome P-450) and II enzymes, which also eliminate endogenous and environmental carcinogens [63]. Sorghum phenolic compounds can promote the elimination of carcinogens from the body by increasing the phase II enzyme activity [58] and possess chemopreventive effects on cancer. There is epidemiological evidence that corroborates their potential to prevent cancer in humans. Replacement of sorghum with corn as a staple food diet increased the incidence of esophageal cancer in South Africans [64].

Phenolic compounds from sorghum can act directly against cancer cells, including inducing tumor cell apoptosis and cell cycle arrest and inhibiting tumor growth and metastasis. The mechanisms by which sorghum's phenolic compounds induce apoptosis include decreasing phosphorylation of signal transducer and activators of transcription (STAT)5 and STAT3, upregulating the expression of apoptotic genes and proteins (BCL2-associated X, apoptosis regulator (BAX)/BCL2 antagonist/killer 1 (BAK) protein, and p53 gene expression), increasing enzyme activity (caspase-9 and caspase-3 activity), and inhibiting the expression of anti-apoptotic factors (BCL2, mitochondrial cytochrome C, and apoptosis-inducing factors) [60, 65]. Cell cycle arrest was induced by increasing cell cycle inhibitors (cyclin D, cyclin E, and retinoblastoma protein (pRb); breast tumor kinase (BRK); p53; and hypoxia-inducible factor 1α (HIF-1α) expression) [65, 66]. Tumor metastasis was inhibited by decreasing the expression and release of insulin-like growth factor 1 receptor and vascular endothelial growth factor.

The cytotoxicity of 3-deoxyanthyanidins from sorghum on cancer cells is higher than anthocyanins present in other foods [67]. Flavonoids can also induce apoptosis of colon cancer cells through their estrogenic activity [68]. Tannins from sorghum can inhibit the activity of human aromatase (CYP19) in vitro with a stronger effect than 3-deoxyanthocyanin [69]. This enzyme is the key to estrogen synthesis and is an important target for breast cancer chemotherapy that depends on this hormone [70].

7.3.3.3 Inhibition of Obesity and Inflammation

Obesity is a pandemic that correlates with various noncommunicable diseases and can induce systemic inflammation. Polymeric tannins and other phenolic compounds in sorghum can be combined with starch and protein to resist enzymatic hydrolysis [71–73]. Proteins rich in proline bind more sorghum tannins than other proteins [74]. By contrast, phenolic compounds can directly inhibit the hydrolytic activities of digestive enzymes, including amylase, glycosides, trypsin, chymotrypsin, and lipase to reduce calorific intake and animal weight gain [26, 73–77]. In addition, phenolic compounds, particularly tannin sorghums with higher degrees of polymerization, can inhibit intestinal brush border bound amino acid transporters, resulting in reduced digestive enzyme activity [78, 79]. In vivo experiments confirmed that ingested sorghum powder could reduce the risk of obesity associated with inflammation. Extruded sorghum flour (ESF) upregulated lipoprotein lipase, inhibited fatty acid synthase gene expression, upregulated peroxisome proliferator-activated receptor gamma, decreased inflammatory factor TNF-alpha, and decreased the Lee index and the percent obesity. Digitoside and 5-methoxy-butyl luteolin are the major flavonoids identified in ESF.

In a study of anti-inflammatory activity in vitro, sorghum extract enriched with 3-deoxyanthocyanidins inhibited the secretion of IL-1β, TNF-α, and nitric oxide in lipopolysaccharide-activated human monocytes [80]. These effects were not observed for varieties with high levels of tannins. However, sorghums rich in tannins were more effective than those rich in 3-deoxyanthocyanidins in inhibiting hyaluronidase, an important enzyme associated with inflammation. The greater inhibitory effect of tannins could be attributed to their ability to complex hyaluronidase via competitive binding to binding sites of this enzyme [81]. The evaluation of the in vivo anti-inflammatory effects of sorghum showed that sorghum extract rich in tannins reduced the formation of edema in rats by downregulating the expression of cyclooxygenase-2 (COX-2), resulting in decreased vascular permeability and edema with neutrophils infiltration [80, 82]. Therefore, both in vitro and in vivo studies indicate that the anti-inflammatory effects of sorghum stem from its effect on enzymes while 3-deoxyanthocyanidins act mainly on cytokines.

7.3.3.4 Antidiabetic Activity

The results of in vivo studies showed that sorghum extracts rich in phenolic compounds could significantly reduce the levels of glucose, TG, TC, and LDL in the plasma of diabetic animals, decrease the area under the glucose curve, regulate plasma insulin, increase the HDL, and improve dyslipidemia and diabetes mellitus [83–85]. Furthermore, studies in animals have shown that phenolic extracts of sorghum have a hypoglycemic effect similar to glibenclamide and antidiabetic medication used in the control group because of its strong effect on plasma glucose and insulin.

Sorghum phenolic compounds exert antidiabetic effects through various mechanisms. First, they decrease the carbohydrate digestion rate by inhibiting digestive enzyme activity. Sorghum extracts enriched in phenolic compounds induced antidiabetic effects in mice fed a high-fat diet by increasing the expression of adiponectin and peroxisome proliferator-activated receptor gamma (PPAR-γ) and reducing TNF-α expression, which resulted in improved insulin sensitivity [85]. Second, by inhibiting expression of phosphoenolpyruvate carboxykinase 2 (PEPCK) and phosphorylation of p38 protein in the liver, and increasing AMPK expression and phosphorylation, hepatic gluconeogenesis was suppressed and the blood glucose concentration decreased [84]. Third, sorghum phenolic extracts with high antioxidant activity could inhibit up to 60% of protein glycosylation, which could reduce the incidence of diabetic complications. However, sorghum bran extracts with a low antioxidant activity and phenolic compound content did not inhibit this process.

7.3.3.5 Improving Dyslipidemia and Decreasing Cardiovascular Risk

Elevated serum cholesterol is a major risk factor for cardiovascular disease (CVD). Sorghum phenolic compounds could regulate lipid and cholesterol metabolism in obese rats, improve dyslipidemia, and reduce the risk of CVD. Intake of sorghum phenolic extracts or whole sorghum could reduce the levels of TG, TC, and LDL cholesterol, increase HDL cholesterol contents in plasma [83, 84, 86], and promote the excretion of bile acids in feces [87]. These functional benefits vary depending on the sorghum variety and the type of extraction solvent used.

HDL and LDL can be further characterized into density subfractions that demonstrate greater efficacy in preventing atherogenesis and ultimately CVD risk [88]. Intake of sorghum cereal rich in condensed tannins by overweight populations increased the area under the curve (AUC) of LDL2 and LDL3 and decreased that of the small dense LDL5. The results indicated that consumption of sorghum tannins could beneficially alter lipoprotein fractions and reduce cardiovascular risk. Excessive intake of trans fat is a risk factor for CVD. Sorghum extracts could inhibit intestinal lymphatic absorption of trans fat and cholesterol in rats. However, none of these studies determined the mechanism of action.

In addition, considering the decomposition and degradation of important components of the blood vessel wall by hyaluronidase and free radicals, the efficacy of sorghum phenolic compounds in inhibiting hyaluronidase activity and scavenging free radicals plays an important role in maintaining blood vessel elasticity and function.

7.3.3.6 Regulating Gut Microbiota

Phenolic compounds in food are not completely absorbed in the gastrointestinal tract. Unabsorbed phenolic compounds and their metabolites contribute to the maintenance of gut health by regulating the gut microbial balance through the stimulation of the growth of beneficial bacteria and the inhibition of pathogenic bacteria, exerting probiotic-like effects [89–91]. Sorghum phenolic compounds can promote the growth of *Bifidobacterium* and *Lactobacillus* and reduce the proportion of *Firmicutes* and *Bacteroidetes*. Studies on other foods rich in phenolic compounds, such as anthocyanins and tannins, have also demonstrated a reduction in the genus *Propionibacterium*, *Salmonella typhimurium*, and *Escherichia coli* [92–95]. The intake of sorghum flour also regulates gut microbial balance and exerts probiotic-like effects, although RS and dietary fiber also play a role in addition to phenolic compounds [96].

7.3.3.7 Alleviation of Colitis

The intake of sorghum brans rich in 3-deoxyanthocyanins or condensed tannins could alleviate dextran sulfate sodium (DSS)-induced colitis in rats and maintain intestinal homeostasis. The mechanism of action is related to the upregulation of the expression of trefoil factor 3 (TFF3), transforming growth factor beta (TGFβ), and SCFA transporters [97].

7.3.3.8 Immunomodulatory Activity

Sorghum water-soluble phenolic compounds can promote the production of cytokines and enhance immune function by promoting the proliferation of spleen cells and stimulating the activation of macrophages. The sorghum ethyl acetate extract inhibits the complement system, which is beneficial for the treatment of diseases caused by excessive activation of the complement system [98].

In summary, the activities of sorghum phenolic compounds have been studied mainly through in vitro and in vivo animal experiments. However, there have been few studies about beneficial effects of sorghum phenolic compounds in humans.

7.4 The Effect of Processing on Availability

7.4.1 Resistant Starch and Slowly Digestible Starch

Research shows that there are many factors that affect the content of SDS and RS in food. These include the plant sources, the crystal structure type, the amylose amylopectin ratio, the starch treatment, the processing conditions, and other factors (such as the starch water content, heat treatment temperature, enzyme concentration, storage temperature, and time). Heat treatment can destroy the internal structure of starch granules and allows the crystallized regions to recrystallize after melting. Heat can also increase the density of amorphous zone and decrease the crystallinity of the crystalline region. Currently, the main methods to prepare SDS and RS are as follows:

1. Chemical methods

Chemical modification is an important and widely applied starch modification method. Wolf studied the effects of chemical denaturation on the kinetics of waxy, high, and common starch digestibility [99]. They found that cross-linking did not cause significant changes in digestibility, while etherification, oxidation, and paste refinement reduced the degree of hydrolysis, and increasing the degree of substitution further reduced starch digestibility. Müller-Röber and Kossmann [100] pointed out that the network structure between starch chains and different chain length substituents can achieve slow release of glucose after modification. Esterification is an effective method to prepare SDS and RS. Jung found that the ability of starch to bind to alpha 2 amylase was weakened after modification of octyl succinic anhydride (OSA), which reduced the digestibility of starch [101]. Other studies point out that the number of hydrophobic octyl long chains increased in starch molecules [102], and the effect of alpha 2 amylase on starch molecules was blocked, making it difficult to hydrolyze it using amylase, thus increasing the content of SDS.

2. Physical methods

Annealing, wet heat treatment (HMT), and autoclaving are commonly used methods to physically modify starch. Annealing treatment is mainly used to keep starch under moisture conditions of 60%, or 40–55%, while the HMT was carried out at 30% moisture and at a higher temperature. The two treatments are carried out between the glass transition temperature and the gelatinization temperature of starch. Autoclaving is the treatment of starch under excessive moisture and at high temperature and pressure. The main principle is the recrystallization of amylose to form a double helix structure. Therefore, high temperatures can destroy the structure of starch granules, making the starch fully gelatinized. These methods lead to obvious changes in starch functional properties, such as particle crystallinity, swelling, solubility, and gelatinization properties. These three methods are also widely used to change the nutritional properties of starch, being the main ways to produce SDS and RS.

3. Enzymological methods

Gelation of high chain starch and recrystallization of branched amylopectin by debranching enzyme treatment are widely used to generate SDS and RS. During the storage of gelatinized starch, the rearrangement of the crystallization of starch chains by hydrogen bonds is beneficial for the formation of SDS and RS. Han and Hamaker [103] hydrolyzed starch with alpha 2 amylase and recrystallized the linear products to effectively synthesize high SDS levels. The patent introduced the preparation of SDS from natural starch or commercialized starch by controlling the degree of hydrolysis of alpha-amylase: using amylase at 1~500 U enzyme activity to hydrolyze gelatinized starch for 1~500 min and storage at 0~20 °C for 6~24 h. Sang et al. [12] pointed out that a product with an SDS content of 27% could be obtained by storage for 3 days at 1 °C after hydrolyzing waxy sorghum starch using isoamylase for 8 h. Currently, a single preparation method can no longer meet the requirements for the preparation of SDS and RS. Methods such as the combination of enzymes and thermal processing have become the latest research hotspot.

7.4.2 *Effects of Processing on Fiber Availability*

Although few studies have focused on sorghum fiber processing, current studies have shown that preparation of sorghum dietary fibers is affected by different food processing technologies. The advent of cereal germination technology, which can increase the content of several active substances, such as gamma-aminobutyric acid, has attracted increasing attention and has been applied to a variety of cereals, including sorghum and brown rice. Studies have shown that germination for 14 h can significantly reduce the content of starch and ash in sorghum; however, the contents of dietary fiber, protein, fat, and other indicators were not affected significantly [104]. When the germination time was extended to 72 h, the dietary fiber content in sorghum was significantly reduced [105, 106]. Fermentation treatment could decrease the content of sorghum dietary fiber significantly, which might be because part of the dietary fiber is used by microorganisms during fermentation [105]. Soaking of dietary fiber from sorghum has little effect. This is because the dietary fiber in sorghum is mostly insoluble dietary fiber. In addition, soluble dietary fiber accounts for only about 5% of the total dietary fiber and is difficult to dissolve in water at room temperature. These features of IDF and SDF make dietary fiber content stable during soaking [105]. Cooking could also lead to a decrease in the dietary fiber content in sorghum, mainly because sorghum dietary fiber contains a portion of soluble dietary fiber that is easily dissolved in hot water during cooking [105].

7.4.3 Polyphenols

The phenolic compounds are the main bioactive compounds of sorghum. The major classes are phenolic acids, tannins, and flavonoids. Recent research shows that different factors affect the bioavailability of phenolic compounds in humans, including environmental factors, food processing, the food matrix, and interactions with other compounds and polyphenols [107, 108].

The phenolic acids in sorghum are mainly combined with arabinoxylan or lignin [24, 109, 110]. These combined phenolic acids are not hydrolyzed by human digestive enzymes, which reduces their bioavailability; however, they can be fermented by the colonic microbiota [110, 111]. The release of free phenolic acids can be significantly increased after fermentation and cooking, resulting in improved bioavailability. Sorghum tannins are also not directly digested and absorbed by animals and humans [112, 113]. Most tannins pass unaltered into the large intestine, where a portion are catabolized by the colonic microbiota, yielding a diversity of phenolic acids [113]. The biological effects of tannins are generally attributed to these phenolic acids [112]. Three classes of flavonoids are present in large quantities in sorghum: anthocyanins, flavones, and flavanones. The total flavones of the sorghum mostly comprise the aglycone forms of luteolin and apigenin [28, 32], and the flavanones are the aglycone forms of eriodictyol and naringenin. Sorghum anthocyanins belong to the class 3-deoxyanthocyanidins [29]. Although no information has been published on the bioavailability of flavonoids in sorghum, the aglycones of flavones and flavanones, the forms most prevalent in sorghum, are highly available and are rapidly absorbed and excreted according studies on other foods [112]. Compared with flavones and flavanones, 3-deoxyanthocyanins have relatively low bioavailability [114], and are dependent on the nature of their glycosyl and aglycone derivatives. The colonic microbiota hydrolyzes glycosides into aglycones and degrades them into simple phenolic acids [108], which can be further fermented in the colon [115].

Condensed tannins have a large influence on the quality of sorghum; therefore, studies to improve availability have mainly focused on them. Processing can improve the digestibility of tannins in sorghum. For example, heat treatment can degrade condensed tannins in sorghum [73], reduce the content of these compounds, and increase the bioavailability and nutritional value of sorghum, because of the higher digestibility of starch and protein. Extrusion cooking also causes degradation of condensed tannins in sorghum and increases the proportion of dimers and decreased oligomers [116]. Besides the total phenol and tannin content, the sorghum-free radical scavenging ability was reduced after extrusion. In extrudates, there was a progressive increase in phenols and tannin content with increasing feed moisture and a decrease in moisture, which resulted in the production of more monomeric and dimeric procyanidins. The extrudates could still inhibit free radical-induced oxidative DNA damage after digestion. Nixtamalization, including lime and cooking treatments, can effectively reduce condensing tannins in sorghum, while retaining other phenolic compounds and their antioxidant capacity [117]. Total phenolic and flavonoid content and antioxidant capacity correlated negatively with the lime concentration and cooking time. Soaking, steaming, and baking also affected the content and activity of phenolic compounds in sorghum. After steam treatment, the ferulic acid (free) and p-coumaric acid (bound) levels were significantly increased in sorghum. Baking resulted in a significant increase in phenolic acids, total phenolics (TPC), total flavones (TFC), and procyanidins (PAC). However, the three treatments all reduced antioxidant and inhibitory activity on α-glucosidase and α-amylase, and baking had less effect on the activity than steam treatment.

7.5 Possible Approaches to Enhance the Health Benefit of Sorghum Bioactive Compounds

7.5.1 Using the Whole Sorghum Powder

The use of whole sorghum powder as a raw material to develop different kinds of special foods for diabetic patients based on its RS and SDS controls product costs and improves competitiveness. However, the biggest problem in the process whole sorghum flour food utilization is its poor applicability in meeting the needs of various food industries. For example, the solubility of whole sorghum flour is relatively poor, making it difficult to use in meal replacement powders, formula foods for special medical purposes, and other formula food industries. Modification by ultrafine pulverization, extrusion, and other methods could improve the solubility of whole sorghum flour. However, it is worth noting that the modification should not have large impact on its digestibility, which is crucial for its health effects. In addition, the proteins in sorghum cannot form unique spatial structures, such as those formed by gluten in wheat, which greatly restricts its application in traditional Chinese food. The addition of whole sorghum powder to flour can result in insufficient proofing of dough, resulting in small volume. Even if dough can be full proofed, it is difficult to effectively maintain the internal gas during storage and transportation of dough, resulting in collapse of the dough. After the collapse, the volume of baked bread is greatly reduced. In addition, the addition of whole sorghum flour will also cause cracking of the surface of the dough, which seriously reduces the quality of the appearance of baked goods. Adding whole sorghum flour to noodles results in a decrease of their gluten content; this in turn results in a significant increase in the strip-breaking rate and the cooking loss rate. The gluten content of sorghum noodles can be maintained or even increased by adding additional gluten to solve the aforementioned problems. However, the current preparation of gluten from wheat flour faces some challenges, and the solubility of gluten is very poor, and it is very difficult to mix into the entire food system. Therefore, more studies are needed to solve these issues and to promote the application of whole sorghum flour in various food systems.

7.5.2 The Utilization of SDS and RS

SDS and RS are the bases for the control of the glycemic index of sorghum starch. There are several approaches that could be used to increase the content and efficacy of sorghum RS in the future. Our previous study showed that there was a great difference in the RS content between different varieties of sorghum, with the largest reaching about 40% and the lowest content being less than 10%. Therefore, the breeding of sorghum varieties with high RS content and establishing matched cultivation measures to ensure raw material supply in the subsequent food processing industry will become a key task in the future. Second, most of the RS currently available in the market are cornstarch and other grain starches modified by phytic acid or enzymatic digestion. These preparation processes are complex, face certain food safety risks, and the production cost is relatively high. Therefore, the development of a specific RS preparation process with matched equipment based on the characteristics of sorghum resources and the current grain starch preparation technology is very important. Meanwhile, the effective separation of RDS, SDS, and RS from sorghum flour is also important. As a native pure RS, sorghum RS could be competitive to replace the current modified starches. Third, and most important, the dynamic changes in digestive performance and processing characteristics of sorghum RS during the typical processing of different foods, such as baked bread, noodles, and food for special medical purposes (FSMP), should be studied systematically to identify the critical influencing points and to establish optimal processes to maintain the low digestibility of RS and its health effect in the final products.

7.5.3 The Utilization of Sorghum Dietary Fiber

There are two major approaches in the sorghum dietary fiber industry, as there are other grain dietary fiber industries. First, there are two kinds of dietary fiber in sorghum, water-soluble dietary fiber and water-insoluble dietary fiber, which have different health effects and different mechanisms. More importantly, the processing characteristics of these two dietary fibers in the course of subsequent food development are very different. Therefore, it is necessary to improve and optimize the current preparation processes of dietary fiber to separate these two dietary fibers effectively from sorghum. The second approach, also the most important, is to improve the taste of dietary fiber. Poor taste is the biggest problem faced by all kinds of insoluble dietary fibers utilized in the food industry. The health benefits of insoluble dietary fiber were recognized decades ago. However, the Chinese high-fiber food industry developed very slowly because the addition of dietary fiber seriously affects the taste of food. In addition, Chinese people are some of the most discriminating people for food taste in the world and rarely choose these high-fiber foods. By contrast, the high-fiber food industry, such as whole-wheat foods and sorghum food, have developed rapidly in Europe and the United States, covering all variety of foods and playing an important role in disease prevention and treatment. There are also some cases of the successful development of high-fiber foods in China. However, the content of sugar and fat is extremely high in these foods. Large amounts of sugar and fat can improve the taste and increase the palatability and selectivity of consumers. However, it is well known that high sugar and high fat contents are typical means of developing diabetes. Therefore, improving the taste by adding more sugar and fat not only greatly reduces the health benefits of dietary fiber but also could exacerbate the metabolic disturbance of glucose and lipids in the body. Therefore, improvement of the taste of foods rich in dietary fiber is very important to increase consumer acceptance and promote the development of the dietary fiber food industry. In the future, appropriate processing methods, such as extrusion, ultrafine grinding, and steam explosion technology could be used to improve fiber's processing characteristics by reducing particle size, improving solubility, and maintaining water quality.

7.5.4 The Utilization of Sorghum Polyphenols

There are two important approaches in the development and utilization of polyphenols and other active substances in sorghum. First, the extraction rate of active substances from by-products, fruits, vegetables, or even medicinal plants is relatively low. In addition, organic solvents are usually used, which results in some risk to food safety. Therefore, the use of pretreatment measures, such as superfine grinding technology, combined with new solvents and equipment, such as supercritical CO_2

extractors and subcritical extractors, to increase the extraction rate of active substances is a very important approach. Meanwhile, the use of green solvents could also reduce the impact of the industry on the environment. Second, Chinese polyphenol and other bioactive substances manufacturing industries are not approved internationally. This problem was caused by several factors, the most important of which is that the bioactive extracts are mostly mixtures of unidentified components. Therefore, the mechanism underlying the health effects of bioactive substances is unknown, which does not meet the recognition criteria for functional food internationally. This problem is particularly prominent for the Chinese traditional medicinal plant industry. Currently, the industrial production from traditional medicinal plants in South Korea, Japan, and other countries, based on the techniques and methods of Western medicine, is far ahead of that of the Chinese industry. Therefore, modern separation methods, such as membrane separation and preparative liquid chromatography, should be fully utilized to ensure the separation and purification of individual components or monomers from the mixture of bioactive compounds. Simultaneously, HPLC-MS and other methods should be used to identify the structure of the isolated compounds, making it possible to analyze the structure-activity relationship between the bioactive compound and its health effect. Finally, bioactive substances are usually not stable in nature, and their health effects are easily destroyed in the subsequent processing of different foods. Therefore, more studies are needed that focus on technology to improve the stability of active substances, such as molecular modification, embedding, and liposomes, either during the storage process or during the production of functional foods, such as tablets, powders, and emulsions.

7.5.5 Evaluating the Efficacy of Sorghum Bioactive Compounds

Compared with developed countries, the Chinese functional food industry and nutritional assessment are lagging behind. Many claims for functional food are only based on formulas instead of efficacy evaluations. Exaggerated publicity often appeared, which had a negative impact on the development of the functional food industry. Therefore, the dose effect, structure effect, and composition effect of sorghum bioactive compounds on different diseases still need to be fully determined. In terms of the dose effect, it is necessary to ascertain the nutritional support of different amounts of sorghum starch on different patients, such as those with prediabetes, diabetes, and diabetes with serious complications. In terms of the structure effect, the relationship between the structure of various polyphenols and their in vitro and in vivo antioxidant activities should be fully explored, which will provide the basis for subsequent structural modification and steady-state studies. In terms of the composition effect, the synergistic effects of bioactive compounds from sorghum combined with other bioactive substances, such as sorghum RS combined with resistant dextrin and functional lipids rich in ALA, or sorghum polyphenols combined with other antioxidants, such as vitamin C, on diseases such as diabetes and hyperlipidemia should be explored. All these evaluations will provide solid support for subsequent product development and will be a key approach in the future.

7.5.6 The Development of Special Foods for Diseases

Currently, edible products are mainly divided into four types: foods, health products, FSMPs, and medicines under the laws and regulations in China. In the order presented in the previous sentence, the product process gradually becomes more complicated, the product cost gradually increases, and the added value of the product is gradually increasing. However, the stability of the process and the risks faced by fluctuations in sales also increase accordingly. Compared with bulk grain crops, the production and utilization systems are insufficient in sorghum and other coarse cereals; thus they are not particularly competitive. Therefore, the development of specific foods with beneficial health effects, such as healthy products, like FSMP, and medicines based on the bioactive compounds in sorghum is the main approach that could provide specific nutritional support for the increasingly large number of patients with nutritional disorders such as obesity, hyperglycemia, and type 2 diabetes mellitus, ultimately enhancing their nutritional status and promoting the prevention and treatment of these diseases.

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Chapter 8
Buckwheat

Hongyan Li

8.1 Introduction

Buckwheat (BW), belonging to the family Polygonaceae, genus *Fagopyrum,* has been a widely eaten food in arid and cold regions. Buckwheat is ubiquitous almost everywhere but grows mainly in the northern hemisphere. Russia and China are the main producers of BW worldwide [1]. Among the BW species, common BW (*Fagopyrum esculentum Moench*) is most commonly grown and used, while Tartary BW (*Fagopyrum tataricum Gaertner*) is grown in mountainous regions [2]. Recently, the consumption of BW has become increasingly popular in the USA, Canada, and Europe [3]. BW is mostly consumed in the form of raw groats (dehulled seeds) and flour. The raw groats are principally used for human consumption as breakfast cereals, while the processed flour is always used to make bakery products (bread, cookies, snacks, and noodles) or BW-enhanced nonbakery products (tea, honey, tarhana, and sprouts) [4].

BW is rich in high-quality protein and starch with properties different from other cereals. Furthermore, it contains high levels of fiber, minerals, vitamins, and other bioactive compounds (e.g. flavonoids, phytosterols, D-chiro-inositol, myoinositol, free and bound phenolic acids, and phenylpropanoid glycosides), which have positive therapeutic effects on the human body. As a consequence, interest in BW as a functional food has gained momentum in the past few years [5]. The consumption of BW and BW-enriched food is related to a wide range of biological and health factors: hypocholesterolemic, hypoglycemic, anticancer, and anti-inflammatory, among them (Fig. 8.1) [3]. Therefore, BW, with both edible and pharmaceutical values, has further potential for use as an important functional food source.

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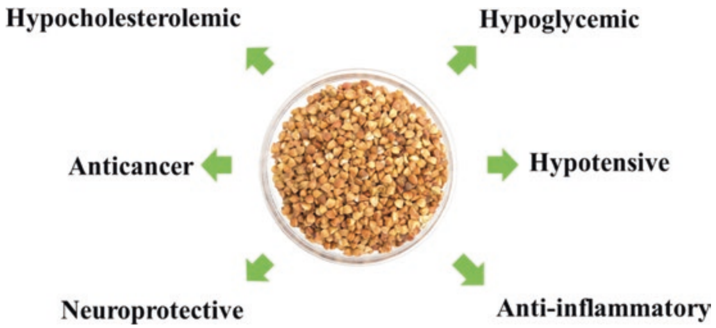

Fig. 8.1 Simplified scheme about the health benefits associated with BW or BW-enriched food. Adapted from Giménezbastida and Zieliński [3]

8.2 Bioactive Components

8.2.1 Major Nutritional Components

BW is most commonly consumed in seed form, with the general composition of BW seeds or groats between different BW-based samples listed in Table 8.1.

8.2.1.1 Carbohydrate

Starch is the major component in BW, accounting up to over 70% of the total dry weight. Similar to other cereal starches, starch contains several different levels of structure, and the relation between starch structures and properties has been extensively reviewed [7–9], so it only requires a brief introduction here. The amylose content of BW starch ranges from 20% to 28%, and starch granules are mostly polygonal, with size ranging from 2 to 15 μm and an A-type polymorph. Besides its role for supplying energy to human bodies, BW also contains a significantly higher proportion of resistant starch, which displays similar nutritional effects as fiber in inhibiting starch digestion.

As listed in Table 8.1, dietary fiber (DF) is another important source of carbohydrates, which can be as high as 12.16% in BW Samara. The DF of BW seeds are about 10.9%, while that of BW groats is 7.3%, indicating that DF is mainly present in the outer seed covering such as seed coat and hull. The total DF content of BW is comparable to other cereal grains, such as oats and wheat [10]. Furthermore, most of BW DF is insoluble; Yang et al. [11] found that, in Tartary buckwheat, the total dietary fiber content was 8.4%, of which 8.2% was insoluble, while 0.2% was soluble fiber.

Table 8.1 Comparison of proximate composition between different BW-based samples

BW product/nutrient (g/100 g)	Common BW groats[a]	Tartary BW groats[a]	Seeds[b]	Groats[b]	Dark flour[b]	White flour[b]	BW Samara[b]	BW semolina[b]	Flour[b]	Flour whole meal[b]	Groats[b]
Carbohydrate	56.1	59.18	73.3	67.8	68.6	79.5	73.82	74.34	75.31	70.74	79.8
Protein	12.3	13.15	12.3	12.2	11.5	6.4	9.66	8.52	8.24	10.86	7
Lipids	3.8	3.84	2.3	3.6	3.2	3.2	2.09	1.57	1.74	2.71	1.4
Dietary fiber	7	10.6	10.9	7.3	10	0.5	12.16	3.22	1	10	2.3
Ash	2	2.7	2.1	2	2.2	0.9	1.91	1.85	1.09	1.59	0.9

[a] Giménezbastida and Zieliński [3]

[b] Krkošková and Mrázová [6]

8.2.1.2 Protein

Protein content of BW ranges from 6.4% to 13.15% depending on variety and processing. Compared to other cereals, such as wheat, BW is rich in albumin and globulin, but very low in prolamin and glutelin, so BW is deemed to be suitable for use in coeliac diets [12]. Furthermore, BW proteins are rich in arginine and lysine, the first limiting amino acid in other plant proteins. Threonine and methionine are the first and second limiting amino acids, respectively, for all buckwheat strains. The low ratios of lysine/arginine and methionine/glycine in BW indicate that BW has a strong cholesterol-lowering effect [13].

8.2.1.3 Lipids

Tartary BW and common BW have similar lipid content, about 3.8%. The lipids of BW are mainly located in embryo (6.4% for Tartary BW), while only 0.2% is in the endosperm [14]. Tartary BW is a source of unsaturated fatty acids, containing 53.8% of oleic acid and 27.9% of linoleic acid (relative to the total fatty acids) [15]. Common BW also shows similar fatty acid composition as Tartary BW.

8.2.2 Minor Bioactive Compounds

8.2.2.1 *D*-Chiro-inositol

D-Chiro-inositol is an epimer of myoinositol which is involved in insulin signaling pathways. Correspondingly, it may have functions such as lowering blood pressure, glucose concentration, and plasma triglycerides in humans. In common buckwheat, *D*-chiro-inositol can be in forms of galactosyl derivatives [16].

8.2.2.2 Vitamins

Tartary BW contains various types of vitamins, including vitamins B (B_1, B_2, and B_6), C, and E [15]. In BW seeds, the majority of vitamin E is in the form of γ-tocopherol (117.8 μg/g), followed by δ-tocopherol (7.3 μg/g) and α-tocopherol (2.1 μg/g). Germination is reported to cause an increase of the content of some vitamins, such as vitamins C and B_1 [17].

8.2.2.3 Polyphenols

It is widely accepted that high dietary intake of polyphenols is associated with lower risks of chronic diseases such as certain types of cancer, neurodegeneration, and cardiovascular diseases. Polyphenols are the most studied phytochemicals in Tartary buckwheat.

Flavonoids. The content and composition of flavonoids are dissimilar in different BW species. Generally, the flavonoid content in *F. tataricum* (~40 mg/g) is higher than in *F. esculentum* (~10 mg/g), accounting up to 100 mg/g in Tartary BW flowers, leaves, and stems. BW seeds and sprouts are an important source of rutin (quercetin-3-rutinoside), and its content is affected by variety and environment. Tatary BW groats contain more rutin than common BW, while the rutin content of Tartary BW sprouts is 2.2-folds higher than that of common BW sprouts. Quercitrin is another glycoside present in BW and ranges from 0.54% to 1.8% in common BW. Isoquercetin (quercetin-3-glucoside) is present in BW hypocotyls, and aglycone quercetin is present in BW groats and hulls at lower concentrations than rutin. The flavone C-glycosides present in BW seedlings (vitexin, isovitexin, orientin, and homoorientin), the content of anthocyanins and proanthocyanidins, and the presence of squalene, epicatechin, and vitamin E make BW a good antioxidant source in human diet [3].

Phenolic acids. The phenolic acids in Tartary BW include *p*-coumaric, syringic, and vanillic acids in all milled samples (hull, coarse bran, and light flour). Phenolic acids are most concentrated in the brans in the free form and to a lesser extent in the bound form. It is reported that the most abundant phenolic acid in bran is *p*-hydroxybenzoic acid (up to 360 mg/g fine bran), followed by caffeic acid (38 mg/100 g fine bran), chlorogenic acid (21 mg/100 g fine bran), and protocatechuic acid (18 mg/100 g fine bran). In the hulls, protocatechuic acid is the most abundant (54 mg/100 g dry weight) [16] (Fig. 8.2).

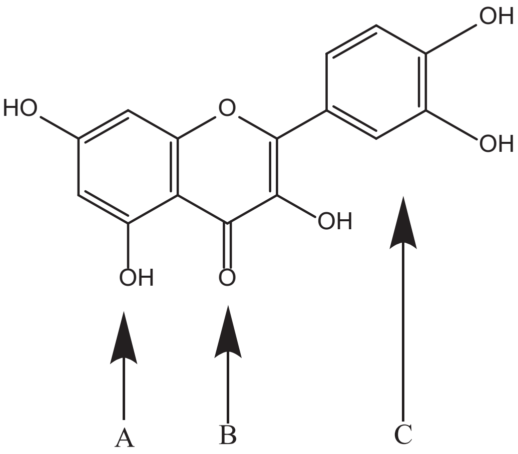

Fig. 8.2 Basic molecular structure framework of polyphenols

8.2.2.4 Minerals

Minerals are important for various physiological functions in human body. Mineral elements in buckwheat are very abundant, mainly trace elements such as K, Mg, P, Fe, Ca, Cu, Zn, Se, Ba and B, I, Pt, and Co. These trace elements are mainly concentrated in the outer layers of buckwheat seeds and shell [6]. K, Mg, Co, Cr, Zn, Ca, Fe, and other contents are all significantly higher than cereal crops, and their contents are greatly affected by cultivated varieties and planting regions. The content of Mg in BW is 3–4 times higher than rice and wheat. Taking magnesium rich buckwheat can regulate the activity of myocardium, prevent arteriosclerosis and myocardial infarction, prevent and treat hypertension, and regulate the nervous system.

8.2.2.5 Active Peptides

Buckwheat contains some peptide and nonprotein amino acids with hypotensive effects. The hydroxylated derivative of nicotinamide, 2″-hydroxy-nicotinamide, is a nonprotein amino acid isolated and purified from buckwheat flour. The substance has high ACE inhibitory activity, and the content in buckwheat flour is 30 mg/100 g. After germination treatment, the content of 2″-hydroxy-nicotinamide was 48 mg/100 g, and the content of nicotinamide was 18 mg/100 g [18].

8.3 Molecular Mechanism of Bioactives in Buckwheat

8.3.1 BW Protein

BW protein displays high biological value due to a well-balanced amino acid pattern and is rich in lysine and arginine. BW protein is reported to have many unique physiological functions, such as curing chronic human diseases, decreasing blood cholesterol, inhibiting mammary cancer caused by 7,12-dimethylbenzene, restraining gallstones, and so on. In humans, consumption of BW is associated with a lower prevalence of hyperglycemia and improved glucose tolerance in people with diabetes. Since many of the health-promoting functions are inherently related to the radical scavenging activity of peptides from the protein digests, it is hypothesized that hydrolysis of buckwheat protein can release peptide fragments capable of stabilizing reactive oxygen species and inhibiting lipid oxidation [19].

8.3.2 Polyphenols

Polyphenols is a generic term for plant components that contain multiple hydroxyl compounds linked to one or more benzene rings in the molecule [20]. The basic molecular structure framework is presented in Fig. 8.2.

It can be seen that the polyphenolic compound generally consists of three rings: the A ring and the B ring are connected to a hydroxyl group, and the C ring is an oxygen-containing carbocyclic ring [21]. Phenolics can be used as antioxidants because the mesogenic group is a phenolic functional group, which can provide hydrogen radicals, while its radical intermediates are relatively stable [22].

It has been widely accepted that polyphenols are an effective antioxidant. Its antioxidant mechanism is as follows [23]:

1. The free radical oxidation process is (RH represents a fatty acid molecule):

   Initiation: RH → R● + H●(heat, light, metal catalyst activation)
   Pass: R● + O_2 → ROO●
   ROO● + RH → R●10 ROOH
   Decomposition: ROOH→RO● + ●OH + R● + ROO●
   Termination: ROO● + AH → ROOH+A● (AH stands for antioxidant)
   Antioxidants functions are displayed in various aspects such as competitively binding to oxygen, delaying the initiation process, terminating chain reaction transfer by destroying free radicals, or in combination with free radicals [24].

2. Antioxidant and peroxide free radical action:

   AH + ROO● → ROOH+A● (AH stands for antioxidant)
   Or AH + R● → RH +A●
   Termination: A● + A● → A-A
   A● + ROO● → ROOA
   In the buckwheat polyphenols, there are generally three rings A, B, and C. The hydroxyl group on the A ring is meta, the B ring is ortho, and the C ring is an oxygen-containing ring, but not all the hydroxyl groups have strong oxidation resistance [22].

Flavonoids. As shown in Fig. 8.3, flavonoids can be divided into four types depending on their molecular structure. Its physiological properties depend on the aromatic rings containing double bonds in its structure, especially the loss of electrons in the aromatic rings [25].

Among rutin, boswellic acid, ellagic acid, and quercetin, rutin is the most active flavonoid in improving glucose tolerance and reducing FBG and serum lipids [26]. Proposed mechanisms for the antihyperglycemic effect of rutin are shown in Fig. 8.4.

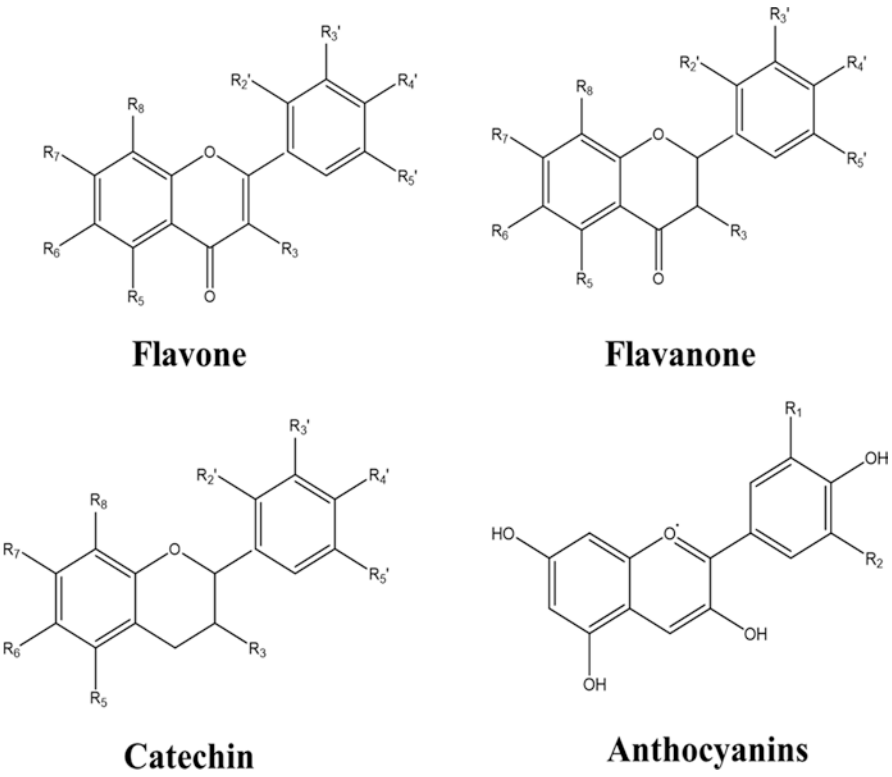

Fig. 8.3 Molecular structure of four types of flavonoids

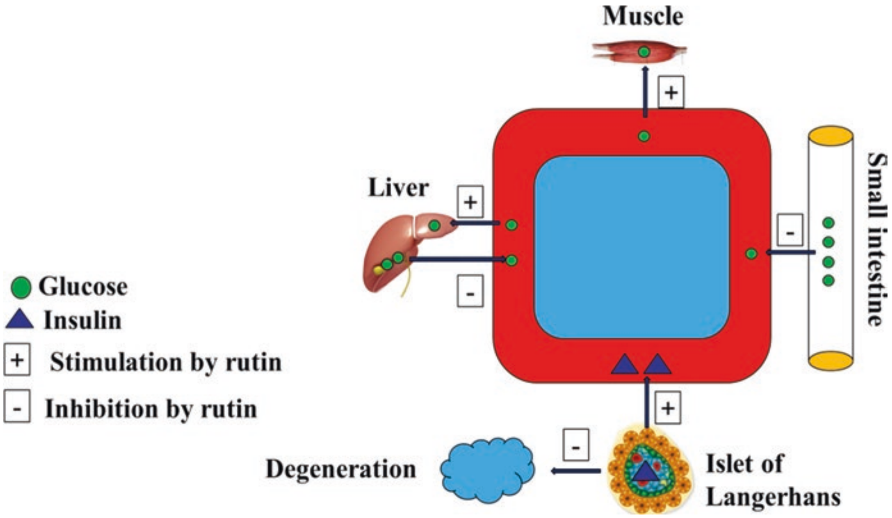

Fig. 8.4 Scheme for the proposed mechanisms for the antihyperglycemic effect of rutin

Rutin reduced glucose absorption in the small intestine by inhibition of α-glucosidases and α-amylase which is involved in the digestion of carbohydrates [26]. The inhibition of intestinal glucose absorption prevents a sharp rise in the postprandial blood glucose level. The decrease in blood glucose also can be achieved by stimulating the secretion of insulin from beta cells and increasing glucose uptake by tissues. Rutin increased the glucose-induced insulin secretion and preserved glucose sensing ability in high-glucose conditions [27]. It stimulated glucose transport into muscles through activating synthesis and translocation of the transporter GLUT-4 [28]. Similar to the insulin signaling pathway, phosphoinositide 3-kinase (PI3K), protein kinase C, and mitogen-activated protein kinase (MAPK) are involved in the intracellular transduction of rutin, leading to a stimulatory effect on tissue glucose uptake. Rutin also increases expression of PPARγ, which thereby improves insulin resistance and glucose uptake in skeletal muscle and adipose tissue [29]. Increased rate of gluconeogenesis is believed to be one of the main causes of hyperglycemia in diabetic patients [30]. Insulin inhibits hepatic glucose output predominantly by inhibiting the gene expression of key gluconeogenic enzymes glucose-6-phosphatase (G6Pase) and phosphoenolpyruvate carboxykinase (PEPCK) [31]. Rutin (50 mg/kg) reduced the activities of liver G6Pase and glycogen phosphorylase [29]. Similarly, treatment with rutin (100 mg/kg) decreased the activity of G6Pase in the liver (31%) and kidney (37%) of diabetic rats [32]. Also, rutin reduced the activity of fructose-1,6-bisphosphatase, another main gluconeogenic enzyme, in the liver (32%), kidney (25%), and muscle (31%). On the other hand, in all these tissues, rutin increased the activity of hexokinase, an enzyme catalyzing glycolysis pathways [32].

8.4 Effects of Processing on BW Bioactives

BW is mostly consumed in the form of raw groats (dehulled seeds) and flour. Two dehulling methods are commonly used: thermal and nonthermal. In thermal treatment, BW grains are saturated with moisture up to 22% of the dry weight and are steamed at 150–164 °C, sometimes from 130 to 160 °C under 5.5–6 bar, and then cooled conditioned, separated by sieving into fractions and hulled, thereby causing a brown color of grain. For nonthermal treatment, raw grains are dehulled directly. BW grains are moistened and dried until hulls become dry and kernels are moist and soft. Then the dried hulls are broken during the rolling process, while moist kernels remain intact and of natural color. Dehulling processes of BW grain affects the content of biologically active compounds and nutritional value of groats. Research evidenced that thermal treatment of BW flour is the cause of changes in protein, lipid, fiber, and ash contents, and thermal process causes a decrease in total phenolics, total flavonoids, and the antioxidative activities of Tartary BW flour extract [33].

Thermal processing of food also affects the composition and bioactivity of BW bioactives. Baking black or white BW flour at 200 °C for 10 min does not affect the total amount of polyphenols, but its antioxidant capacity is slightly decreased. Twin-screw extrusion of black BW flour shows a significant change in total polyphenol content; polar polyphenols is increased, but its antioxidant capacity is not significantly changed [34]. Heat treatment of Tartary BW powder can reduce the enzymatic activity for degrading rutin. Steam-cooking Tartary BW flour for 1 min can completely inhibit the enzymatic activity for degrading rutin, indicating steam treatment is a good way to reserve the bioactivity of rutin [35].

Germination is another process affecting the composition and bioactivity of BW bioactives. During germination, the contents of free sugar, fatty acids, free amino acids, water-soluble vitamins, and flavonoids all change. The monosaccharide content increases rapidly, while the contents of disaccharides, trisaccharides, and tetrasaccharides gradually decrease. Oleic acid is the most important fatty acid in buckwheat seedlings. After 7 days of germination, its content increases to 52.1% (of total fatty acids), and the total unsaturated fatty acid content exceeds 83%. Free amino acid content in buckwheat seedlings is almost four times that of buckwheat seeds. With the increase of germination time, the content of rutin and quercitrin increases significantly, while chlorogenic acid increases moderately; vitamin C increases more significantly than vitamins B_1 and B_6 during germination [36].

8.5 Possible Approach to Enhance Health Benefits of Buckwheat Bioactives

8.5.1 Nonthermal Processing

Emerging nonthermal processing is a potential way to develop functional BW products [37]. High hydrostatic pressure (HHP) and pulsed electrical field (PEF) processing are two typical nonthermal techniques of foods, which have been revealed as useful tools to extend the shelf life and quality [38]. These are novel food preservation techniques for microbial and enzyme inactivation as well as preservation of their nutritional and functional characteristics and bioactive components in comparison with the traditional thermal processing [39, 40]. These two techniques are successfully applied in fruit juices and functional soft drinks. For example, in HP-treated beverages, high ascorbic acid retention and high anthocyanin (cyanidin, pelargonidin, and their glycoside derivatives), petunidin, peonidin, and malvidin glycosides were observed. Therefore, HHP and PEF could be feasible technologies to attain BW products with high bioactive content and antioxidant potential [41].

8.5.2 Microcapsule Technology

Microcapsule technology is a technique that coats solids, liquids, or gases with a film-forming material to form microparticles [42]. This technique was rapidly developed and is now widely used. Microcapsules are micro-containers with polymeric wall shells or other film-forming materials. The embedded material is called core material, and the embedding material is called wall material. The advantage of microencapsulation is that it can maximize the preservation of the activity of the core material, reduce the influence of external factors, control the release of core material, and improve the operability of the core material [43]. Thus, applying microcapsule technology in preserving BW bioactive compounds for developing BW functional products is also a potential way to enhance the availability of BW bioactives.

8.6 Conclusion

Overall, buckwheat has major potential as food ingredient, especially for the functional and clinical food industry. BW in various forms (hull, seed, leaf, flower, and sprout) has unique composition of various bioactive components. It contains a significant amount of polyphenols (especially flavonols). It can be a good source of essential amino acids, dietary fiber, minerals (Zn, Fe, K, and Mg), vitamins (B, C, and E), and D-chiro-inositol. Much attention has been paid to the molecular mechanism, the processing on bioavailability, and the potential approach to enhance and preserve the health benefits of BW bioactives.

To better utilize BW, considering the requirements of improving our living quality, the main trends in recent future are expected:

- Improving traditional BW foods
- Developing new functional BW foods and further investigating its mechanisms
- Developing food additives with exclusive biological effects from BW
- Fully utilizing the by-products of BW

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Chapter 9
Rye

Guangli Feng

9.1 Introduction

Rye is the most winter-hardy crop of all the small grains. It is mainly grown in Europe and, to a lesser extent, in South America, Oceania and Northern China. Unlike wheat and other cereal grains, rye grows well in poorer soils, tolerating low pH and poor fertility. Thus, rye is a valuable crop in sandy or peaty soils.

Rye seeds are very similar to wheat seeds but are smaller and darker. Rye grain is used for the production of beer and spirits, such as whiskeys and vodkas, and is also consumed as human food and animal feed. Rye can be eaten whole, either as boiled rye berries or as rolled rye, which is similar to rolled oats. Rye is most commonly consumed as bread, made of rye flour. Rye flour is high in gliadin and low in gluten when compared to wheat flour. Though some wheat allergy patients can tolerate rye food products, they are generally not suitable for people with gluten-related disorders.

Most common grains have similar structures. For example, the bran is the outermost layer which protects the grain; the endosperm, which is mainly starch, supplies nutrients for the germinating seed; and the germ is the plant embryo [1]. The bran itself also has several layers, including the pericarp, testa and aleurone layer, as shown in Fig. 9.1 [2].

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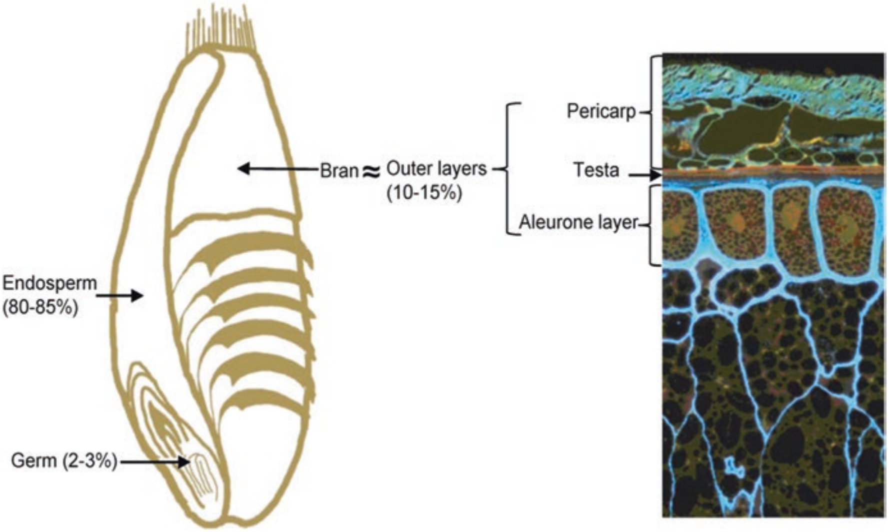


Fig. 9.1 A schematic structure of rye grain (left) and a microstructure of sections of rye grain (right). Figure is reproduced from Kamal et al. (2009) [2] and Gliwa et al. (2011) [30] with permissions. From a nutritional point of view, whole rye flour mainly contains starch (62.2%), a relatively high amount of dietary fibre (20% dry matter) [43], a medium amount of proteins (11.4%) and a small amount of fat (2.7%) [6]

9.2 Bioactives in Rye

Apart from dietary fibres, rye grains are also rich in bioactive compounds, such as sterols, folates, tocopherols and tocotrienols, alkylresorcinols, lignans, phenolic acids and total phenolics. They are mainly concentrated in the bran layers of the grain. In contrast, the rye flour, which is constituted mainly from endosperm cells, presents low levels of bioactive compounds [3].

9.2.1 Dietary Fibre in Rye

Dietary fibres are defined as carbohydrate polymers with three or more monomeric units, which are either digested or absorbed in the human small intestine and have beneficial physiological effects [4]. Of the 20% dietary fibres in wholemeal rye, 60% are arabinoxylans and cellulose, with β-glucans and lignin each constituting less than 10%. The chemical structure of arabinoxylan consists of a β-1,4-xylopyranose backbone, in which some of the xylose units are substituted with α-L-arabinofuranose at C(O)2 and/or C(O)3 (Fig. 9.2). The arabinofuranosyl residues can also be further esterified with ferulic acids, which might cross-link arabinoxylan chains or link arabinoxylan to lignin to make it insoluble [5]. However, rye

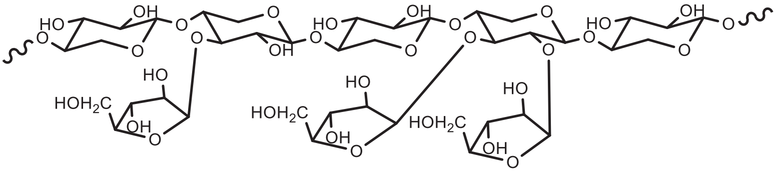


Fig. 9.2 A schematic structure of arabinoxylan [44]

Table 9.1 Arabinoxylan (AX) content in wholegrain rye and rye products (g/kg of dry matter) [7]

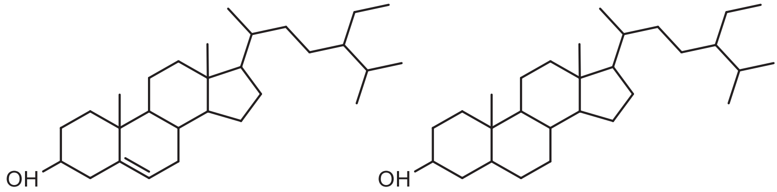
	WE AX	Total AX	References
Whole grain	36	67–121	[8]
	22	73	[9]
	22–47	90–110	[10]
	26–40	80–121	[11]
	24	90	[12]
Endosperm	–	36–43	[13]
	29	42	[6]
Aleurone[a]	46	171	[6]
Pericarp/testa	55	359	[6]
Bran	44	291	[10]
	–	206–251	[2]

[a] Aleurone-enriched fraction. *WE AX* water-extractable arabinoxylan

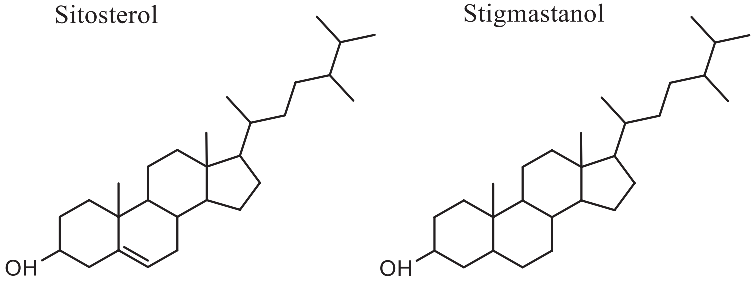
grains contain a relatively high proportion of soluble fibre; up to 41% of the arabinoxylan is water extractable [6]. In comparison, rye whole grain and endosperm contain more total arabinoxylan than wheat, whereas wheat pericarp contains more total arabinoxylan than rye pericarp. The amount of arabinoxylan from aleurone and bran is similar for both wheat and rye. However, for all arabinoxylan from wheat and rye fractions, pericarp contains the highest amount of arabinoxylan, followed by aleurone, whilst endosperm contains the least. Table 9.1 shows both soluble and total arabinoxylans in rye grain and rye products.

9.2.2 Sterols

Plant sterols, also called phytosterols, are a group of natural compounds in plants that have similar structures to that of animal cholesterols. More than 250 different sterols and related compounds in land and marine plants have been reported. In general, vegetable oils and related products are the richest natural sources of plant sterols, followed by cereal grains and nuts. However, considering the high amount of cereal products we consume, cereals are one of the most important natural sources of plant sterols in human diets, which accounts for more than 40% of the daily intake of plant sterols [14]. Rye whole grain contains higher total sterols than



Sitosterol Stigmastanol



Campesterol Campestanol

Fig. 9.3 Chemical structure of sitosterol and campesterol and their saturated forms stigmastanol and campestanol

wholegrain wheat, 99.5 mg versus 78.3 mg per 100 g dry weight. In cereals, the most common species of sterol are sitosterol and campesterol and their corresponding saturated forms, stigmastanol and campestanol (Fig. 9.3). Of the 99.5 mg total sterols, sitosterol, campesterol, stanols and other sterols are 48.5 mg, 16.7 mg, 17.9 mg and 16.5 mg [15], respectively. In terms of the biological function of plant sterols, they regulate the fluidity of membranes of plant cells. They might also play a role in the response of membranes to temperature, in cellular differentiation and in proliferation [16]. Consistent to their biological functions in plants, cereal sterols are unevenly distributed among grains, with germ and bran fractions being the richest source of plant sterols, whilst starchy endosperm is the lowest source.

9.2.3 Folates

Folates are a group of compounds exhibiting similar chemical characteristics and biological activity to folic acid. Figure 9.4 shows the structures of folic acid and most commonly folate vitamers. The basic structure of folates consists of a pteridine ring, a para-aminobenzoate, and one or more L-glutamic acid residues. In addition, the number of glutamyl residues can vary greatly, whilst folates in vivo exist mainly as folyl-poly-glutamates. Wholegrain cereals are the main natural source of folate in human diets, especially in Finland and other Nordic countries, as well as many central European countries, where the consumption of rye bread is common.

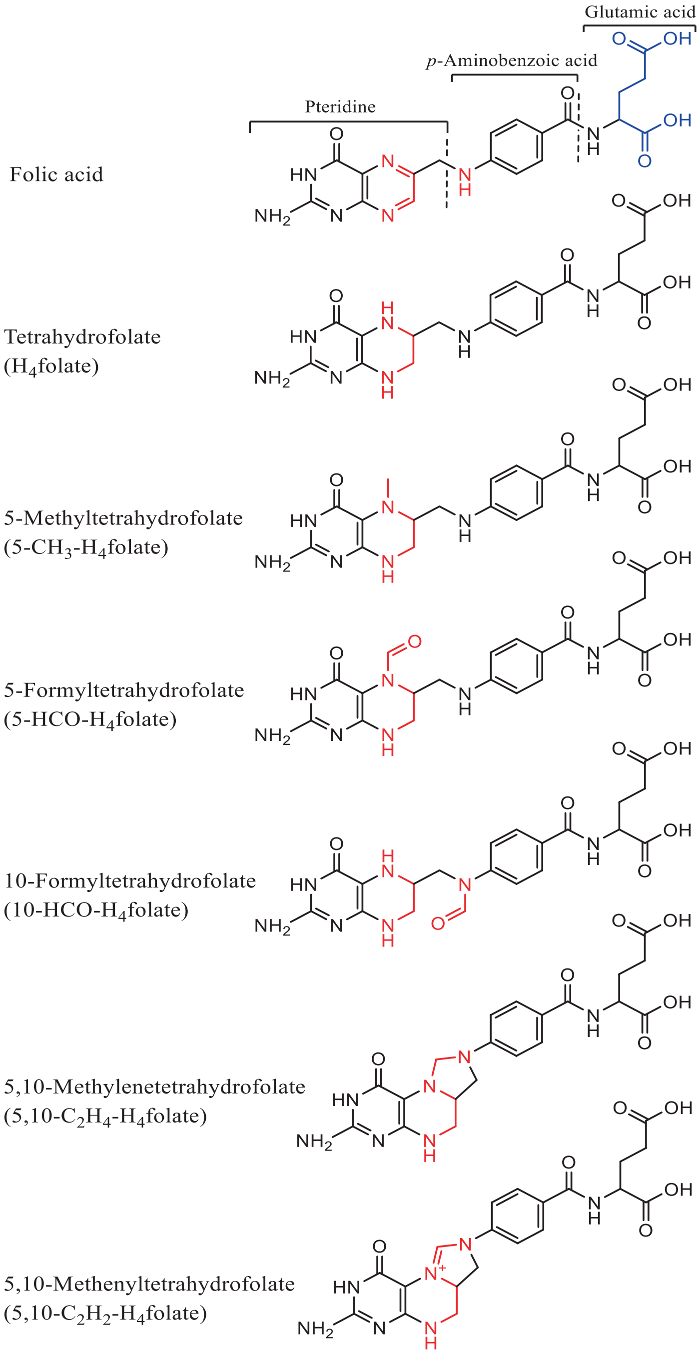


Fig. 9.4 Chemical structures of folic acid and folate vitamers

Rye products, along with orange juice, are considered an efficient way to correct folate deficiency. In comparison with wheat flour, rye flour contains considerably high amount of folates, ranging from 72 to 143 μg/100 g [17]. More than 60% of the total folates are formylated vitamers, whilst 5-methyltetrahydrofolate (5-CH_3-H_4folate) accounts for about 25%. This vitamer pattern in rye is very different to most vegetables, with 5-CH_3-H_4folate being the dominant vitamer and other vitamers accounting for less than 20% of the total vitamer [17].

9.2.4 Tocopherols and Tocotrienols

Tocopherols and tocotrienols are vitamin E homologues, which consist of a 6-hydroxychroman group and a phytyl side chain made of isoprenoid units. Tocopherols and tocotrienols are structurally similar, except that the former contains a saturated phytyl side chain, whilst the latter has three carbon-carbon double bonds (Fig. 9.5). These vitamin E homologues commonly exist in whole grains in α- and β-forms. In comparison, rye grains contain less total tocols than wheat grains, around 27.87 and 35.02 μg/g dry matter, respectively (Table 9.2). However, the biological activity of vitamin E in whole rye grains is higher than that of wheat grains, which might be because of the different vitamers in these two types of grains [18]. α-Tocols are the dominant form of tocols in rye grains, whilst β-tocols dominate in wheat grains. In addition, the distribution of tocols in wheat and rye grains is different. Wheat bran and wheat endosperm (with embryo) have similar levels of tocols, whilst the tocol level concentrates in the rye bran fraction. The concentration of tocopherols and tocotrienols is 2–3 times higher in rye bran than in rye grain, with α-tocotrienol concentration especially high in rye bran. Contrarily, the vitamin E activity of rye flours is much lower than that of rye grain.

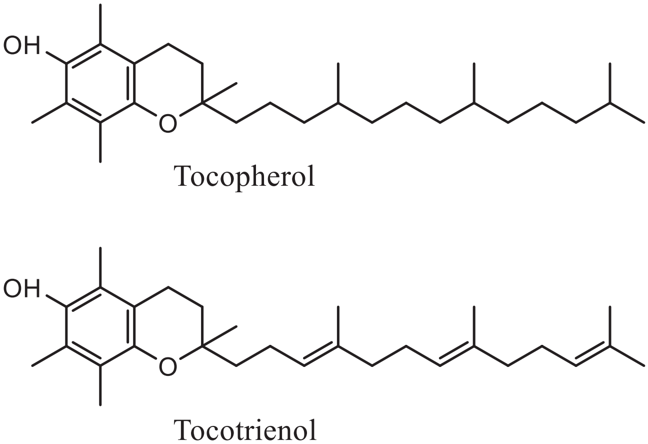
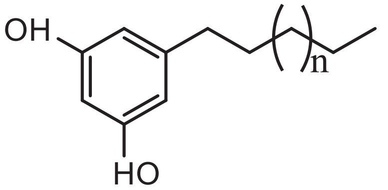


Fig. 9.5 Chemical structure of tocopherol and tocotrienol

Table 9.2 The content of tocopherols and tocotrienols in different wheat and rye fractions (μg/g dry matter) [18]

	Tocopherols		Tocotrienols			
Material	α-Form	β-Form	α-Form	β-Form	Total	Vitamin E (IU/kg)
Wheat						
Whole grain	6.06	4.23	1.05	23.68	35.02	13.8
Endosperm with embryo	3.65	1.13	0.92	21.60	27.30	8.1
Pericarp and testa	6.07	2.93	–	22.37	34.18	12.5
Rye						
Whole grain	11.46	2.28	5.94	8.19	27.87	21.2
Endosperm with embryo	1.89	–	3.97	12.80	18.66	5.5
Pericarp and testa	52.22	14.67	2.87	5.04	74.80	88.2



n = 11, 13, 15, 17, 19, 21

Fig. 9.6 Chemical structure of alkylresorcinols present in rye

9.2.5 *Alkylresorcinols*

Alkylresorcinols are one of the major groups of phenolic compounds in cereals. Although alkylresorcinols have been reported in various kinds of plant food, they are only present in high amounts in wheat and rye. Analyses show that rye contains a slightly higher amount of alkylresorcinols than wheat, 500–1300 μg/g. Structurally, alkylresorcinols are 1,3-dihydroxybenzene derivatives. An odd-numbered alkyl chain is decorated at 5 position of the benzene ring, a structure that gives alkylresorcinols amphiphilic properties (Fig. 9.6) [19]. The length of the saturated alkyl tail varies between 15 and 27 carbons, in which the alkyl chain can be mono-, di- and tri-unsaturated (mostly at positions C8, C11 and C14), or may have a keto or hydroxyl group decorated on the alkyl tail. The homologue profile between wheat and rye alkylresorcinols is different. About 90–95% of alkylresorcinols from wheat have a saturated alkyl tail with a chain length of 17–25 carbons, with a chain length of 21 in the largest proportion. In comparison, rye alkylresorcinols have relatively short chain length, mainly between 15 and 25 carbons, with a length of 19 being the dominant homologue. In addition, a proportion of 15–20% of the rye alkylresorcinols have identified with modified alkyl tails, which have been suggested to be either unsaturated or keto and hydroxyl derivatives. Despite the different structures of alkylresorcinols present in wheat and rye, their locations are similar in both cereal grains, with 99% of the total alkylresorcinols being reported present in the intermediate layer of the caryopsis, including hyaline layer, testa and inner pericarp. Therefore, alkylresorcinols are considered biomarkers of wholegrain wheat and rye intake. There were no measurable alkylresorcinols found in the endosperm or in the germ [20].

9.2.6 Lignans

Lignans are a group of natural polyphenols commonly distributed in a variety of cereals, vegetables and fruits. There is an especially high amount of lignans in rye grains. Seven dietary lignans, secoisolariciresinol, matairesinol, lariciresinol, 7-hydroxymatairesinol, pinoresinol, medioresinol and syringaresinol, are present in rye grain (Fig. 9.7). Syringaresinol is the dominant lignan in rye grain, which constitutes nearly 80% of the total lignans. Medioresinol and pinoresinol each account for less than 10%, and only small amounts of secoisolariciresinol, matairesinol and 7-hydroxymatairesinol are found [21]. The total amount of lignans ranges from 2500 to 6700 μg/100 g, depending on genetic and environmental differences [21]. In particular, larger grains are reported to contain significantly higher amounts of syringaresinol, lariciresinol and total lignans. This is the opposite trend to the hypothesis that smaller grains contain a higher proportion of lignan-rich cell walls which results in higher lignan content. Similar to the other bioactives, lignans are concentrated in the outer layers of the rye kernel, which might be associated with the plant cell wall matrix.

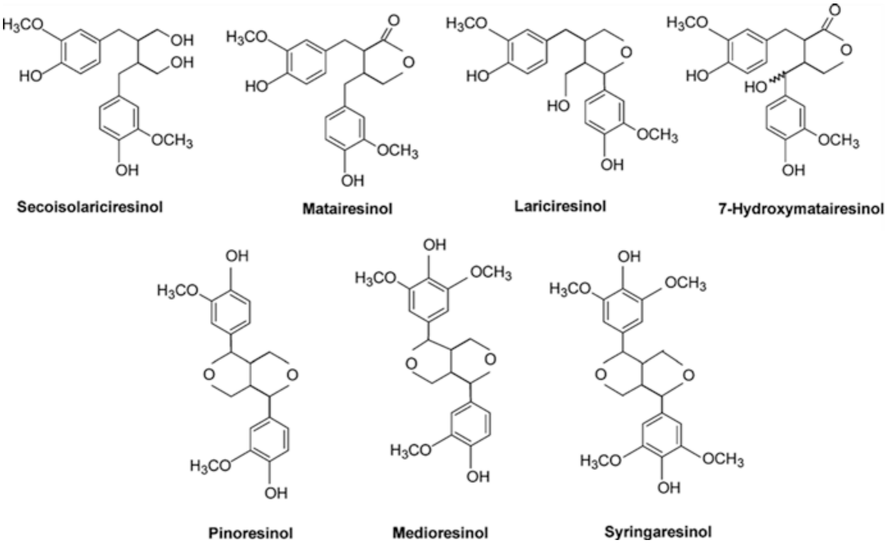
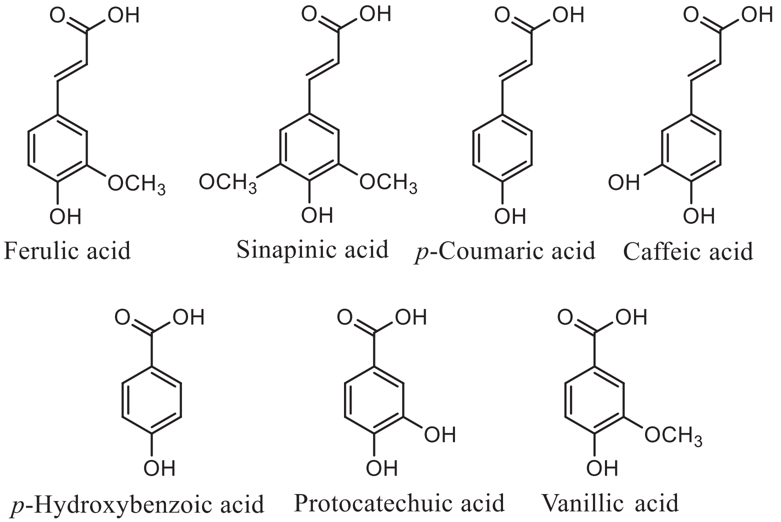


Fig. 9.7 Chemical structure of lignans. (Figure is adapted with permission [21])



Ferulic acid Sinapinic acid *p*-Coumaric acid Caffeic acid

p-Hydroxybenzoic acid Protocatechuic acid Vanillic acid

Fig. 9.8 Chemical structure of phenolic acids identified in rye

9.2.7 Phenolic Acids

Phenolic acids, also named phenolcarboxylic acids, are a group of aromatic acid compounds, which consist of a phenolic ring and an organic carboxylic acid function (C6–C1 skeleton). Seven phenolic acids have been identified (Fig. 9.8) in rye. Among them, ferulic acid is the most abundant, followed by sinapinic and *p*-coumaric acids. Analyses of 17 rye varieties showed that the concentration of ferulic acid ranges from 900 to 1170 μg/g in dry matter milled rye whole grain. The content of sinapinic acid ranges from 70 to 140 μg/g, and *p*-coumaric acid ranges from 40 to 70 μg/g. Concentrations of caffeic, *p*-hydroxybenzoic, protocatechuic and vanillic acids were below 20 μg/g [22]. Similar to other bioactives, the content of phenolic acids in the bran is proximately 15 times higher than that in the flour. Ferulic acids, which are present in the cell wall matrix, are often esterified to the O-5 position of arabinofuranose of arabinoxylan. The esterified diferulic acid links adjacent arabinoxylan chains together. Cross-linked wheat arabinoxylans have a higher water binding capacity than purified arabinoxylans and form viscous solutions. Therefore, cross-linking of polymers through diferulic dimers may be an important determinant for dough handling and bread quality, including bread baking [22].

9.3 Molecular Mechanism of Bioactives in Rye

9.3.1 Dietary Fibre

Numerous epidemiological, intervention, in vitro and in vivo mechanistic studies have shown health benefits throughout the gastric-intestinal tract, associated with the intake of dietary fibre in daily food. In the stomach, dietary fibres might slow down gastric emptying and prolong the timescale of nutrient delivery, thus potentially increasing the perceived satiety. In the small intestine, dietary fibre slows down the digestion and absorption rate of nutrients by either increasing the viscosity of digesta or by encapsulating macronutrients such as starch, proteins and lipids in the cell. These effects increase satiety, decrease energy intake, slow down lipid digestion and smooth glucose uptake, which in turn are thought to reduce the risk of obesity, cardiovascular diseases and diabetes [23, 24].

In the large intestine, dietary fibres are widely recognised "prebiotics" and exert a multitude of beneficial effects. In the large intestine, dietary fibres are (partly) broken down into smaller and absorbable nutrients by the microflora. The fermentation of dietary fibre on one hand provides energy to the microbes. On the other hand, the microflora produces smaller and absorbable by-products for the gut epithelium cells. Short-chain fatty acids, such as acetate, propionate and butyrate, are the main by-products of dietary fibre fermentation, which provide around 10% of our daily energy intake. Acetate and propionate are absorbed by the liver, and the ratio of acetate to propionate might contribute in modulating cholesterol synthesis [25]. Butyrate is the preferred energy source for the gut epithelium cells, which helps in preventing colonic cancer by promoting cell differentiation, cell-cycle arrest and apoptosis of transformed colonocytes [25]. In addition, carbohydrates are the preferred energy source for microflora growth, which, in turn, decrease the unfavourable fermentation of protein and peptides and decrease the subsequent toxic metabolite such as ammonia. Finally, the production of short-chain fatty acids provides an acidic environment in the colon, which is beneficial in inhibiting some pathogenic microbes such as *Clostridium* spp., decreasing the absorption of bile acids and ammonia and increasing the absorption of minerals [25]. Therefore, the intake of whole grains has been prescribed as beneficial in dietary guidelines worldwide. Although the recommended intake of wholemeal grains varies in different countries, it is the main intake of a healthy diet, being 250–400 g per day for an adult in China.

9.3.2 Sterols

Plant sterols are steroid alcohols, which are chemically and biologically similar to cholesterol, the predominant sterol found in animals. They function as an essential component of the membranes of all eukaryotic organisms by controlling membrane fluidity and permeability. Some plant sterols also relate to cell signal transduction.

Plant sterols can either be synthesised de novo or taken in from diet. Due to the resemblance of plant sterols and animal cholesterol, dietary intake of plant sterol inhibits the absorption and subsequent compensatory stimulation of the cholesterol synthesis. Therefore, the higher the dietary intake of plant sterols, the lower cholesterol absorption and serum cholesterol level. The usual human dietary intake of plant sterols is around 200–300 mg per day. The optimal daily intake of plant sterols for lowering cholesterol level has been reported to be 2 g [16].

9.3.3 Folates

Folate polyglutamates, the main folate vitamers in rye, need to be hydrolysed to monoglutamyl folates in the mucosa before absorption. The produced monoglutamyl folates are absorbed mainly in the jejunum through an active carrier-mediated mechanism. After absorption, folates are reduced to tetrahydro derivatives and methylated by the mucosal cells before entering the hepatic portal vein.

Folates are vital for cell division and homoeostasis because of the critical role of folate coenzymes in various biosynthetic reactions that involve the transfer of one-carbon units, including the biosynthesis of DNA and RNA through the nucleotide synthesis cycle and the metabolism of amino acids through the methylation cycle [17, 26]. In the case of folate deficiency, all the reactions involve one-carbon metabolism are affected in various degrees, depending on the relative affinities of the enzymes with the respective folate molecules. As a consequence, various substrates and metabolic intermediates will accumulate and may cause health risks. For example, in the methylation cycle, in cases of a lack of folates or vitamin B_{12}, the level of plasma homocysteine will be elevated, which has been reportedly associated with a significantly higher risk for numerous types of vascular diseases [17, 26]. Folate deficiency generally impairs nucleic acid synthesis during cell division, especially in rapid turnover tissues. Severe folate deficiency may lead to megaloblastic anaemia, which inhibits DNA synthesis during red blood cell production, resulting in the production of large immature and dysfunctional red blood cells in the bone marrow. Apart from the effect on red blood cell division, the numbers of white cells and platelets are also decreased [26]. Whilst megaloblastic anaemia is still a common consequence of folate deficiency, more attention has been given to the positive effects of folates in preventing neural tube defects in the early developmental stage of embryos. The World Health Organization has recommended a daily intake of 400 μg folates for pregnant women in early pregnancy stages to prevent maternal diseases.

9.3.4 Tocopherols and Tocotrienols

Free radicals are a group of atoms with unpaired electrons which are highly unstable and reactive. Free radicals can be formed in the human body, such as low-wavelength electromagnetic radiation (e.g. gamma rays), and can split water in the body to generate hydroxyl radical, $^{\bullet}OH$. The most commonly generated free radical in the human body is superoxide ($^{\bullet}O_2$) which is produced by adding one electron to an oxygen molecule. Superoxide is produced unavoidably in the human body due to the extensive involvement of oxygen in various biological reactions. Thus, it is essential to keep a balance between free radicals and antioxidants to enable proper physiological function. Excess free radicals might cause oxidative stress, which might adversely alter lipids, proteins and DNA and trigger ageing and numerous diseases, such as cardiovascular diseases and cancer [27]. Consumption of dietary antioxidants is important in maintaining the balance. Tocopherols and tocotrienols, as vitamin E homologues, exert antioxidant activity in vivo. Tocopherols and tocotrienols exhibit similar activity towards peroxyl radicals, with the α-forms higher than the β-forms [28]. In addition to their antioxidant function, tocopherols and tocotrienols are incorporated into the membrane and interact with unsaturated fatty acids, which play a role in membrane structure, affecting biophysical properties such as the membrane fluidity [29].

9.3.5 Alkylresorcinols

Both human and animal studies suggest that alkylresorcinols are absorbed in the upper intestine via the lymphatic system [19]. For a long time, alkylresorcinols had been considered an antinutritional factor responsible for poor growth in animals fed with rye. However, most studies investigating the antinutritional qualities in rye have concluded that the soluble fibre fraction of rye, mostly arabinoxylan, is responsible for the decreased growth of animals fed with high-rye diets.

Alkylresorcinols only show weak antioxidant activity in vitro compared to α-tocopherol. Treatment of PC-12 cells with rye outer layer extract increases mitochondrial biogenesis, and the cells are better protected from radical attack in the presence of a pro-oxidant (AAPH). However, the protective effect decreases from the outermost to innermost fraction extracts. The results suggest that higher alkylresorcinol content in bran fractions confers antioxidant protection against free radical damage [30].

In addition, alkylresorcinols can be incorporated into biologic membranes and form hydrogen bonds with neighbouring phospholipids, which may interfere with the structure of these membranes and influence the effects of membrane-bound antioxidants. Due to their hydrophobic nature, alkylresorcinols are able to bind to some proteins and affect their properties. Therefore, instead of being effective antioxidants, they may modulate oxidation reactions in membranes [19].

9.3.6 Lignans

The dietary lignans are converted into mammalian lignans, enterolactone (Enl) and enterodiol (End), by the gut microflora, and the latter is oxidised to the former after the conversion. Enl and End are absorbed through passive diffusion which is similar to the absorption of short-chain fatty acids. Therefore, serum Enl has been used as a crude biomarker of lignan intake.

Lignans exhibit weak oestrogenic, antioxidant and inhibitive activity of certain enzymes, which reduce symptoms of high lipids, hyperglycaemia and hypertension and decrease the oxidative stress and inflammation. A growing body of evidence shows that the consumption of lignans is associated with a low risk of cardiovascular diseases, metabolic syndrome and a number of cancers (e.g. breast cancer and prostate cancer) [31].

9.3.7 Phenolic Acids

Phenolic acids are health beneficial due to their antioxidant, antitumour and antimicrobial properties. Table 9.3 is a summary of the functional properties of each phenolic acid [32].

Table 9.3 Functional properties of phenolic acids [32]

Phenolic acid	Functional properties
p-Hydroxybenzoic acid	1. Antioxidant activities against free radicals. 2. Antimicrobial activities against pathogenic bacteria and fungi. 3. Oestrogenic and antimutagenic properties
Protocatechuic acid	1. Antioxidant. 2. Antimicrobial. 3. Cytotoxic. 4. Chemopreventive. 5. Apoptotic. 6. Neuroprotective. 7. LDL oxidation inhibition
Vanillic acid	1. Antisicking and anthelmintic activities. 2. Suppression of hepatic fibrosis in chronic liver injury. 3. Inhibition of snake venom 5′-nucleotidase
p-Coumaric acid	1. Antioxidant activities against free radicals. 2. Antitumour activities against breast carcinoma cell lines. 3. Antimicrobial activities by disrupting bacterial cell membranes and binding to bacterial genomic DNA to inhibit cellular functions. 4. Antimicrobial activity against pathogenic bacteria and fungi
Caffeic acid	1. Antioxidant activities performed by DPPH, ABTS and ORAC assays. 2. Antimicrobial against pathogenic bacteria and fungi
Ferulic acid	1. Antioxidant activities performed by DPPH, ABTS and ORAC assays. 2. Antimicrobial against pathogenic bacteria and fungi
Sinapinic acid	1. Antioxidant activities against free radicals such as $^{\bullet}OH$, $^{\bullet}OCCl_3$ and $^{\bullet}OOCCl_3$ [33]. 2. Antitumour by inhibiting cell growth in a non-small lung cancer cell line and colon and cervical carcinoma cell lines. 3. Antimicrobial activities against Gram positive, Gram negative and fungi

DPPH, 2,2-diphenyl-1-picrylhydrazyl radical; ABTS, 2,2-azino-bis(3-thylbenzothiazoline-6-sulphonic acid); ORAC, oxygen radical absorbance capacity

It should be noted that the bioavailability of phenolic acids is crucial to their biological properties. Free phenolic acids are rapidly absorbed and conjugated in the small intestine and delivered to the liver to be metabolised. However, in our diet, phenolic acids are present significantly in the form of polyphenols. The binding of polyphenols with plant cell wall components significantly affects the bioaccessibility and bioavailability of phenolic compounds.

9.4 Effects of Processing on Availability

Processing is a prerequisite for consuming whole rye grains. Processes such as milling, fermentation, baking and other heat treatments might have effects on the availabilities of bioactive compounds in grains.

Food processing is reported to have little effect on the amount of alkylresorcinols [34], but it decreases the extractability of alkylresorcinols, because they form complexes with starch during food processing.

9.4.1 Milling

After harvest, the hulls of rye grains are removed before their usage in food production. After hulling, rye grains are used as whole, cracked or milled into flour. Because of the unevenly distributed nutrients in rye grains, milling has a profound impact on the nutritional values of rye flour. Different mailing fractions differ in nutritional profiles. The endosperm fraction is the highest in starch (78.2%), low in fat (1.5%), proteins (6.8%) and dietary fibre (6.5%). In contrast, the pericarp/testa fraction is rich in dietary fibre (73.3%) and has the least starch (3%). Aleurone, which is between the endosperm and the pericarp/testa, is high in protein (17.6%), relatively low in starch (34.5%) and high in dietary fibre (28.3%) [6]. In addition, most of the bioactives, such as sterols, folates, tocopherols and tocotrienols, alkylresorcinols, lignans, phenolic acids and total phenolics, are concentrated in the bran layers after milling and are low in the endosperm fractions. Therefore, a significant quantity of the bioactives may be lost by removing the bran layers during milling.

9.4.2 Germination

Germination usually occurs under hydrothermal treatment in ambient conditions. During germination, a number of hydrolytic enzymes are synthesised which leads to structural changes and synthesis of new compounds. It has been reported that germination increases the levels of total phenolics, plant sterols, lignans and particularly folates, which increases more than three folds [36], whereas the amount of alkylresorcinols decreases slightly [3].

Germination temperature affects the folate content in germinated rye. With a lower temperature, more time is needed to enable complete germination, which may destroy folates through oxidation. Therefore, moderate temperatures (14–16 °C for 7 days) during germination and low temperatures during the subsequent drying (below 75 °C) enable better retention of the total folates. The folate content in the hypocotylar roots is especially high after germination. A level of 600–1180 μg/100 g dry matter folates has been detected in the hypocotylar roots, with 5-CH_3-H_4folate being the dominant folate vitamer, accounting for 67–77% of the total folates. This pattern is similar to that of most vegetables, where 5-CH_3-H_4folate usually accounts for 90% of the total folates [17].

Prolonged germination (up to 160 hours) of wheat grain increases soluble dietary fibres at the expense of insoluble fibres [37]. Although the effect of germination on rye grains hasn't been reported, dietary fibre profiles between rye and wheat are similar; germination of rye grains might also have a similar trend.

9.4.3 Fermentation

Fermentation is generally done by adding yeast starters, such as *Saccharomyces cerevisiae* (baker's yeast). Fermentation of sourdough with *S. cerevisiae* for 20 h at 30 °C dramatically increases the content of folates and total phenolics, particularly folate that increases to 2–3 folds during fermentation with yeast and microbes. The increase is mainly due to folate synthesis by yeast [36, 38], because fermentation without yeast did not change the content remarkably.

In addition to improving the bioaccessibility of many bioactive compounds, fermentation also increases the extractability of rye pentosans and produces prebiotic oligosaccharides [39]. However, fermentation of sourdough might decrease the total dietary fibre, which may be attributed to endogenous enzymes and acidic hydrolysis, because of the low pH [40].

However, fermentation has little effect on the levels of plant sterols, alkylresorcinols and lignans, whereas it slightly decreases the level of tocopherols and tocotrienols, which is probably due to oxidation [3].

9.4.4 Baking and Temperature Treatment

Baking and heat treatment have profound effects on many bioactives.

Tocopherols and tocotrienols are sensitive to heat processing. The losses of tocopherols and tocotrienols in rye wholemeal flour are variable and noticeable in baking, with the losses of α-tocopherol, α-tocotrienol, β-tocopherol and β-tocotrienol being 49%, 44%, 37% and 33%, respectively. After baking, the contents of α-tocopherols, β-tocopherols, α-tocotrienols, and β-tocotrienols in rye bread are 2.51, 0.61, 1.85 and 1.53 μg/g dry matter, respectively [41]. Extrusion cooking also dramatically decreases the levels of tocopherols and tocotrienols, with 63–94% of vitamin E activity decreased. The tocopherol and tocotrienol losses are particularly high if degradative reactions have already started in flours or if the preparation time for dough is lengthy [42].

The total folate loss during baking is around 25%. The vitamer of H_4folate is completely destroyed, whilst 5-CH_3-H_4 folate and 5-HCO-H_4folate are relatively stable, losing 67% and 76%, respectively [17].

Baking has little effect on the content of dietary fibres or phenolic acids in rye, although the total phenolic acids in rye bread decrease slightly in wholemeal bread crumb (1472 μg/g dry matter), in comparison to rye wholemeal flour (1575 μg/g dry matter). The decrease is mainly caused by the diminution of ferulic acid, the dominant phenolic acid in rye, in the preparation of imitated sourdough. Nevertheless, phenolic acids are relatively stable in the bread-making process [40].

9.5 Possible Approach to Enhance Health Benefit of Rye Bioactives

As discussed in the previous section, dietary fibres and bioactives are present in different fractions in the bran layer after milling. It is therefore essential to consume wholemeal rye to improve health benefits. One of the benefits of eating rye grains in comparison to wheat is that rye is usually included in food products in the form of wholemeal flour or whole grains, such as wholemeal rye bread and wholegrain rye flakes.

Germination is another approach to enhance the health benefits of rye products. Although germination and malting (limited germination) are normally used in brewing and distilling industries, they can also be used to produce ingredients enriched with health-promoting compounds. Germination is usually carried out by soaking grains in water (steeping), and the grains are germinated under controlled conditions. The germination is terminated by drying with hot air (kilning). The metabolic activity in the embryo increases during germination, which leads to formation, release or metabolisation of various compounds. For example, germination increases the amount of folates and soluble dietary fibres and the bioaccessibility of phenolic acids, which enhance the health benefits of rye products. In addition, germination provides raw material that is rich in enzymes and microbes that might be useful in later processing steps, such as fermentation. Along with the increases of bioactives, germination also renders food products with different flavour and colour.

Fermentation of rye sourdough by yeasts and endogenous enzymes, a common approach in rye bread making, also increases the levels of some bioactives, therefore providing health benefits. In particular, fermentation of sourdough made of germinated rye increases the levels of many bioactives – the plant sterols increase more than two folds, folates increase more than eight folds, total phenolics increase more than four folds, and free phenolic acid increases nearly ten folds [36]. The two folate vitamers 5-CH_3-H_4folate and 10-formyltetrahydrofolate (10-HCO-H_4folate) are mainly responsible for folate increases. The significant increase of the bioactives might be because germination provides raw materials that are rich in enzymes and yeasts and are able to carry out further fermentation.

In order to obtain the maximum health benefits of rye products, it is not merely enough to increase the bioactive levels through germination and fermentation. The latter processes, such as proofing after fermentation, dilute the increased effect during fermentation. Baking, on the other hand, greatly decreases many bioactives. Therefore, bioactives might be better retained through a low-temperature treatment. For example, the losses of tocopherols and tocotrienols in cooking rye porridge are under 5%, whereas baking and extrusion decrease the amounts by more than 30%.

In conclusion, when prepared and consumed wisely, rye products are very healthy.

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Chapter 10
Bioactives from Millet: Properties and Effects of Processing on Bioavailability

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10.1 Introduction

Millets are one of the most drought-tolerant and high-yielding cereal crops. They are vital for most people living in Africa and Asia. Although there are various types of millet, five types are most commonly grown in different parts of the world: common or proso millet (*Panicum miliaceum*), foxtail millet (*Setaria italica*), finger millet (*Eleusine coracana*), pearl millet (*Pennisetum typhoideum*) and barnyard millet (*Echinochloa frumentacea*) [1]. Common or proso millet is cultivated mostly in India, Central Europe, Russia, China and the Middle East [2, 3]. This crop has a short growing period of about 10–11 weeks and is able to grow at a wide range of altitudes with little water [2, 3]. Foxtail millet is cultivated in 23 countries but China, India and Japan are the chief growing countries [4]. It is not only a crop of short growth duration but also is highly resistant to pests and diseases. Its grains make nutritious and healthy food [4] and have been found to have medicinal properties [5]. Finger millet is widely grown in the semiarid areas of Africa and in the Indian subcontinent. It plays a key role in the livelihood of farmers in those regions [6, 7]. Finger millet has been reported to have some hypoglycemic, hypocholesterolemic and antiulcerative properties [6]. Barnyard millet is a fast-growing variety that is mainly grown in India, Japan, China, Malaysia, East Indies, Africa and the USA [8].

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Pearl millet is the most widely grown type of millet with cultivation mainly in developing countries. India is known to be the single largest producer of pearl millet in the world [9]. In the USA, pearl millets are cultivated in the Great Plains of the Dakotas, Colorado and Nebraska [10].

The commercial processing of millets into value-added food and beverage is a major driver for the economy in developing countries [11]. For instance, millet ranks sixth in production after wheat, rice, maize, sorghum and bajra in India. It is generally used as whole meal for preparing traditional foods, such as *roti* (unleavened breads or pancake), *mudde* (dumpling) and *ambali* (thin porridge) [12]. Other foods prepared from millets include porridges, steam-cooked products, boiled rice-like products, alcoholic and non-alcoholic beverages and snacks [13, 14]. With the increasing world population, millets represent important cereal crops for human consumption because unlike wheat, barley or rye, millet is gluten-free [11]. The number of people suffering from gluten allergy is increasing globally and thus demand for gluten-free cereals is escalating dramatically. In developed countries, there is a growing demand for gluten-free foods and beverages from people with coeliac disease and other intolerances who cannot eat products from wheat, barley or rye [11].

Millets are a rich source of protein, carbohydrate, minerals and bioactive polyphenols [15–17]. Compositional analysis of millet showed that it contains all the major nutrients that are common to other cereal grains. Depending on the variety, climatic conditions, growing conditions and type, millet contains 60–70% carbohydrates, 7–11% protein, 1.5–5% lipids, 2–7% fibre and an abundance of minerals and vitamins [14]. Millet protein contains most of the essential amino acids except lysine and threonine but relatively high quantities of methionine [18]. Individual components of millets have beneficial health effects. Since millets are often prepared as whole grain or whole meal, a combination of its intact structure, dietary fibre, minerals, phenolics and vitamins has synergistic effects on human health. Therefore, this chapter will focus on the health benefits and their molecular mechanism and effects of bioprocessing on the retention and bioavailability of bioactive compounds from millets.

10.2 Structure of Millet Grain and Distribution of Bioactives

As described earlier, there are several varieties of millet around the world; however, the basic structure of the grain is almost identical in all millet types. Similar to other grains, millet consists of a pericarp, an endosperm and a germ (schematic diagram is shown in Fig. 10.1). The pericarp is the outermost and protective layer that surrounds the endosperm and germ of the seed. The endosperm consists of starchy endosperm and aleurone layer. The starchy endosperm is the largest component of the grain and consists of floury and horny portions. The aleurone layer that surrounds the starchy endosperm contains protein, lipids, vitamins and minerals. The germ of the grain includes the embryo and scutellum and is rich in lipids, proteins and minerals. Compared to other cereals, millet has a comparatively larger germ,

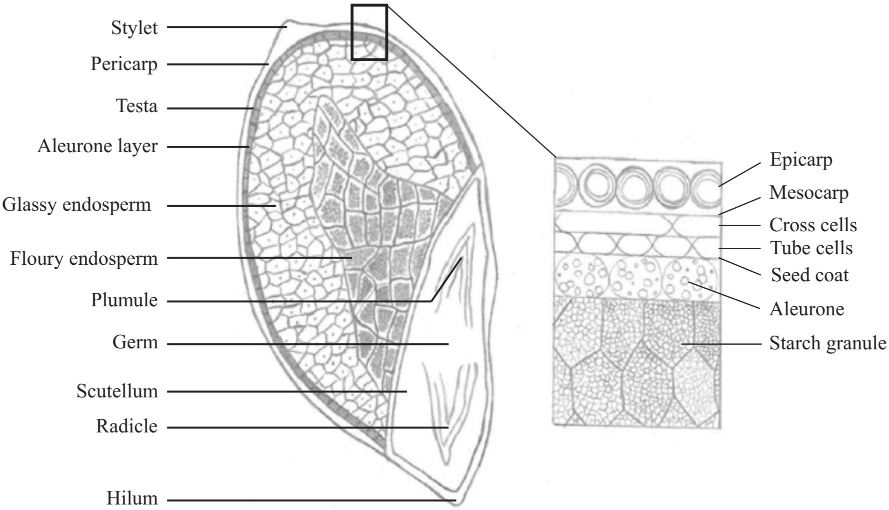


Fig. 10.1 Schematic diagram showing the structure of millet grain. The figure concept is based on the detailed structure of the grain reported by Mcdonough and Rooney [20]

thus reducing the amount of starchy endosperm. For example, proso millet has 70% by weight of grain as endosperm whereas its close relative sorghum has more than 80% endosperm in grain. In-depth structural characteristics of millet and other cereals grains are reported elsewhere [19, 20]. However, it is to be noted that the fine structure such as pericarp thickness and germ-to-endosperm ratio vary significantly among varieties.

It is well established that majority of the bioactives in millet are located in the seed coat. The endosperm is mainly comprised of starchy portion and contains negligible quantity of bioactives [6]. The ensuing section describes the major bioactives in millet and effect of processing on the availability of these compounds.

10.3 Polyphenols: Major Bioactive Compounds in Millet

Apart from being rich in carbohydrate, protein, crude fibre, fat, calcium, iron and niacin [14], several studies have shown that millets also have a broad range of bioactive phytochemicals that are beneficial to human health. Notable among these phytochemicals are polyphenols [1, 12, 14–16]. Polyphenols are naturally occurring plant-derived antioxidants with known health benefits [21]. Polyphenols often act as antioxidants within the human body to protect against oxidative stress and to reduce the risk of non-communicable diseases [16, 22]. Polyphenols have also been shown to reduce the incidence of oxidative stress and related conditions, including chronic fatigue syndrome, neurodegenerative and cardiovascular diseases and sickle cell anaemia [23–25]. Other bioactive properties of polyphenols include anticarcinogenic,

Table 10.1 Major polyphenolic compounds in different types of millet

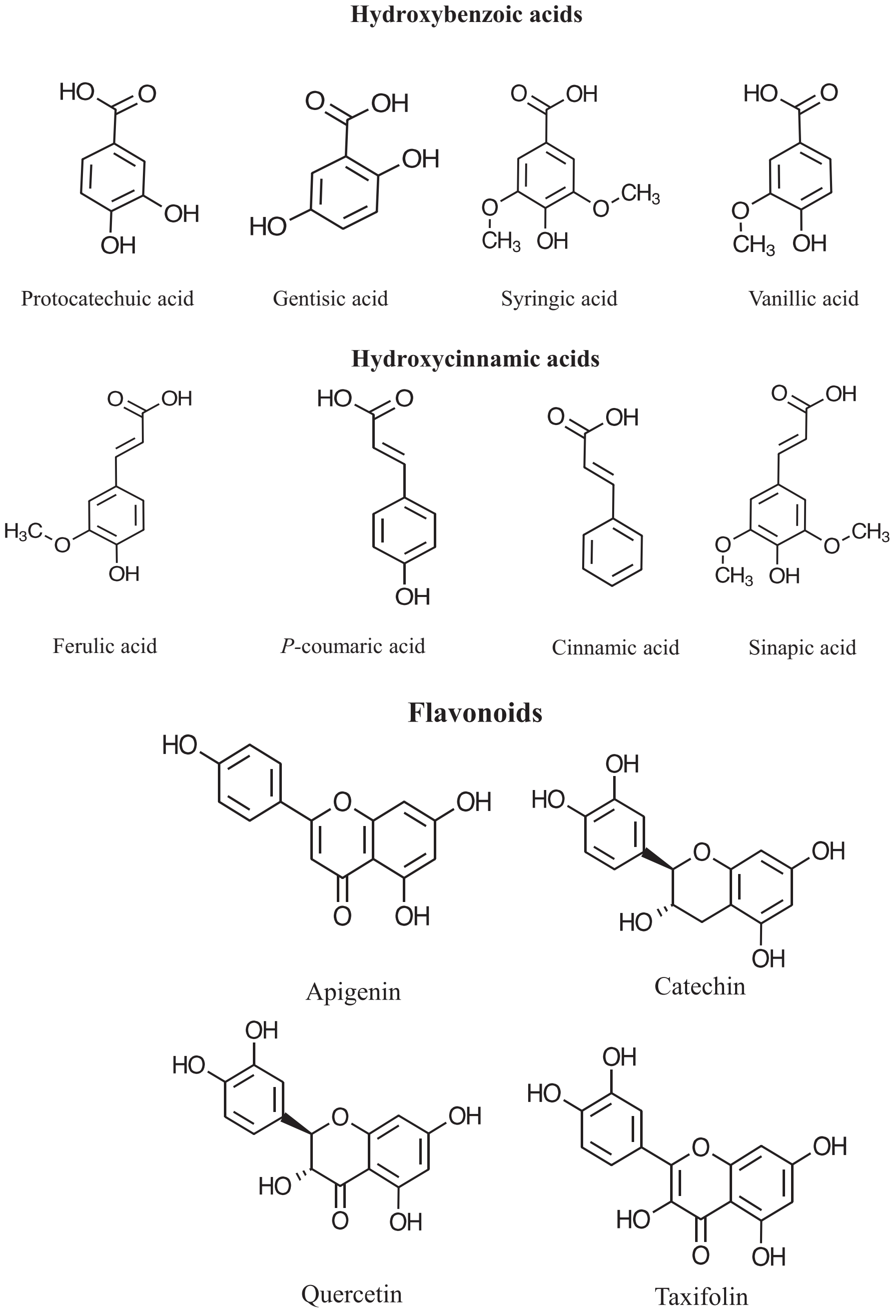
Millet type	Polyphenolic compounds	References
Common millet	Gallic, *p*-hydroxybenzoic, gentisic, vanillic, chlorogenic, sinapic and ferulic acids	Chandrasekara and Shahidi [28]
Foxtail millet	Ferulic, chlorogenic, caffeic, *p*-coumaric, syringic acids	Pradeep and Sreerama [55] and Zhang and Liu [63]
Finger millet	Quercetin, gallic, protocatechuic, vanillic, *p*-hydroxybenzoic, syringic, ferulic, trans-cinnamic, caffeic, sinapic and *p*-coumaric acids	Devi et al. [12] and Pradeep and Sreerama [55]
Pearl millet	Methyl vanillate, apigenin, ferulic, caffeic, *p*-hydroxybenzoic and *p*-coumaric acids	Chandrasekara and Shahidi [28]
Barnyard millet	Gallic, *p*-hydroxybenzoic, vanillic acid, caffeic, chlorogenic, ferulic and *p*-coumaric acids	Pradeep and Sreerama [55]

anti-inflammatory, antiviral and neuroprotective activities [25]. Dietary intake of polyphenols could be as high as 1 g/day, which is much higher than any known dietary antioxidant [26, 27].

Millet contains different types of polyphenols. These are mainly hydroxybenzoic acid, hydroxycinnamic acids and flavonoids [14]. The distribution and concentration of these phenolic compounds varies with the type and variety of millet [28]. For instance, a study found that finger millet phenolics are found more in the seed coat than in the endosperm [6]. There are even variations in the phenolic contents of brown and white varieties of finger millets [6, 28]. A study also showed significant variation in the polyphenol contents of two pearl millet cultivars from Sudan. These were the Standard and the Ugandi cultivars [29]. The total polyphenols in the whole and dehulled Ugandi cultivar were 444 mg/100 g and 326 mg/100 g, compared to those of the Standard cultivars which were 304 mg/100 g and 235 mg/100 g, respectively [29]. Other millet types including foxtail and barnyard millets have also been reported to be rich in polyphenols [30, 31]. The major polyphenolic compounds that are present in different types of millets and their chemical structures are presented in Table 10.1 and Fig. 10.2, respectively.

10.4 Molecular Mechanism of Health-Promoting Effect of Millet Bioactives

As mentioned in the previous section, millet is a rich source of various bioactive phytochemicals including feraxans, lignans, β-glucan, inulin, resistant starch, sterols and phytates and phenolic compounds (e.g. ferulic acid, caffeic acid and quercetin). Due to the presence of these phytochemicals, consumption of millet exhibits a number of health benefits such as lowering the risk of cancer and cardiovascular disease, diabetes, high blood pressure, high cholesterol, inflammatory diseases, metabolic syndrome and Parkinson's disease and delaying gastric emptying and fat



Hydroxybenzoic acids

Protocatechuic acid

Gentisic acid

Syringic acid

Vanillic acid

Hydroxycinnamic acids

Ferulic acid

P-coumaric acid

Cinnamic acid

Sinapic acid

Flavonoids

Apigenin

Catechin

Quercetin

Taxifolin

Fig. 10.2 Chemical structures of some phenolic compounds found in millets absorption [18]. Phytochemicals present in millet are also reported to have antimicrobial and DNA damage protection activities [32, 33]. Substantially high content of minerals (e.g. iron, potassium, magnesium, manganese, zinc), vitamins (e.g. niacin, riboflavin, thiamine, folic acid) and dietary fibres also makes it a better choice over other cereal grains. Possibly for this reason, finger millet used to be highly popular for infant and geriatric nutrition in ancient times.

Although consumption of millet is associated with improvement of health such as reduction of incidents of blood pressure, type 2 diabetes, cardiovascular and inflammatory disease and even cancer, the exact mechanisms of how these phytochemicals induce beneficial effects in consumers' health are still not clearly identified due to the involvement of huge number of phytochemicals and biological processes associated with it [34]. The ensuing section provides some fundamental information about the absorption and utilisation of polyphenols in the body and associated mechanism of action.

(a) Enzyme Inhibitory Activity

Millet polyphenols are known to inhibit the activity of digestive enzymes such as amylase, glucosidase, pepsin, trypsin and lipases [35, 36]. Inhibition of amylase and glucosidase lead to a decrease in postprandial hyperglycaemia by partially inhibiting the enzymatic hydrolysis of glycaemic carbohydrates and hence may delay the release and absorption of glucose. Alpha-amylase inhibition induces carbohydrate tolerance, satiety and weight loss and prolongs gastric emptying effects that may be useful in treatment of obesity and non-insulin-dependent diabetes mellitus [36]. Inhibition of amylase takes place in several ways, for instance, by competing with the substrate during binding to the active site of the enzyme or by disrupting irreversibly the catalytic process. Phenolics react with proteins/enzymes and alter various properties of biopolymers such as the molecular weight and solubility and thus modulate their digestibility [35]. It is important to note that mode of inhibition is dependent on the substrate specificity of the enzymes, structural make-up of the phenolics, enzyme concentration as well as the number and position of the hydroxyl group of the phenolics. In a study, Chethan et al. [37] demonstrated that *trans*-cinnamic acid exhibited a higher degree of inhibition (79.2%) as compared to other phenolic compounds and syringic acid was found to be the weakest inhibitor (56%). Similarly, protocatechuic acid and *p*-hydroxybenzoic acid were found to be less effective in inhibiting the amylase activity.

(b) Antioxidant Activity

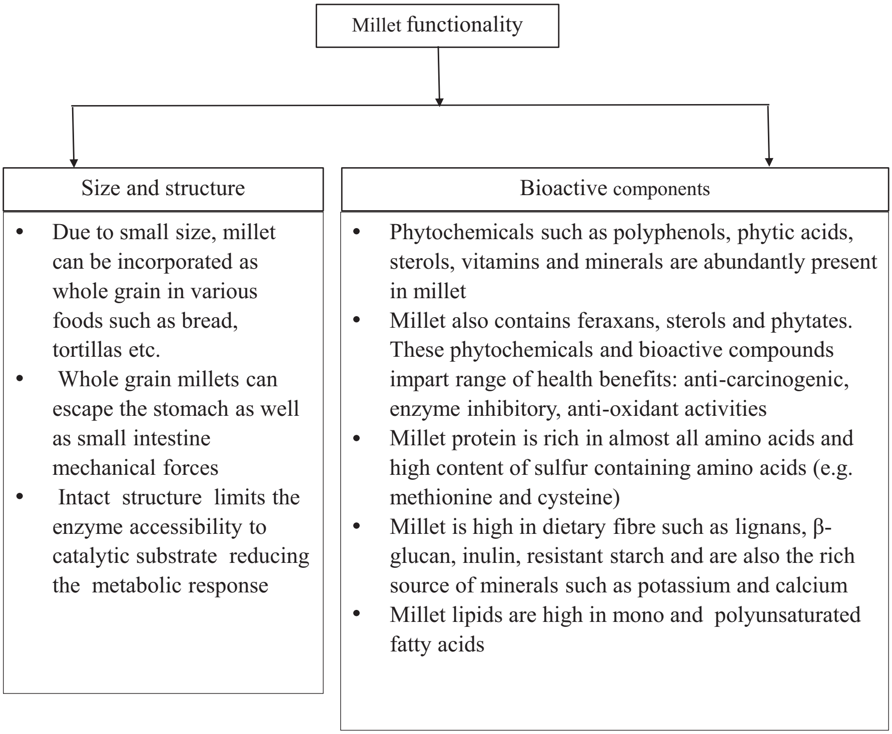
Polyphenols are potent antioxidants although they are not readily absorbed in the small intestine. The primary effect of antioxidants from food sources is in the digestive tract. These phytochemicals protect the intestinal epithelial cells from the attack of free radicals [26, 38]. These polyphenols are found to be involved in cell signalling pathways so that they can modify gene regulation and redox status of the individual. Signalling pathways are regulated up and down by polyphenols via activation or inactivation of transcription factors such as NF-kB or activator protein-1 (AP-1) [39].

(c) Whole Grain Effect

Whole grains have been reported to possess several health benefits [40, 41]. Whole grains are most minimally processed and have several levels of intact structures that retain the numbers of bioactive compounds. Processing of grains, e.g. milling, disintegrates the structure and is often associated with reduction of bioactive components such as dietary fibre and phytochemicals. In case of millet, specific nutritional functionality comes from its size. Millet is one of the smallest whole grain cereals with 1–2 mm in diameter. Due to the large surface area with thicker pericarp and aleurone layer, the ratio of outer layer to endosperm is higher in millet compared to other grains, e.g. wheat and rice. Therefore, swelling ratio of millet is lower than that of other cereals. Even on complete hydration, the size of millet does not exceed 2–3 mm. This is regarded as an optimum size that is less affected by mechanical forces during oral processing (chewing) as well as due to peristaltic movements of the stomach and thus passes through the pyloric splinter to small intestine as intact grains. The details of food structural breakdown during oral processing and gastric digestion are reviewed recently [42, 43]. Considering other cooked cereals with larger size, e.g. rice or wheat, the grain particles are broken to smaller pieces during both oral and gastric processing. Passage of less disintegrated foods (structured foods) to the small intestine is a prominent and holistic approach to reduce the glycaemic response from the ingested food [34]. Structured grains have intact cellular structure (outer bran layers as well as endosperm cell walls) that encapsulate the starch and protein and are mostly impervious to digestive enzymes [44, 45], thus reducing the rate and extent of digestion of metabolic macronutrients. The encapsulated starch in whole millet grains remains undigested in intestinal lumen and passes to the large intestine where this is fermented by colonic microorganisms. The fermentation of starch and fibre in the colon are associated with numerous physiological benefits [46]. A schematic diagram showing different aspects of health benefits of millet grain is presented in Fig. 10.3.

10.5 Effects of Millet Polyphenols on Oxidative Stress

It has been reported that excessive production of reactive oxygen species (ROS) causes oxidative stress in humans. Oxidative stress can damage cellular proteins, lipids and DNA [47]. Polyphenols from millets are known to have potent antioxidant properties [14], as such they can prevent excessive formation of ROS. Soluble and bound phenolic extracts of widely consumed millets such as kodo, finger, foxtail, proso, little and pearl were investigated for their abilities to inhibit radicals and ROS [48]. Authors found that phenolic extracts from all millet varieties displayed effective radical and ROS inhibition activities. Ferulic and *p*-coumaric acids were the major polyphenols in the extracts and were responsible for the observed effects [48]. Several in vitro and in vivo tests have shown that ferulic and p-coumaric acids provide neuroprotection against oxidative stress [49–54].



- Due to small size, millet can be incorporated as whole grain in various foods such as bread, tortillas etc.
- Whole grain millets can escape the stomach as well as small intestine mechanical forces
- Intact structure limits the enzyme accessibility to catalytic substrate reducing the metabolic response

- Phytochemicals such as polyphenols, phytic acids, sterols, vitamins and minerals are abundantly present in millet
- Millet also contains feraxans, sterols and phytates. These phytochemicals and bioactive compounds impart range of health benefits: anti-carcinogenic, enzyme inhibitory, anti-oxidant activities
- Millet protein is rich in almost all amino acids and high content of sulfur containing amino acids (e.g. methionine and cysteine)
- Millet is high in dietary fibre such as lignans, β-glucan, inulin, resistant starch and are also the rich source of minerals such as potassium and calcium
- Millet lipids are high in mono and polyunsaturated fatty acids

Fig. 10.3 Overview of beneficial effects of millet

Finger and kodo millet-based diets have been also reported to be beneficial in protecting against oxidative stress and this may be largely due to the presence of polyphenols [27]. Therefore, the ability of millet polyphenol extracts to inhibit ROS formation suggests their usefulness in offering protection against oxidative stress.

10.6 Effects of Processing on Functionality

In order to prepare millet-based foods, several processing steps are carried out, including but not limited to soaking, cooking, germination, fermentation, milling, decortication and dehulling. These processing steps, depending on the techniques and severity, can have significant impact on the nutritional functionality of millets. For example, milling can alter the food structure increasing the glycaemic response, whereas other processing techniques can decrease the stability and bioactivity of health-promoting bioactive compounds in millet [55].

For instance, in Indian sub-continent, where fermented cereal products are widely consumed, millets are generally fermented using mixed cultures of lactobacilli and yeasts [29]. In Burkina Faso, pearl millets are fermented to produce a traditional millet-based gruel called *ben-saalga* [56]. Also, in Asia and some parts of Africa, millet hulls are removed traditionally using wooden mortar and pestle [29]. Since most of the bioactive phytochemicals are concentrated in seed coats of millet processing steps that involve removal of seed coat have significant negative impact on the contents of these bioactives [6].

It has been reported that dehulling of millet reduces approximately 80% of phenolic content citing the concentration of phenolics in the seed coat. Hydrothermal treatment and germination were also reported to have a pronounced effect on the phenolic content of millet. Chethan et al. [37] reported nearly 44% reduction in phenolics during the first 24-h germination period and approximately 80% loss during further germination period of 120 h. Similar findings were also reported in other studies.

The total polyphenol content of two pearl millet cultivars, Standard and Ugandi, obtained from El Obeid Research Station in Sudan was found to significantly decrease under different fermentation conditions. For instance, the total polyphenol in the standard pearl millet before fermentation was 304 mg/100 g; after 14 hours of fermentation, the total polyphenol contents had decreased to 122 mg/100 g. A similar pattern was observed in the Ugandi cultivar. Its total polyphenol decreased from 444 mg/g (whole millet) to 306 mg/g after 14 h of fermentation [29]. This reduction was theorised to be due to the microbial activity during fermentation [29]. Contrary to these findings, a study that involved mixed cultures of *Saccharomyces diastaticus*, *Saccharomyces cerevisiae*, *Lactobacillus brevis* and *Lactobacillus fermentum* during the fermentation and germination of pearl millets did not show significant change in the concentration of polyphenols [57]. Interestingly, authors found that the polyphenol contents of millet decreased when fermentation was carried out only by mixed cultures of *S. diastaticus* and *L. brevis* [57]. These observations suggest that certain microorganisms have capacity to utilise polyphenols during germination and fermentation, whereas others do not possess such ability.

Malting of finger millet was reported to cause changes in the content of polyphenols [58]. The authors found a threefold decrease in protocatechuic acid content of finger millet after malting for 96 h. However, the content of other free phenolics such as gallic, vanillic, coumaric and ferulic acids increased [58]. Another study also found that malting and blanching can affect the contents of polyphenols in millet [59]. For malting pearl millet was steeped for 16 h, germinated for up to 72 h and kilned for 24 h at 50 °C; meanwhile blanching was done for 30 s in a boiling water at 98 °C. Results showed that blanching caused a 28% reduction in the polyphenol content while up to 40% loss was observed after 72 h of malting. Authors attributed these polyphenol losses to leaching during the blanching and steeping processes [59]. It is believed that the aqueous environment that is present during steeping and germination facilitates the solubilisation of phenolic compounds, thus leaching out into the steep liquor [60]. Also, polyphenol oxidases (PPO) mobilised during germination of millet may have degraded the polyphenols because these compounds are suitable substrates for PPO [60]. Other authors have also found that malting and blanching can decrease polyphenol content in millets [61, 62]. Table 10.2 summarises the effects of processing on the phenolic contents of millets.

Table 10.2 Effects of processing on phenolic compounds in millet

Processing method	Millet type	Effects on polyphenol	References
Fermentation	Pearl	Significant reduction in polyphenol content	El Hag et al. [29]
	Pearl	Increase in the polyphenol contents of fermented millet flour was noticed	Kheterpaul and Chauhan [64]
Dehulling and decortication	Pearl	Polyphenol contents reduced by up to 51%	Mohamed, et al. [65]
	Finger	Polyphenol contents reduced by up 75%	Shobana and Malleshi [66]
	Foxtail, proso, finger and pearl	Varying degrees of phenolic compound losses were observed in all millet types	Chandrasekara et al. [67]
Malting	Finger	Threefold decrease in protocatechuic acid content was observed while the contents of others increased	Rao and Muralikrishna [58]
Blanching/ boiling	Pearl	Caused a 28% reduction in the polyphenol content	Archana et al. [59]
	Finger	Significant reduction in total phenolics after boiling whole finger millet grains	Towo et al. [68]

10.7 Concluding Remarks and Future Perspectives

Although millets have a promising nutritional and health-promoting potential, its consumption is still limited to rural low-income families in Asian and African continent. Therefore, it is sometimes known as poor man's crop. In addition, they are not commonly incorporated into commercial foods and thus remain underutilised cereals due to lack of novel product development technologies and awareness about their health benefits among the vast majority of consumers. Since the phytochemicals present in millet have anti-oxidative, anticarcinogenic and enzyme inhibitory activities, millets are capable of preventing various pathophysiological conditions. Furthermore, millets' small size makes it possible to use them as whole grain in other foods. Therefore, appropriate processing technologies are essential in order to utilise them in infant formula, geriatric nutrition, complementary food products and therapeutic foods to combating current and emerging health problems.

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Chapter 11
Oats

Sumei Zhou, Litao Tong, and Liya Liu

11.1 Introduction

Oat (*Avena sativa*) is a species of cereal grain grown for its seed, which is classified into common oat and naked oat (*Avena nuda*), according to whether it has a hull. Oat, a worldwide cultivated crop, is distributed in 42 countries on five continents but is concentrated in temperate zones in the northern hemisphere. The north latitude from 41 to 43 degrees is recognized as the optimal latitudinal zone of oat gold growth. The best natural environment for growth is 1000 m above sea level, with an average annual temperature of 2.5, and 16 h. Oat contains13~20% protein, 2~12% crude fat, 2.0~7.5% β-glucan, and about 60% starch [1–3].

Oat's health efficacy has been confirmed in both animal experiments and human trials and is thus recognized as a healthy grain. In 1997 the US Food and Drug Administration (FDA) releases health claim, "Soluble fiber from foods such as oats, as part of a diet low in saturated fat and cholesterol, may reduce the risk of heart disease." Products that contain at least 0.75 g of β-glucan per serving fall under the umbrella of this claim. It is reported that dietary oat oil reduces plasma cholesterol and LDL cholesterol in rats by promoting excretions of fecal lipids. The hypolipidemic effects of oat oil could be attributed to its higher contents of tocotrienols and sterols [4]. Furthermore, the research team further confirmed that dietary oat proteins reduced plasma lipids levels through elevating the excretion of fecal total lipids and regulating the activity of liver cholesterol-metabolizing enzymes [5]. It has been reported that oat avenanthramides as phenolic compounds are bioactive, including anti-inflammatory effects and induction of apoptosis [6]. Viewed through the lens of present research, the major functional components of oats include β-glucan, protein, oil, starch, and minor components including avenanthramides, tocols, etc.

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Numerous studies indicate that dietary oats reduce plasma total cholesterol and low-density lipoprotein (LDL) cholesterol, lower obesity, prevent coronary heart disease, and improve symptoms of diabetes, immune enhancement, and antioxidation effects [7–10]. The multifunctional uses of oats and its extracts include common foods, functional foods, cosmetics, and animal feed. The most common oat foods are crushed into oatmeal or ground into oat flour. Oatmeal, besides being chiefly eaten as porridge, is also used in bakery goods such as oat bread, oat cookies, and oatcakes. Steamed oat noodles and thin-walled rolls called "you mian" are processed using oat flour and are consumed as staple food particularly in western Inner Mongolia and Shanxi province in China.

In the process of food processing, cooking, extrusion, crushing, and so on, the content and structure of its functional components have changed greatly, which affect the biological activity of the food. There are reports that soluble dietary fiber in oat content is influenced by pearling, milling, extrusion cooking, malting, and baking [11, 12]. Ban et al. [13] reported that cooked oatmeal can lower plasma and liver lipid concentrations in rats, and boiled oatmeal is more effective than the brewed. Furthermore, the hypocholesterolemic effects of boiled oatmeal were proven to be positively correlated to its higher soluble β-glucan content and apparent viscosity as compared to the brewed oatmeal. Therefore, in order to give full play to the physiological activity of functional components, it is necessary to fully analyze the variation of the in the process of oat and to maintain or improve the function of oat based on this process.

11.2 Bioactive in Oat

11.2.1 β-Glucan

Oat is well known for their soluble dietary fiber and β-glucan (beta-glucans), which is naturally occurring in the cell walls of cereals, bacteria, and fungi, with significantly differing molecular weight, solubility, viscosity, branching structure, and gelation properties depending on the source. The mixed linkages of β-(1 → 3) and β-(1 → 4)-glucans (Fig. 11.1) of oats are important parameters which contribute to their physicochemical properties and physiological effects in animals. The hypercholesterolemia is a major factor for cardiovascular diseases (CVD), the primary cause of human death in the world. Prevention of CVD by alternative medicinal foods is of increasing interest to scientists. Various studies show that oat β-glucan as soluble dietary fiber lowers the level of plasma total cholesterol and LDL cholesterol effectively without affecting the HDL cholesterol level in plasma or triglyceride and reduces the risk of developing cerebrovascular disease (CVD) in hypercholesterolemic animals [14, 15]. In 1997, the FDA approved oat β-glucan

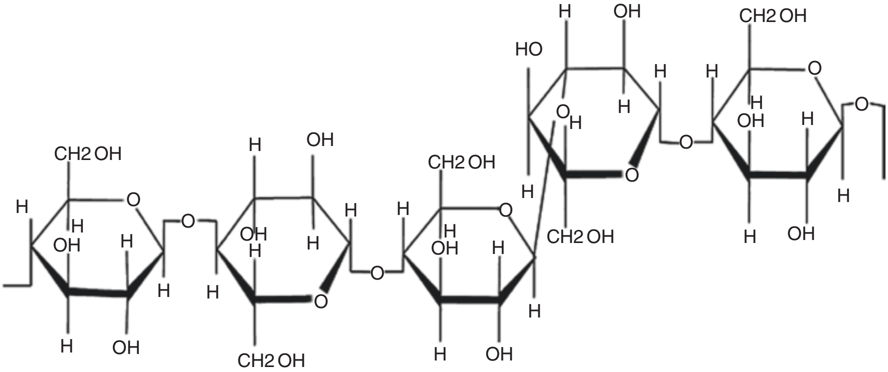


Fig. 11.1 Chemical structure of oat β-glucan [16]

soluble fiber for lowering LDL cholesterol in plasma and risk of heart disease. Seven years later, the United Kingdom Joint Health Claims Initiative (JHCI) approved similar cholesterol-lowering health claims for oat β-glucan. Othman et al. [16] reviewed the follow-up studies and concluded that intake of 3 g of oat β-glucan per day may lower the total and LDL cholesterol concentrations by 5~10% in hypercholesterolemic conditions. The present review based on last 13 years of research is also in agreement with the FDA and JHCI Instead of lowering the levels of plasma total cholesterol and LDL cholesterol. Similar effects of oat β-glucan on glycometabolism have also been reported. Wood [17, 18] showed that oat β-glucans can reduce the blood glucose and insulin responses. The author also found a highly significant linear relationship between the β-glucans viscosity and the glycometabolism indexes. Therefore, intake of oat β-glucan exerts beneficial effects on health in patients having type 2 diabetes through modification of the viscosity of chyme in the upper part of the gastrointestinal tract that affects food digestion and nutrient absorption [19].Several studies showed that oat β-glucan is physiologically active against tumors and cancers. Hong et al. [20] reported that orally administered β-(1, 3)-glucans enhance the tumoricidal activity of antitumor monoclonal antibodies in murine tumor models. At the same time, orally administered β-(1, 3)-glucans induce proliferation and activation of monocytes in the peripheral blood of patients with advanced breast cancer [21]. In addition, Murphy et al. [22] reported that when oat β-glucan is taken orally, it has beneficial effects on infections and on macrophage effects of antiviral resistance. Both oral and parenteral administrations of oat β-glucan play an important role in providing resistance against bacterial and parasitic infections; this may contribute to its strong immunity-enhancing effects because oat β-glucan has its own many physiological activities and related functions that focus on functional food development.

11.2.2 Proteins

Oat contains higher content of protein (13~20%), and the composition of oat amino acid is more reasonable compared with other cereals. Several studies on humans and experimental animals indicate that the dietary plant proteins, such as in rice, soybean, and buckwheat, could significantly reduce serum cholesterol levels and prevent cardiovascular diseases. Tong et al. [5] reported that the dietary oat proteins markedly decreased plasma LDL cholesterol levels and significantly enhanced plasma HDL cholesterol levels in hypercholesterolemic hamsters. These hamsters were fed with a hypercholesterolemic diet containing 1.47% oat proteins indicating that increased intake of oat protein can prevent the development of cardiovascular diseases. It is interesting enough that the total cholesterol levels in the plasma and liver of oat proteins. In addition, β-glucan groups were lower than those without the protein or β-glucan group. Similarly, the ability of intake of oat proteins plus β-glucan to increase the activity of liver cholesterol 7 α-hydroxylase was also higher than that of the single intake of proteins or β-glucan. Therefore, dietary oat protein and β-glucan together can play a synergistic role in the cholesterol-lowering effect.

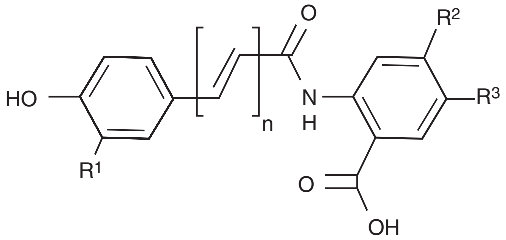
Tsopmo and Jodayree [23] reported that both tryptic and alcalase digests of oat flour protein show remarkable antioxidant activity in 2,2′-diphenyl-2-picrylhydrazyl (DPPH), oxygen radical absorbance capacity, linoleic acid emulsion system, and ferrous ion-chelating assays, indicating that trypsin and alcalase hydrolysates can be used to produce antioxidant peptides. At the same time, these results also indicate that oat peptides are the core component for its radical scavenging activity and enzymatic digestion may be used to obtain bioactive peptides from oat flour with potential application in food products to improve health. When we talk about bioactive peptides, angiotensin converting enzyme (ACE) inhibitory peptides are the most important and studied. Keenan et al. [24] described that oat ingestion has beneficial effects of lowering blood pressure by reducing systolic and diastolic blood pressure in patients with mild or borderline hypertension. Maki et al. [25] stated that dietary oat exerts beneficial effects on blood pressure, carbohydrate metabolism, and biomarkers of oxidative stress in men and women with elevated blood pressure. These effects are attributed to the ACE inhibitory activity of oat functional components, especially protein and peptides. It is also reported that strong ACE inhibitory activity of oat peptide was produced under suitable hydrolysis conditions, and its IC_{50} value can reach 30 μg/mL in silico and this was also testified with in vitro experiment [26]. Moreover, this study also shows that the molecular weight of potent ACE inhibitory oat peptides was below 3 kDa.

11.2.3 Oils

Although oats have not been used as a source of edible oil, it is an excellent source of functional food applications because it contains much higher levels of crude fat (2–12%) compared with other cereal grain, and oat oil itself shows the nutritional and technological potential [27–29]. Many studies have showed that fat intake is the most critical factor in lowering serum cholesterol concentrations and there is much evidence that supports the functionality of oils such as rice bran oil and other oils in reducing plasma cholesterol and preventing cardiovascular and cerebrovascular diseases in both humans and animals [30–32].Gold and Davidson [14] demonstrated the intake of oat bran muffins resulted in a 8.3% reduction in serum triglycerides as compared with an overall increase of 6.4% in the other groups, indicating that oat bran taken daily can significantly lower lipid concentration in young and healthy persons. Rice bran was used as a positive control effect of full-fat oat bran on the cholesterol metabolism in normal and hypercholesterolemic humans, reported by Gerhardt and Gallo [33]. The results of the study showed that ingesting full-fat oat bran and rice bran lowers plasma total cholesterol and LDL cholesterol concentrations. After that another scientist investigated the extraction of carbon dioxide from oat oil and checked the effects of oat oil metabolism in Wistar-Lewis rats by giving them a hypercholesterolemic diet [4]. Their results confirmed that intake of oat oil has the same effect as rice bran oil which lowered total plasma cholesterol, LDL cholesterol levels, liver cholesterol, and triglyceride levels. It was indicated that oat oil is an important component in full-fat oat bran which is directly responsible for the effects on lipid metabolism in humans and animal models. In plants, the sterols such as campesterol, stigmasterol, and β-sitosterol and vitamin E like α-tocopherol, α-tocotrienol, and γ-tocotrienol are minor functional components which are abundant in oat oils. It has been widely reported that the plant sterols and vitamin E are able to exert beneficial effects on cholesterol metabolism through competition of inhibition or regulation of cholesterol-metabolizing enzymes. Therefore, the effect of lowering total cholesterol in plasma by oat oil can be partially attributed to the fact that they contain high content of plant sterols and vitamin E.

11.2.4 Avenanthramides

Avenanthramides such as anthranilic acid amides are a group of phenolic alkaloids that are mostly found in oat. They were firstly isolated from oat and named by a Canadian scientist named Collins in 2003 as the alkaloids [34]. At present, more than 20 different forms of oat avenanthramides have been isolated from oat bran and grains. As displayed in Fig. 11.2, the alkaloids include alkaloids A (N-4′-hydroxycinnamyl-5-hydroxyo-aminobenzoic acid), alkaloids B (N-4′-hydroxy-3-methoxycinnamyl-5-hydroxyo-aminobenzoic acid), and alkaloids C (N-3′,4′-dihydroxycinnamyl-5-hydroxyo-aminobenzoic acid) accounting for 35%, 21%, and 44% of oat avenanthramides, respectively. There were clear differences in alkaloids in different varieties of oat, different locations, cultivation conditions, and nitrogen levels that all affected the contents of oat avenanthramides. The average content of avenanthramides in oats was 2–300 mg/k, as reported by [34]. Oat avenanthramides have many physiological effects, such as antioxidation, lowering blood lipids, reducing inflammation and itching, inhibiting cell proliferation, and many others.



Collins	**Dimberg's original**	**Dimberg's modified**	***n***	**R^1**	**R^2**	**R^3**
A	Bp	2p	1	H	H	OH
B	Bf	2f	1	OCH_3	H	OH
C	Bc	2c	1	OH	H	OH
O		$2p_d$	2	H	H	OH
P		$2f_d$	2	OCH_3	H	OH

Fig. 11.2 Chemical structure of avenanthramides

The prevention and treatment of colon cancer and skin pruritus is important [35, 36] and is also an important focus of health products in modern healthy life and the effective component of new drugs for skin care. Ren et al. [37] found that oat avenanthramides could significantly reverse oxidative stress induced by D-galactose in mice by increasing the activities of superoxide dismutase and glutathione peroxidase and upregulating their gene expression. The results of human experiments also showed that oat avenanthramides could significantly increase the superoxide dismutase (SOD) and glutathione peroxidation (GSH) in the blood. Meydani [36] also found that the synergistic action of extraction, rich in oat avenanthramides and vitamin C, also inhibited oxidation of low-density lipoprotein in vitro.

The biological activities of different oat avenanthramides are different and their functional diversity is closely related to the structural diversity. As scientific and technological techniques advance and become more sophisticated, the structure and function of oat avenanthramides will be studied more and more deeply, promoting high-quality research and expanding industrial applications of oat.

11.3 Molecular Mechanism of Bioactive in Oats

11.3.1 Mechanism of Physiological Functions of β-Glucan

Oat β-glucans regulate cholesterol metabolism through a variety of different mechanisms. It is generally accepted that the primary function of β-glucan is lowering plasma cholesterol concentrations which is contingent on water solubility and viscosity [38]. β-glucans adsorbed bile acid of micelles in the intestine so the bile acid did not enter in enterohepatic circulation system and intervene in the required interaction with the luminal membrane transporters on the intestinal epithelium. The absorption of triglycerides, cholesterol, bile acid, and other lipids in the small intestine is greatly reduced, which leads to increased fecal output of lipids and significantly lowers the plasma cholesterol concentrations. At the same time, due to the decrease in exogenous cholesterol intake and bile acid reabsorption, the liver compensates by increasing the absorption of cholesterol in order to maintain stability of cholesterol and further reduce the LDL cholesterol concentration in the plasma. High molecular weight may produce higher intestinal viscosity compared with low molecular weight, so the molecular weight of β-glucan may influence its hypocholesterolemic effect. The liver, as an important organ of cholesterol synthesis and excretion, contains 3-hydroxy-3-methylglutaryl-coenzyme A (HMG-CoA) reductase and cholesterol 7 α-hydroxylase (CYP7A1) as rate-limiting enzymes that regulate cholesterol synthesis and excretion in the liver, respectively [39]. There are reports that dietary oat β-glucan may regulate activity of CYP7A1 but does not affect the activity of HMG-CoA in hypercholesterolemic hamsters. So, oat β-glucan can only promote cholesterol decomposition, not inhibit cholesterol synthesis [4]. Humans and animals lack small intestine enzymes that can digest a mixed β-(1 → 3) and β-(1 → 4) linkage of oat β-glucans and they pass undigested into the large intestine. Therefore the oat β-glucan as soluble fiber entering the colon is fermented almost completely by the intestinal microflora, and the end products of major fermentation are short-chain fatty acids (SCFAs) such as lactate, acetate, propionate, and butyrate. These SCFAs are absorbed through the portal vein, inhibiting hepatic cholesterol synthesis by limiting the action of cholesterol-metabolizing enzymes or by increasing catabolism of LDL cholesterol [40, 41]. These results suggested one mechanism for cholesterol reduction is the effect of SCFAs.

Similar to the mechanisms reducing plasma cholesterol, oat β-glucans can reduce blood glucose and insulin responses. The hypoglycemic effect is also directly related to the viscosity of oat β-glucans. Behall et al. [19] reported that the oat β-glucan exerts beneficial effects in lower postprandial glycemic and insulin responses for healthy subjects and patients with type 2 diabetes through modification of chyme viscosity in the intestine and lowers the rate of glucose absorption. Many studies have shown that oat β-glucan has physiological antitumor, anticancer, antiviral, antibacterial, and antiparasite effects. These may be attributed to its strong immune-enhancing activity. Because the oat β-glucan has significant physiological activity to enhance immunity, it has been used in immune-adjuvant therapy for tumors and cancers.

11.3.2 Proteins

Lowering cholesterol concentration in the liver is one of the ways to reduce serum cholesterol, because the decrease in liver cholesterol will compensate the blood. Tong et al. [5] reported that the oat β-glucan was able to significantly reduce liver cholesterol ester, triglyceride, without effecting free cholesterol concentrations. The CYP7A1 and HMG-CoA reductase activities in the liver were measured to elucidate the mechanism of oat β-glucans which regulates plasma and liver cholesterol metabolisms. The result showed that the oat β-glucan was able to significantly increase liver CYP7A1 activity but did not significantly affect the activity of the HMG-CoA reductase. Many studies have shown that the inhibition of cholesterol absorption in the small intestine increased fecal bile acid excretion, so as to reduce the synthesis of cholesterol which was thought to cause hypolipidemic mechanisms of oat β-glucans. Further analysis showed that oat protein significantly increased the excretion of total cholesterol, bile acid, and total lipids in feces. These results confirmed that intake of oat β-glucan could reduce the concentrations of plasma LDL cholesterol and liver total cholesterol by increasing the excretion of cholesterol and the inhibition of reabsorption of bile acids in feces.

The antioxidative effect of oat peptides has been confirmed by some reports. It is generally believed that the antioxidant activity of antioxidant peptides is related to the relative molecular weight of peptides, amino acid sequences, amino acid side-chain groups, and metal salt complexation. The antioxidant activity of antioxidant peptides is determined by the ability of their molecules to supply hydrogen and the stability of their own structures. The mechanisms of antioxidant peptides are directly acting on free radicals or indirectly consuming substances that are easy to generate free radicals to prevent further reactions. Therefore, the antioxidative mechanisms of oat protein and peptides may be attributed to its molecular weight, amino acid sequence, and structure, but the specific peptide sequence of oat peptides has not been reported.

ACE is an angiotensin-converting enzyme. It exists widely in the body and has the effect of constricting blood vessels, which can cause a rise in blood pressure. Functional components in foods inhibit the activity of ACE, which can reduce blood pressure and reduce the risk of cardiovascular and cerebrovascular diseases. At present, except for some triterpenes, ACE inhibitors reported are mainly bioactive peptides. ACE inhibited peptide bins at competitive sites, which prevents angiotensin I from converting to angiotensin II and increases the level of soothing peptides and encephalin, thus achieving the effect of hypotension. So far, all the reported ACE inhibitory peptides are 2–20 amino acids with a molecular weight between 200 and

2 kD. Numerous studies have reported that there are functional peptides with significant ACE inhibitory activity in oat protein [24–26], but the specific peptide sequences still need further clarifying.

11.3.3 Oils

There are some reports that the hypocholesterolemic effect of dietary functional oil may result from increasing upregulation of LDL-receptor mRNA which thereby exerted beneficial effects on catabolism/output of LDL cholesterol, which lead to an increase in cholesterol and bile acid concentration in feces [9]. In the reports of Tong et al. [5], the fecal weight, total lipids, cholesterol, and bile acid concentration in the oat oil group were significantly increased more than in soybean oil groups, which indicated that the beneficial effects of oat oil on cholesterol lowering can be partly attributed to the promotion of lipid excretion in feces. It is well known that excellent fatty acid composition is beneficial to body health. Long-chain polyunsaturated fatty acids are also beneficial for human health. On the other hand, the functional components are small molecules in oils that can play a key role in their physiological activities. For example, it has been reported that the hypolipidemic effects of rice oil are not due to its fatty acid composition but mainly its γ-oryzanol [31]. The cholesterol-lowering effect of oat oil can be partly attributed to its high content of γ-tocotrienols, which has a clear effect on regulating the metabolism of cholesterol through an inhibition of HMG-CoA reductase. At the same time, their results showed that the concentration of total plant sterols in oat oils is approximately 1.5 times higher than that in soybean oil. The plant sterols can reduce the absorption of intestinal cholesterol by competitive inhibition because they do not participate in collective cholesterol synthesis in the body, thus playing the role in regulating the cholesterol metabolism.

11.3.4 Avenanthramides

Oat avenanthramides could significantly inhibit the expression of pro-inflammatory cytokines in a dose-dependent manner. The mechanism of inhibition of oat avenanthramides on the expression of pro-inflammatory cytokines was mediated by the regulation of the activity of nuclear transcription factor NF-κB [42]. Further study showed that oat avenanthramides reduce the binding activity of IL-1 β-induced NF-κB P50 to DNA and inhibit the activation of NF-κB in human arterial endothelial cells in a concentration-dependent manner, thus inhibiting the expression of pro-inflammatory cytokines. A series of studies by Guo et al. [43] have also shown that oat can inhibit the effect of inflammatory cytokines in endothelial cells by inhibiting the phosphorylation of IKK and inhibiting protein (IkB) and decreasing the activity of IkB in endothelial cells. Similarly, Sur et al. [44] have also reported that oat avenanthramide extract could inhibit the effect of inflammatory cytokines in endothelial cells by inhibiting phosphorylation in IκB kinase inhibitor of kappa-B kinase (IKK) and inhibitor of κB (IκB).

The clinical symptoms of contact allergic dermatitis and neuroinflammation were alleviated by local administration of oat alkaloid extract (3) × 10~3 mg/m/L in mice. In addition, studies have showed that the synthetic dihydroxy oat alkaloid-D can reduce skin diseases such as pruritus, erythema, and water sores, caused by histamine changes, and has been used as an active ingredient in cosmetics. These results suggested that oat avenanthramides have great potential in relieving pruritus.

The results of Peterson et al. showed that the level of blood lipid and malondialdehyde decreases the activity of serum antioxidant enzymes. The effect of trypsin messenger RNA was significantly increased in mice fed with oat bran alkaloid extract [45].Nie et al. [46] study showed that oat avenanthramides can inhibit the proliferation of vascular smooth muscle cells, which prevent atherosclerosis and restenosis after angioplasty and have the effect of anti-vascular smooth muscle cell proliferation and can be used to prevent restenosis after percutaneous transluminal coronary angioplasty.

11.4 Effects of Processing on Availability

As a nutritious food, oats have attracted a lot of significance over the years. Most of the studies focus on their nutritional value, especially in the profiles of its excellent lipids, abundant proteins, and higher amounts of soluble β-glucans. However, oats undergo considerable changes in composition during food processing operations occurred either commercially or at the consumer level. Previous research reveals that the availability of nutritional ingredients in oat product depends upon food processing operations, such as milling, cooking, baking, storage, etc. These factors may play a positive or negative role on the availability of nutrients in oats. For example, β-glucans content of cereals is influenced by the food processing of pearling, milling, malting, extrusion cooking, and baking [47]. Certain food processing operations such as steaming and flaking of dehulled oat groats result in a moderate loss of tocotrienols compared to tocopherols [47]. Therefore, it is critical to better understand the influences of different processing operations during the manufacturing of oat products.

11.4.1 Milling

Oat kernels are not completely digested in gastrointestinal tract, and thus they must be utilized in milled form for maximum utilization of nutritional benefits [48]. Milling of cereal grains removes the bran and germ layers, which are rich in fiber and phytochemicals. After milling, foreign materials are removed, groats are isolated and stabilized, and then it is converted into a form that can be used to easily cook. However, milling of cereal grains causes severe losses of nutrient substances, which move to the by-products, including hulls and polish waste. A dramatic decrease of 71% in tocol levels has been reported after the milling of dehulled rice, probably due to the higher loss of tocols in the form of by-products, and a significant loss of tocols was also observed following an increase in the degree of milling [49, 50]. Nevertheless, the availability of the final product is also strongly dependent on the milling method. Compared to the roller-milled whole wheat flour, stone-milled wheat flour showed higher tocol content [51].The oat bran soluble dietary fiber from superfine ground oat bran showed good physicochemical properties that might be of potential use in the food industry [52].

11.4.2 Inactivate Lipid-Related Enzymes

Oats yield a high percentage of lipids, around two to five times than wheat, and are also rich in lipase, lipoxidase, and other hydrolytic enzymes [53]. The effects of enzymatic activity on oat lipid stability would deteriorate its sensory quality, resulting in rancid taste. Therefore, it is necessary to inactivate these enzymes during the oat processing, especially before oat milling, which is considered as the most important step involved in oat production [54, 55].

Generally, hot air roasting and steaming, including both normal pressure steaming and autoclaved steaming, have been adopted as most efficient hydrothermal treatments to inactivate enzymes, which also facilitate flaking of the oat groat [55, 56]. There have been extensive researches on the effectiveness of thermal treatments to eliminate these enzymes but avoiding the changes of β-glucan, lipids, as well as other active components in oats [55, 57, 58]. It has been reported that enzyme-deactivated oat bran concentrate produced an oat gum with an increased β-glucan content and solution viscosity, but the yield was decreased [59]. Moreover, hydrothermal processing applied to oat materials with the purpose to inactivate enzymes resulted in varied and complex rheological properties, especially when particulates are present [60]. The tocopherols are reported to be very sensitive to the heat treatment and tend to undergo degradation during food processing, especially in water solutions [61], while avenanthramides are rather stable to heat treatment under certain conditions [62]. Ovando-Martínez et al. [63] reported that thermal treatments can cause the reorganization of amylose and amylopectin chains, which in turn lead to the changes to their physicochemical and digestibility properties.

11.4.3 Fermentation

Sourdough fermentation is one of the most important methods to modulate the nutritional quality by increasing the contents of bioavailability of bioactive compounds and retarding starch digestibility [64]. However, sourdough may result in a significant decrease in the molecular weight of β-glucan. Degutyte-Fomins et al. [65] found that the solubility of the β-glucan and the proportion of low molecular weight β-glucan were both enhanced without changing the total β-glucan content of the slurry by the treatment of the incubation of oat bran-water slurry with rye sourdough for 4 h at 30 °C. Aman et al. [66] also reported the reduction of the content and molecular weight of β-glucan for the rye sourdough fermented with oat bran.

11.4.4 Cooking

Different cooking methods, including baking, steaming, and boiling, are widely used in processed oats to enhance the nutritional value and acceptability [67]. Various factors controlling these processes such as mixing time, pH, temperature, and heat all influence the levels of nutritional compositions and active substances in the final products [68]. Many adverse effects occurred after heat treatment, such as nutrient destruction. Chemistry reactions, such as the Maillard reaction and lipid oxidation promoted after heat treatment, can lead to undesirable appearance and taste. Oenning et al. [69] reported that avenacosides were stable when heated up to 100 °C for 3 h at pH 4–7; overheating (>140 °C) caused partial destruction of oat saponins; the addition of catalytic amounts of iron and stainless steel caused saponin degradation significantly. This could partly interpret the reduction of saponin in canned and roller-dried products.

Wennermark and Jagerstad [70] have reported that the tocopherols and tocotrienols decreased 20–60% during the oat sourdough bread making process, which might be attributed to the direct oxidation or enzymatic oxidation catalyzed by lipoxygenase. Similarly, Leenhardt et al. [71] reported 30% loss of vitamin E in bread baking and also an insignificant varietal difference for tocols during kneading, despite large varietal differences for lipoxygenase activity. It was concluded that tocol losses during bread making might be induced by the incorporation of air during dough making, as well as the heat destruction during baking. Short mixing and kneading time seemed like to be efficient to lower the oxidative degradation of tocols and retain higher molecular weight of β-glucan during bread making [72]. Besides, the bread quality can also be improved by the addition of germ to improve the tocol level in bread, but it should be stabilized to avoid oxidative rancidity [68, 71].

Hidalgo Vidal et al. [73] observed that tocopherols migrated from the bran and germ fractions to the endosperm of einkorn under the treatment of steaming. Bryngelsson et al. [56] reported that moderate decreases of tocotrienols, caffeic acid, and avenanthramide Bp were induced by steaming and flaking of dehulled oat groats, while the contents of ferulic acid and vanillin increased after the treatments. Although the structure of soluble β-glucan was not influenced by cooking and baking, cooking is beneficial to increase the amount of soluble β-glucan, but baking decreased its content. Thus, cooking appears to be the most favorable process when health effects are concerned [74].

11.4.5 Extrusion

Extrusion also plays a critical role in cereal availability. For example, tocols are not severely influenced by the processing because of their water solubility, but the losses are in close relationship with lipid degradation [75]. Moreover, this kind of lipid degradation could be affected by the cooking temperatures, time, and exposure to light and oxidative conditions [76]. Zielinski et al. [77] found that extrusion cooking led to a 30% decrease in tocopherol and tocotrienol in cereals including oat, barley, wheat, rye, and buck wheat, and the reason mainly can be attributed to the short thermal treatment of cereal grains during extrusion. Shin et al. [78] demonstrated greater losses of tocols during extrusion while the temperature was increased from 110 to 140 °C. Significant decreasing of tocols also appeared during the processing of tortilla [79].

11.4.6 Sterilization and Storage

Cereal-based beverage products are diffused staple food resources worldwide, especially oat-based beverages, which represent a promising field in the beverages market for innovation. The raw cereal materials carry a large number of microbes like bacterial spores which are hard to kill and might cause food spoilage. In order to prolong the shelf life of oat beverages and improve the safety of product, it is necessary to sterilize effectively. Sterilization methods and process parameters have showed different effects on product quality and component availability. Zhang et al. [80] demonstrated that during the processing of oat-based beverages, the decanting step induced a 45–74% loss of phosphorus, zinc, calcium, and iron but caused a 47% increase of vitamin B_6. The steam-injection UHT treatment caused a 60% loss of vitamin D-3 for both holding times and a 30% loss of vitamin B-12 for 20 s [80]. After storage of 1 year, oleic and linoleic acids remained stable, whereas linolenic acid showed a slightly decrease, even for the iron-enriched variety [80]. Therefore, the authors suggested that oat-based beverages can be manufactured by adding vitamins prior to direct UHT treatment with a shorter holding time to obtain highly retained vitamin products, and the iron-enriched oat beverages can be achieved by filter sterilization without affecting the fatty acid profile [80].

11.4.7 *Drying*

After lipase and lipoxygenase were inactivated by heat denaturation before milling, heat is always applied for an extended period, known as kilning. Kilning is beneficial to the oat quality due to the inactivation of bacteria, yeasts, and molds, which can shorten the shelf-life of the products and cause food safety risks [81]. Moreover, kilning can also increase the Maillard reaction between proteins and carbohydrates and produce desirable flavors, browning, and the formation of antioxidant compounds, which can increase the stability of lipids [82]. Although it was known that kilning may destroy some heat-labile vitamins, the benefits of kilning to extend shelf-life far outweigh these undesirable effects.

The tocopherols and tocotrienols in the steamed rolled oats were almost completely loss after drum drying treatment, and the total cinnamic acids and avenanthramides also decreased significantly [56]. Nevertheless, less pronounced losses were observed while the process was applied to the whole meal made from autoclaving groat [56]. It is worthy to note starch gelatinization might occur during oat processing, such as while steam was applied followed by drying in oat flake processing, and the pre-gelatinized starch easily and rapidly absorbs water than unprocessed starch, thus decreasing the cooking time.

11.5 Possible Approach to Enhance Health Benefit of Oat Bioactives

Food processing can first render food into a suitable form and good palatability and also play an important role in increasing the health benefit of bioactives [83]. It may affect both the levels of the bioactive compounds and their bioavailability of the grain as reviewed previously by Slavin et al [84] Up to now, a number of methods have been applied to improve the nutritional qualities of cereals, such as genetic improvement and amino acid supplementation with protein concentrates or other protein-rich sources [85]. Additionally, many processing technologies including cooking, melting, milling, and fermentation have been put into practice to enhance the nutritional properties of cereals. Among these technologies, fermentation is recognized as one of the most effective methods.

11.5.1 *Fermentation*

Fermented oat-based food has become the most popular part of a healthy diet in the functional food market. The significant potential of yoghurt and sourdough fermentation to improve the nutritional properties of oat and other cereals has gained much attention, and the interest at present is still increasing. It has been reported that after appropriate processing, oat is a suitable substrate for fermentation with lactic acid bacteria [86, 87]. Recently, Yu et al. [88] observed that the oat vinegar products revealed more favorable in vitro antioxidant as evaluated by 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging abilities. Moreover, oat vinegar comparably decreased D-galactose-induced oxidative damage in mice serum and liver. Importantly, the different fermentation processes of oat vinegars were accompanied by the dynamic migration and transformation of specific phenolic acids across bound, esterified, and free fractions. Thus, the antioxidant activities of oat vinegars could be improved through targeted modulation of the generation of specific phenolic acid fractions during production processes.

11.5.2 Utilization of Pearling By-products

Pearling or debranning is used to remove the remainder of hull as well as endosperm, which might lead to a reduction of 7–14% grain weight [89]. This process can be efficiently utilized as abrasive technique to gradually remove the seed coat (testa and pericarp), aleurone and sub-aleurone layers, and the germ, to produce a polished grain and by-products including high levels of bioactive compounds like β-glucans, tocopherols, and tocotrienols [90, 91]. These by-products can be used as potential sources of bioactives and enhance the nutrition and health benefits of the end product. Compared with milling, pearling is considered more effective to concentrate bioactives in oat flour as reported by Wang et al [92]. That is a pearling fraction consisting of 20% of the original kernel weight exhibited the higher concentrations of α-tocotrienols, α-tocopherol, and total tocols in comparison with whole hull-less barley grain. Borrelli et al. [79] also found the same results for the pearling of wheat.

11.5.3 Extrusion

Extrusion is a high-temperature, short-time process of intense mechanical shear processing, which has been widely used to ready-to-eat cereals, snacks, and so on [93]. In a recent study, extrusion exhibited great significance for formulation and development of healthy snacks with minimal loss of nutrients during processing [94].Interestingly, extrusion has proved to enhance the functional properties of oat bran, with the bran exhibited more aggregates, higher gelatinization temperature, higher solubility, swelling capacity, etc. The modification in rheological behavior might be due to the slower gut transit and the perceived “fuller for longer” of satiety effects [95]. Min et al. [52] found that the extraction rate of oat bran soluble dietary fiber increased after the extrusion processing, and the proportion of high molecular weight granules was higher in oat bran soluble dietary fiber from extruded oat bran compared with steam heating and superfine grinding treatment. Camire and Flint

[96] demonstrated that the total non-starch polysaccharides increased in oatmeal with extrusion cooking and baking processes; however the ratio of soluble to insoluble non-starch polysaccharides was higher in the extruded samples. Similar observations were also reported by Min et al. [52]

Gopirajah and Muthukumarappan [94] demonstrated that extrudate protein availability and water absorption capacity were improved with a single-screw extruder. Extrusion also showed potential application in the replacement of traditional heat treatment in production of whole meal oats with stable lipids. Enzymatic degradation of lipids could effectively be prevented by extrusion even at its lowest temperature of 70 °C [53].

11.5.4 Malting

Steeping, germination, and the kilning process involved in the malting of grains always cause some physiological changes of cereal grain [97]. Therefore, malting can be used to improve the texture, flavor, as well as the nutritive value of grains [98].The content of some vitamins and antioxidants can be increased and some anti-nutritional factors are decreased. Additionally, only fermentable sugars and starches present in the grain can be utilized by the enzymes during malting; thus, the spent grain can remain, keeping a high level of tocols [99].

Phytate is a main anti-nutrient in coarse cereals. It is a myoinositol molecule esterified with phosphate group on all six hydroxyl groups and with strongly negative charge. Although phytate has been reported with good antioxidant activity and can prevent certain types of cancer, it has been widely accepted that phytate forms complexes with some metal ions and therefore lowers their bioavailability. Due to the mineral-phytate complexes in the grains, it cannot be efficiently utilized by humans, as they lack the necessary phytases to break down the complexes [100]. It has been reported that malting can increase the phytate activity in cereals and cause a breakdown of phytate [101]. Larsson and Sandberg [102] reported that in whole malted grains, the phytate content was reduced at most by 79% after soaking whole kernels. The absorption of iron and zinc was proved to improve by the decrease of the phytate content from whole grain oat products [103].

Recently, it is reported that higher moisture, ash, crude fat, energy, amylase activity, and in vitro protein digestibility were observed in malted oat flour [104]. Hübner et al. [98] also found the content of insoluble fiber was enhanced after applying long germination periods for oat malts. Furthermore, the increasing of protein content for the germinated grains can be attributed to the quantitative reduction in anti-nutritional factors (tannin, polyphenols, and phytic acid) as well as other macromolecules of the grains particularly carbohydrates.

On the other hand, malting can also cause some undesirable side effects, such as it causes the breakdown of β-glucans, which is detrimental to the functional properties of β-glucan. Therefore, malting parameters (germination time, germination temperature, degree of steeping, etc.) should be seriously considered without substantial loss of the most important bioactives like high molecular weight β-glucan. According to the research of Wilhelmson et al. [105], a short malting schedule (72 h, 15 °C) was developed to produce germinated oats, retaining 55–60% of the β-glucan, because the decrease in the molecular weight of β-glucan was initially very slow.

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Chapter 12
Quinoa

Jie Liu

12.1 Introduction

Quinoa (*Chenopodium quinoa Willd*) is an annual self-pollinated dicotyledonous plant and belongs to the Chenopodiaceae family, also known as *Chenopodium album*, Indian wheat, and quinoa. It is originally from the Andean region of South America, mainly distributed in Bolivia, Ecuador, and Peru, with cold-resistant, drought-tolerant, barren-resistant, and salt-tolerant characteristics. It is a cool, high-altitude crop and is the main traditional food of indigenous Incan peoples. It has a planting history of 5000–7000 years. It is a kind of cereal that is used for both medicine and food. It has both rich nutritional value and medicinal value. As understandings of the nutritional value and health functions of quinoa have grown, its consumption demand has also increased.

Quinoa has a high nutritional value. It is the only food that the United Nations Food and Agriculture Organization (FAO) recognizes as a single plant to meet the basic nutritional needs of the humans and is called “the mother of grain” by the ancient Incan peoples [1]. Quinoa is listed as one of the ten most nutritious foods in the world and is one of the ideal space food choices of the US space agency (NASA). Quinoa, as a “whole grain,” is not only rich in protein and calcium, iron, and zinc but also rich in many bioactive substances, such as saponins, flavonoids, polyphenols, and anthocyanins. It has good adjuvant therapy for the prevention of obesity, cardiovascular disease, diabetes, and cancer but also has anti-inflammatory, anti-oxidizing, and immune system-enhancing effects [2]. Because of its rich and comprehensive nutritional value and medicinal value, quinoa has received extensive attention both by food scientists and consumers in recent years. However, as a new crop to the world stage and public consciousness, there are few reports on its nutri-

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tional active ingredients. To this end, combined with the latest research trends at home and abroad, and based on previous studies, this reivew explained the nutrients and active ingredients of quinoa which could provide theoretical basis for quinoa in nutrition, healthcare, and medicinal purposes.

12.2 Bioactive Ingredients

Quinoa is the only monomer plant identified by FAO as meeting the basic nutritional needs of the human [3] and listed as the ten most healthy and nutritious foods in the world. Quinoa is not only rich in protein, fatty acids, and minerals but also rich in bioactive ingredients such as polyphenols, saponins, and flavonoids. It plays a very important role in both preventing and treating diseases and maintaining human health. With a deeper understanding of the nutritional value and health functions of quinoa, scientists have paid increasingly close attention and studied the active ingredients.

12.2.1 Polyphenols

Plant polyphenol is a kind of secondary metabolite with polyphenol structures that are widely found in plants. It mainly exists in the skin, roots, leaves, and fruits of plants and is biologically active in scavenging free radicals and antioxidants [4]. Plant polyphenols include a variety of natural phenols such as tannins, catechins, quercetin, gallic acid, ellagic acid, and arbutin [1], which are natural antioxidants. Nowadays, quinoa is attracting increased attention due to the high content of polyphenols in its tissues and organs.

Repo-Carrasco-Valencia et al. [5] have measured the content of total phenol and soluble phenolic acid in quinoa, amaranth, and pallidicaule. They found that phenol content varied from 16.8 to 59.7 mg/100 g, the proportion of soluble phenolic acids ranged from 7% to 61%, and polyphenols showed strong antioxidant activity in vitro. Paweł et al. [6] determined the content of anthocyanin and polyphenol in quinoa and leek. Through the comparative analysis of DPPH free radical scavenging ability, ferric reducing ability of plasma (FRAP), and ABTS radical scavenging ability, they determined that the total phenol content in quinoa and leek was (3.75 ± 0.05) mg/g and (2.95 ± 0.07) mg/g, respectivley. The total polyphenol content of quinoa is higher than that of leeks. Both have good antioxidant capacity.

12.2.2 Saponins

Saponin, also known as alkali soap, is a compound composed of one or more sugar chains and one triterpene aglycone or steroidal glycoside and is an anti-nutrient material. The main saponins of quinoa are oleanolic acid, ivy saponin, phytolaccagenic acid, and serjanic acid. Its carbohydrates include glucose, arabinose, and galactose [7]. Saponins are mainly distributed in plants grown at high elevations, and trace amounts also exist in marine life such as starfish and sea cucumbers. The saponin content in quinoa is very high and it has highly biologically active. It has analgesic, anti-inflammatory, anti-microbial, antioxidation, anti-virus, and anti-cytotoxicity functions. Quinoa can be divided into sweet quinoa (<0.11%) and bitter quinoa (≥0.11%) based on saponin content. The saponin of quinoa is mainly located in the seed coat. Sweet quinoa contains 0.02%–0.04% of saponin and bitter one contians 0.47%–1.13%. Both varieties contain higher levels than soybeans or oats [8].

Estrada et al. [9] studied the effect of saponin extracted from quinoa on the gastric and nasal mucosa of mouse antigen model. When quinoa saponins were combined with cholera toxin or ovalbumin and carried in the stomach or nose, specific immunoglobulin G (Ig G) and Ig A antibodies in the blood, small intestine, and lung triggered antigen responses, suggesting that saponins have a positive effect on human immune regulation. Although saponins have a variety of positive effects on the human body, it is also an anti-nutrient material and affects the taste of quinoa. Therefore, before consuming quinoa, water is needed to remove saponin from the seed surface [10].

12.2.3 Flavonoids

Flavonoids are compounds that exist in nature and have a 2-phenyl flavonone structure. Its hydroxyl derivatives are mostly yellow. Flavonoids usually bind to sugars in the plant body as glycosides, and small fractions exist in free form. Most plants contain flavonoids, which play an important role in plant growth, development, flowering, production, and antibacterial and disease prevention. Quinoa has high flavonoid content ranging from 36.2 to 144.3 mg/100 g [11]. According to reports [12], flavonoids are often present in the form of flavonoid glycosides in the plant family. Quinoa is rich in flavonoid glycosides, including quercetin, isorhamnetin, kaempferol, aglycones, and disaccharides and trisaccharides, whose sugar groups are attached at the C-3 position. According to reports, the scavenging capacities of quinoa flavone extracts for DPPH and ·OH were 89.3% and 86.6%, respectively, and the inhibition rate for amylase was 41.38%. It has been proved that flavonoids effectively scavenge free radicals and have antioxidative functions [4].

12.2.4 Anthocyanins

Anthocyanins are water-soluble natural pigments widely found in plants. They are colored elements derived from the hydrolysis of anthocyanins. Most of the major coloring matter in fruits, vegetables, and flowers is related to it. Anthocyanin content in quinoa is very high, in the form of glycosides. Paweł et al. [6] found that the content of anthocyanin in the grain of quinoa was 120.4 ± 7.2 mg cyanidine-3-glucoside equivalent (CGE)/100 g DW, higher than that of many grains and legumes. Furthermore anthocyanin content was increased with the germination process. Studies have shown that anthocyanins have certain antioxidant and therapeutic effects, such as antitumor, anticancer, anti-inflammatory, and cardiovascular disease prevention [7].

12.2.5 Phytic Acid

Phytic acid is also known as creatine, cyclohexanol hexahol-dihydrogen phosphate, which is found mainly in the seeds, roots, and stems of plants. The content in bran and germ of quinoa is the highest, which can produce insoluble compounds with metal ions such as calcium, iron, magnesium, and zinc and reduce the effectiveness of metal ions. Phytic acid can also form complexes with proteins, making metal ions even more unusable and affecting the availability of mineral elements. It is an antinutritional component.

12.2.6 Lipids

Quinoa is rich in fat, the content of which is much higher than common grains. The fat content of quinoa was twice that of corn, but fatty acid composition was similar to corn. Therefore, quinoa has great potential in vegetable oil extraction and utilization. There are many essential fatty acids in quinoa, which are mainly polyunsaturated fatty acids omega-6 and omega-3 [14]. Omega-6 content was significantly higher than wheat and rice, and the content of omega-3 was about three times that of wheat. According to the study, the proportion of unsaturated fatty acids in quinoa accounts for more than 83% of total fatty acids, which can reduce low-density lipoprotein and increase high-density lipoprotein. The ratio of high unsaturated fatty acids can also maintain lipid membrane fluidity. Most of the omega-3 and omega-6 unsaturated fatty acids contain carbon-carbon double bonds, including linoleic acid, linolenic acid, and arachidonic acid, all of which are essential for the human body [13]. Linoleic acid can be metabolized to arachidonic acid, which can be further metabolized to eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). EPA and DHA play an important role in the prevention and treatment of prostaglandins, thrombosis, atherosclerosis, immunity, anti-inflammatory, and membrane function [14].

12.2.7 Carbohydrates

Quinoa is rich in soluble and insoluble cellulose, and some of them have a very important role in regulating blood glucose levels and reducing cholesterol. The most common carbohydrate in quinoa is starch, which accounts for 58%–64.2% of the total dry matter [15]. In addition, the physical properties of starch in quinoa are different from other crops. For example, quinoa starch has similar expansion capacity to wheat, but its freeze-thaw stability is much higher than that of wheat, and the onset temperature and the maximum temperature of starch gelatinization are lower than that of barley [16]. Studies have shown that soluble sugar content in quinoa is very high, up to 15.8%, and glucose, fructose, and sucrose contents were 4.55%, 2.41%, and 2.39%, respectively [17]. Quinoa is low glycemic index (GI) food that can play a beneficial role in the metabolism of glucose and lipids [18]. There are many studies on the extraction methods of quinoa polysaccharides, in which YIF93 (YIF91) and YGF93 (YGF91) have significant antioxidant and immunomodulatory activity, which can be used as potential antioxidants and immunomodulators [19].

12.3 Nutrition and Functions

12.3.1 Gluten-Free

Gluten is a group of proteins in grains, especially in wheat. For most people, gluten is an unremarkable protein that is easily digested in the gastrointestinal tract. However, there is a small group of people who cannot digest gluten protein as most people do. These people have trouble with gluten protein digestion and commonly suffer from celiac disease (a type of intestinal disorder that is not resistant to gluten) [20].

The protein content of different quinoa varieties is different and it is mainly present in the endosperm. Quinoa has much more protein than rice, wheat, barley, and many other common grains. The protein of quinoa is mainly composed of albumin and globulin (account for 44%–77% of the total protein), both of which have good stability due to their disulfide bonds. Alcohol-soluble glutenin and gliadin content in quinoa is comparatively much lower and is commonly called gluten-free [21], so it has better solubility and absorption effects than others [22]. It is an excellent source of nutrition for patients with celiac disease [23–27].

12.3.2 Antioxidant Activity

Many of the bioactive ingredients in quinoa are antioxidant, such as phenols and carotenoids, making quinoa an excellent source of antioxidants [28]. The antioxidant components in quinoa were determined by DPPH, FRAP and ORAC, and unsaturated fatty acid (UFAs), total carotenoid index (TCI) and total tocopherol index (TTI) were found to have a positive correlation with the antioxidant capacity [29].

Polyphenols play the most important role among all the antioxidants. Polyphenols are the secondary metabolites of plants related to their antioxidative property and are widely present in plant roots, stems, skins, leaves, and fruits. They exhibit certain biological activities such as free radicals scavenging ability and antioxidative function [30]. Paweł et al. [6] found that the polyphenol content in quinoa kernel and bud seedling was positively correlated with its antioxidant capacity. Phenolic compounds in most foods exist in the form of esters, glycosides, or polymers that cannot be edible. These polyphenols must be hydrolyzed first in the intestine by intestinal enzymes or bacterial degradation and then they can be absorbed by human body. Nearly 80% of the total polyphenol compounds in quinoa remain biologically active in vitro [31].

Among the evaluation methods for antioxidant capacity, a cell-based antioxidant assay (CAA) was selected which could highlight the bioavailability, absorption properties, and antioxidant metabolic compounds of the antioxidant active substances [32, 33].

Another method for assessing antioxidant capacity is to determine antioxidant enzymes activities, such as glutathione (GSH), superoxide dismutase (SOD), glutathione peroxidase (GPx), and catalase (CAT) in vitro [32, 34]. At present, although many studies have shown phytochemicals such as saponins and flavonoids exhibit strong antioxidant activity, the mechanisms of these compounds are not fully understood, and further studies on the regulation of bioactive components of quinoa in vivo are needed [35].

12.3.3 Anti-inflammatory Activity

There are many bioactive ingredients in quinoa that have anti-inflammatory and antifungal functions. Noratto et al. [36] found that polyphenols extracted from quinoa had the effect of lowering inflammatory cytokines expression such as IL-1β, IL-8, and TNF-α, and protecting against inflammation caused by obesity and maintaining a healthy environment in the cecum of mice.

Flavonoid compounds that exist in quinoa possess anti-inflammatory functions. Formica and Regelson [37] found that flavonoids had many biological activities, including inducing apoptosis; resisting mutagenesis; inhibiting protein kinase C, superoxide dismutase, and lipoxygenase activity; and inhibiting histamine release through vitro experiments.

Quinoa is also an important and active anti-inflammatory substance, which can inhibit macrophages from producing harmful metabolites NO, tumor necrosis factor-alpha, and interleukin-6 [19].

Woldemichael and Wink [12] have isolated and identified 16 saponins from quinoa seeds and detected the hemolytic activities and antifungal activities of these compounds through NMR, mass spectrometry, and chemical methods. Alkaline treatment could destroy cells member which helps to enhance the antifungal activities of quinoa saponins.

12.3.4 Skin Care Activity

Quinoa's proteins exist in its endosperm, which is generally 8%–22% higher than common grain, such as rice, wheat, and barley. It does not contain glutenin. The protein of quinoa is a kind of acid protein, mainly composed of albumin and globulin (they account for 44%–77% of the total protein). The two proteins have good stability because of the two sulfur bonds it contains. The content of gliadin and glutenin is lower than other grains, and it is easy to be absorbed in and utilized by the human body.

On skin care and beauty products, plant's protein mainly has the effect of horniness removing, firming, antiaging, whitening, antioxidant, moisturizing, and anti-inflammatory functions. In recent years, due to plant protein's active ingredients and mild side effects, natural beauty products based on it have becoming more and more popular. Thus quinoa protein is a kind of excellent cosmetic raw material. Hydrolyzed quinoa protein can be used as a natural skin nutrition and hair conditioner. Quinoa saponins are natural and mild plant surfactants. Quinoa seed oil is edible, and it has potential medicinal beauty uses. The rich mineral elements in quinoa are also the nutritional ingredients of human skin [38].

Quinoa is also rich in vitamins and amino acids [6], which can be used for skin care products, cosmetics, and other raw materials.

12.3.5 Anti-obesity and Diabetes Treatment

Quinoa contains low fat, low sugar, and low starch. The regular consumption of quinoa not only reduces the occurrence of type II diabetes mellitus but also has the function of reducing weight. The rich mineral elements of quinoa that regulate glucose levels in the human body act as an inhibitor or activator of key enzymes in glucose metabolism. The rich contents of quinoa's isoflavones and VE contribute to blood circulation, softening blood vessels, promoting sugar and lipid metabolism and insulin secretion, and reducing blood glucose levels [5]. Ruales and Nair [39] reported that quinoa contains 11% of insoluble fiber and 2.4% of soluble fiber. These two kinds of cellulose have a very important role in regulating blood glucose levels, lowering cholesterol levels, and protecting the heart. Furthermore, cooked quinoa's volume is 3–4 times larger than raw, which makes the absorbing capacity of dietary fiber stronger and produces a strong feeling of satiety after eating. Thus, it is helpful for weight control. Quinoa is a kind of low sugar and low calorie food. Experiments with mice found that blood glucose and blood lipids were significantly decreased after feeding with quinoa [32]. Quinoa is also a healthy food for hypertensive patients, hyperlipidemia patients, hyperglycemia patients, obese people, and diabetics.

12.3.6 Cardio-cerebrovascular Diseases and Other Diseases

Many active ingredients in quinoa can regulate human diseases. The consumption of quinoa can regulate fructose metabolism in the human body, which plays an important role in oxidative stress reactions. Thus it has a protective effect on the heart, kidney, liver, and other important organs. Gawlikdziki et al. [40] found that ferulic acid, mustard acid, gallic acid, kaempferol, isorhamnetin, and rutin extracted from quinoa could inhibit the activity of fatty acid enzymes, hinder intercellular communication, and inhibit the proliferation of cancer cells.

12.4 Summary and Outlook

In the recent years, with the rapid development of functional foods, the international market of quinoa is expanding gradually, from its origins in South America to the United States and later to Europe, Asia, and beyond. The annual production of quinoa is rising steadily. The planting areas of quinoa are growing in the United States, Britain, France, Italy, Germany, and other countries. Quinoa, just one single plant, could meet the basic nutritional needs of the human body and is officially recommended by the United Nations Food and Agriculture Organization (FAO) as the most suitable food for human consumption because of its "full nutrition." Therefore it was listed as one of the world's ten healthiest nutritional foods. The year of 2013 was marked as the "International Quinoa Year" [41]. Although quinoa contains some anti-nutritional factors, it can be removed during processing or applied better through appropriate treatments.

The cultivation of quinoa has also developed rapidly in China. It has been introduced and researched since the beginning of the 1990s, and its cultivation has been expanded rapidly. However, since its introduction to China is in a relatively short time, research on it is still at initial stages.

There are few studies on the breeding of new varieties, the nutritional components, and the bioactivities of quinoa. Thus, there is still a long way to go in the research and development of quinoa production.

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Chapter 13
Amaranth

Maryam Iftikhar and Majid Khan

13.1 Introduction

People nowadays are far more concerned about their diet in daily life. Many people are allergic to some elements of food which may cause severe illnesses such as celiac diseases. Overconsumption of the protein gluten, mainly found in barley, rye, and wheat, causes celiac disease. It is a genetic autoimmune disorder which cuts back or permits nutrient absorption in the blood stream [1]. This illness can only be controlled by eliminating gluten from one's daily diet. To deal with this problem, the market is now providing gluten-free products that are prepared by removing protein. However, these products have less nutritional value compared to the food items which contain gluten [2]. Food that is free from gluten contains smaller quantity of fiber, vitamin B, and iron [3]. There are several plants that are being used as alternatives to cereals containing gluten, e.g., amaranth, buckwheat, and quinoa. Furthermore, these gluten-free plant alternatives are quite similar in dietary nutrients to the cereals containing gluten and are referred to as pseudocereals [4].

In recent years, pseudocereals amaranth, buckwheat, and quinoa have attracted a lot of interest. Their exceptional nutrient profile is one of the reasons for this renewed concern. Due to high starch content, these pseudocereals provide an excellent energy source and also provide dietary fiber, lipids high in unsaturated fats, and good proteins. Moreover, they comprise sufficient levels of essential micronutrients such as vitamins and minerals and significant amounts of different bioactive elements such as squalene, phytosterols, fagopyritols, polyphenols, and saponins [5].

Amaranth plant (also known as kiwicha or *Amaranthus*) originated in Central America (Mexico and adjoining countries) and is, along with corn beans, an essential crop. The grains provided by this plant are mostly processed into flour for baking. They are also used to prepare beverages, including alcohol [6]. Many European

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countries have strong interests in amaranth exploration and production, particularly Austria, Slovak Republic, Czech Republic, Germany, Poland, Hungary, Russia, Slovenia, and Italy. In the sixteenth century, amaranth was first introduced to Spain from which it spread all over the Europe and, by end of the eighteenth century, reached Asia and Africa in the mid-1970s [7]. Nowadays amaranth is primarily planted as a vegetable in Africa and Asia and only cultivated as minor crop in the Himalayan region [8].

Grain amaranth belongs to the order Caryophyllales, amaranth family Amaranthaceae, sub-family Amaranthoideae, and genus *Amaranthus* [8]. In botanical terms, it is opposite of the majority of the cereals (e.g., wheat, rice, barley) which are monocotyledonous. Buckwheat, quinoa, and amaranth are not considered as true cereals, as they are dicotyledonous plants. Their seeds have similar composition and function than those of the actual cereals [5]. In terms of utilization of cultivated amaranths, the species can be divided into vegetable amaranths and grain for individual consumption. Most of the *Amaranthus* species have edible leaves, and some species such as *A. blitum*, *A. viridis*, *A. lividus*, *A. tricolor*, *A. gracilis*, and *A. gangeticus* are already commonly used as boiled greens called potherbs [8]. Though the leaves are edible, seeds are the key yielded items for which amaranth is grown. Typical *Amaranthus cruentus*, *Amaranthus hypochondriacus*, and *Amaranthus caudatus* are the species of the seeds that are cultivated. Amaranth is also an ornamental, flowering plant and recognized as a weed too. In this respect, the red root species of amaranth, i.e., *Amaranthus retroflexus*, is one of the most renowned in the world and at the same time one of the most troublesome species [6] (Table 13.1).

Amaranth's mild spinach-like flavor, ability to grow in hot weather, and high nutritive value have made them a widely used vegetable crop and possibly the most commonly eaten vegetables in the humid tropics of Asia and Africa [8].

The amaranth plant has almost 60 species, but most of them are not usually seen on daily menus. Mostly the young leaves of the *Amaranthus blitum*, *Amaranthus cruentus*, *Amaranthus tricolor*, *Amaranthus dubius*, *Amaranthus hypochondriacus*, and *Amaranthus edulis* plants are used in soups and salads. Some of the species like *Amaranthus retroflexus*, *Amaranthus spinosus*, and *Amaranthus viridis* are not safe to consume for either humans or livestock. The grains of *Amaranthus hypochondriacus*, *Amaranthus caudatus*, *Amaranthus hybridus*, *Amaranthus cruentus*, and *Amaranthus mantegazzianus* are used to develop taste and nutritious value of

Table 13.1 Comparison of the content of basic chemical components in amaranth seeds (*A. cruentus*) as well as in wheat, rye, corn, and rice [6]

	Amaranth	Wheat	Rye	Corn	Rice
Chemical components	Content in % s.m				
Total carbohydrate	62	68	71	67	75
Total protein	15.7	12	9	10.3	8.5
Fat	7.2	1.9	1.9	4.5	2.1
Raw fiber	4.2	1.8	1.9	2.3	0.9
Total ash	3.3	1.9	1.7	1.4	1.4

cookies, breads, confectionary, cakes, and soups [9]. Favorable chemical content and the resulting high nutritional value as well as great potential for practical usage caused UN/FAO nutritional experts to recognize amaranth as the plant of the twenty-first century [6].

Amaranth seeds (as shown in Fig. 13.1a) are small (1–1.5 mm diameter); they are lenticular in shape and weigh 0.6–1.3 mg per seed [5]. Amaranth may be found in diverse forms, from broad-branching (bushy) to absolutely lateral shoots, with creeping stems (lying) up to perfectly vertical, with a variety of colors of stems and seeds, which can be yellow, white, brown, or entirely black, as well as colors of leaves that may vary from different shades of red to green. In the same way, plant height also has great diversity, which can differ from 0.3 to 3.0 m. Generally, the height of the seed forms lie between 1.0 and 2.0 m, and vegetable forms can be found from 0.3 to 1.0 m. Amaranth generally has alternate or opposite leaf arrangements and considered an annual plant. It has single inflorescences (as shown in Fig. 13.1b) with unisexual or bisexual flowers; however, abundant and thick inflorescences are the characteristic traits of amaranth, particularly among the seed forms. One plant can produce over 500 grams of seeds, and the vegetable forms, comparatively pastures, produce a smaller amount of seeds but at the same time a large amount of green matter, i.e., leaves. Generally, it is a plant that has characteristics to adapt to soil and climate conditions extremely well. Amaranth grows well in high concentrations of nitrogen. The amount of green matter will increase rapidly, when the nitrogen content of the soil is of a reasonable amount, and as a result cultivation of vegetable or pasture species will be significant [6].

These crops are highly nutritious and environmentally resistant. They can be adapted to different environmental conditions, being cultivated in poor soils and high altitudes [7]. Amaranth is a C4 photosynthesis plant, which means that it can bind CO_2 with specific utilization of solar energy [6]. This ability to grow in a warm climate was attributed to the anatomical features and C4 metabolism of the plant. Amaranthus species can also tolerate salinity stress [10]. Amaranth has potential for functional and bioactive ingredients in food products because of their high dietary fiber content and natural antioxidants, such as phenolic compounds [7].

Fig. 13.1 (**a**) Purple amaranth seed; (**b**) An inflorescence of purple amaranth

13.2 Bioactive Compounds in Amaranth

Amaranth (*Amaranthus mangostanus* L.) is an annually grown herb from the family of Amaranthaceae; in Chinese it is commonly called "xiancai." As a vegetable high in antioxidants, amaranth is ranked as one of top five vegetables. It contains a bounty of bioactive components, such as beta-carotene, *L*-ascorbic acid, polyphenol, lutein, and anthocyanins. It has been used in traditional medicines, as an antipyretic in India and Nepal to lessen labor pain. As diuretic, astringent, hepatoprotective, and hemorrhage agent, amaranth has also been used in the treatment of bladder distress, toothache, blood disorders piles, and dysentery. In vivo, evaluation of amaranth shows anti-inflammatory, anthelmintic, and antioxidant agent properties.

13.2.1 Protein

An excellent amino acid balance has been found in the storage proteins of amaranth grains, which are also known to have antioxidant, antihypertensive, antiproliferative, antithrombotic, cholesterol lowering, and immune regulatory properties. Due to the sensitivity to hydrolysis by gastrointestinal proteases, biologically active peptides in functional foods do not always reach the target organs, which is one of the main drawbacks of such foods. According to a number of studies, the storage proteins of amaranth also have good film forming, gelifying, foaming, and emulsifying properties, as well as excellent water retention capacity [11].

Various bioactive peptides having diverse bioactivities related to health, such as hypertension and cancer, can also be obtained from amaranth seeds. Amaranth also contains an anticancer peptide, which is a bioactive peptide like lunasin, previously found only in barley, soy, and, most recently, wheat. Lunasin has a reasonably high concentration of aspartic acid. Amaranth glutelin also has a relatively high concentration of aspartic acid, 10.6% of the total protein, suggesting that the acidic regions may be related to a lunasin epitope in the protein fractions of the seed. Antihypertensive peptides are the most frequent in amaranth, especially globulin 11S, which showed properties with potential to reduce the angiotensin-I converting enzyme (ACE). In the renin-angiotensin system, the ACE inhibitor plays an important role and helps to regulate blood pressure. Inhibitors of this enzyme lower blood pressure, and many antihypertensive drugs are compelling ACE inhibitors.

Proteins found in amaranth seed could be a substitute source of lunasin-like isoforms or lunasin. In addition, amaranth seeds are a potential source of other bioactive peptides with biological functions that could be beneficial to health, particularly antihypertensive activity. Since high amount of amaranth seed proteins found in globulins and glutelins, amaranth could provide a great potential source of antihypertensive peptides. Proteins in amaranth contain active peptides which perform 12 major activities: antithrombotic, antiamnestic, immune modulating, ligand, antioxidant, opioid, regulating, activating ubiquitin-mediated proteolysis (AUMP), embryotoxic, protease inhibiting, immune stimulating, and antihypertensive [12].

The amaranth is easy to digest because it is a gluten-free grain. About 90% of amaranth grain is digestible, and due to its ease it provides in digestion, it has traditionally been of use to patients who are recovering from long fasting period or illness [13].

The use of its seeds has also increased the production of flakes, flour, popped seeds, and several sorts of bread and confectionery. The products obtained from amaranth are a valuable source of nutrients, minerals, and lipids. Moreover, amaranth provides an attractive source of protein due to its high amino acid profile. Amaranth flour is often used in mixtures with maize or wheat when it is consumed with other cereals; it is a reasonable source of protein. It has also been reported that instead of amaranth flour, the addition of 10–20% amaranth seeds might be used to improve the nutritional value of bread. Furthermore, amaranth products and seeds are a very balanced source of bioactive substances which perform antioxidant activities. The grain lipids of non-saponifiable substances include tocopherols, squalene, sterols, and others [14].

13.2.2 Polyphenol

For the protection of plants against pathogens, herbivores, and ultraviolet radiation, polyphenol plays an important role as a secondary metabolite. A number of molecules in a polyphenol structure (i.e., benzene rings with one or more hydroxyl groups) have been recognized in the edible parts of plants [2].

Bioactive phytochemicals, functioning as a chemical defense against microorganisms and insects, are mainly found in the outer layers of the amaranth seeds. These compounds may be lipophilic or hydrophilic in nature. Phenolic compounds, particularly phenolic acids, are primarily located in the seed coat of the amaranth seeds. Phenolics may include tannins, phenolic acids, and flavonoids and are relatively hydrophilic in nature. They formulate the majority of the plants secondary metabolites that contribute to various physiological effects. Phenolic acids varied from 168 to 329 mg/kg in amaranth seeds found in free, conjugated, and bound forms, whereas the fraction of extractable phenolic acids varies from 7 to 14% of the total phenolic acid. Amaranth seeds and sprouts rutin also contain phenolic acids including *p*-hydroxybenzoic acid, gallic acid, and vanillic acid. Three primary free phenolics in seeds are gallic, protocatechuic, and *p*-hydroxybenzoic acid that are present in amaranth at 11.0–440, 4.7–136, and 8.5–20.9 mg/kg dry seed, respectively. After alkaline and enzyme hydrolyses ferulic acids, mainly *trans*-ferulic acid (620 mg/kg) and *cis*-ferulic acid (203 mg/kg) were found in amaranth seeds [15].

Phenolic compounds are important phytoconstituents and classified into different components including organic or phenolic acids and bioflavonoids. Phenolic compounds are reported to play an important role in the prevention and treatment of different diseases like cancer, diabetes, and cardiovascular (CVS) diseases. Initial findings confirmed that *Amaranthus* leaves are important sources of antioxidants. Red amaranth cultivars having different flesh color or same color may differ in their phenolic content and antioxidant activity. Ecological parameters like light, humidity, and temperature play significant role in plant's antioxidant metabolism. Phenolic compounds act as antioxidants, reducing agents and hydrogen donors because they have redox properties [16]. It has been reported that red amaranth is a rich source of polyphenol. It has been observed red-fleshed cultivars with a better color index are an important source of phenolic compounds and have significant antioxidant potential. Although antioxidants present in vegetables such as ascorbate, proteins, and carotenoids are not a potent source of antioxidants, it has also been reported that total polyphenol and antioxidant activity in amaranths (*Amaranthus* spp.) were higher than or similar to malabar spinach, basil, and sweet potato vine.

Although some fruits and vegetables have an astringent taste attributed to phenolic compounds or tannins, amaranth has an acceptable taste as is consumed as a popular and tasty vegetable in many parts of the world. Therefore, red amaranth would be a healthy food choice for consumers, as well as a potential source of natural antioxidants, namely, polyphenols. Total polyphenols were significantly higher, and antioxidant activity was more than six times higher in the leaves of plants grown in full sunlight than triple black net-shaded leaves. Plants grown under average temperature, 29 ± 2 °C and without shading, accumulate a higher concentration of polyphenols and antioxidants than plants grown under comparatively lower temperature and shaded conditions. Leaves matured under shade have fewer amounts of phenolic compounds due to less stimulation of phenolic production by light. Red amaranth has significant antioxidant capacity due to its high concentration of betacyanin along with phenolic compounds [16].

13.2.3 Squalene

Seeds of *Amaranthus* contain high amount of fiber and also serve as important source of triterpene-like squalene. Squalene is an important antioxidant and also very active against cancer and hypercholesterolemia and as cardioprotectant [17]. Squalene is an important intermediary component of cholesterol synthesis. In amaranth seeds, squalene concentration is high as 620 mg/kg that is significantly higher than maize, buckwheat, and barley [15].

Squalene is commonly used in cosmetics due to its photoprotective activity and also used in computer disks as lubricant due to its heat stability. It is hypothesized that squalene present in olive oil is responsible for the decreased risk for various cancers. Squalene is reported to be effective in reducing serum cholesterol level. Diets containing 20% *Amaranthus cruentus* (Ac) grains and 5% crude amaranth oil played an important role in reducing cholesterol and low-density or very low-density lipoproteins [18]. It has important role in reducing lung, skin, and colon cancer as it has chemopreventive effects. Other valuable health effects are due to its hypocholesterolemic action, in combination with the administration of tocotrienols [19].

13.2.4 Tocopherols

Tocopherols and tocotrienols are vitamin E homologs. Amaranth seeds are reported to contain all four (α, β, δ, and γ) of tocopherol. Common tocopherols in amaranth seeds are α-tocopherol (1.40–31.4 mg/kg), γ-tocopherol (0.01–48.79 mg/kg), δ-tocotrienol (0.06–8.69 mg/kg), and β-tocotrienol (0.51–43.83 mg/kg). Tocopherols have anti-inflammatory and anticancer properties and played an important role in regulation of the metabolism. Recent research studies have reported that tocotrienols have anticancer, neuroprotective, and hypocholesterolemic properties [13, 15].

13.2.5 Minerals and Vitamins

Amaranthus species contain high amount of vitamins such as riboflavin, vitamin B6, vitamin C, and folate. *Amaranthus* is also reported to contain high concentrations of essential amino acids and nutritional minerals such as P, Ca, Fe, K, Zn, Mg, Cu, and Mn [20]. Red amaranth is also especially nutritious and rich in easily digestible minerals, i.e., iron and calcium, as well as protein, vitamin C, and beta-carotene. The vitamins and minerals present in plants as natural or synthetic antioxidants play an important role in reducing infections and different diseases like eye diseases, coronary artery diseases, and cancers because these antioxidants are associated with the removal of injurious molecules called free radicals from body [16]. Different minerals such as Ca, Mg, Cu, and Zn are associated with building of strong bones and muscles [13]. *Amaranthus* species contain high amount of dietary fiber (14.2%) which have water-retaining capacity [13, 21].

Amaranth vegetables are commonly used after home cooking such as frying, boiling, simmering, bleaching, and baking. The advantageous properties of amaranth are due to the presence of antioxidants. Food preparation does not reduce the concentration of total bioactive components except the reduction of anthocyanins content. However, cooking significantly increases the concentration of antioxidants like carotenoids, especially by baking. Baking also increases the concentration of polyphenol, *L*-ascorbic acid, which was critically lost after simmering. However, simmering and bleaching increase the concentration of lutein and beta-carotene in cooked amaranth [22].

13.3 Molecular Mechanism of Bioactives in Amaranth

Foods from animals and plants are important sources of bioactive compounds. Plant sources contain cereals (wheat, barley, corn, and rice), pseudocereals (buckwheat and amaranth), legumes (soybean, bean, and pea), *Brassica* species, and others (sunflower). The presence of bioactive peptides in cereals and legumes can contribute to increase their protein quality and add “functionality” to food consumed on a daily basis [23].

The amaranth seed is high in protein (17%). The leaves of amaranth contain a high-protein level (28–49%), unsaturated oil (45% linoleic acid), fiber (11–23%), and minerals such as potassium, iron, magnesium, and calcium [24]. Amaranth seeds also contain protease inhibitors, antimicrobial peptides, lectins, and antioxidant compounds that play important biological parts in our daily diet.

ACE inhibitory peptides can be easily obtained from amaranth protein. The peptides of amaranth show ACE inhibitory activity which is a mixture of peptides. Angiotensin I-converting enzyme (ACE; peptidyl-peptide hydrolase, EC 3.4.15.1) performs a vital role in the regulation of blood pressure and cardiovascular function. Angiotensin II is also produce by ACE that eliminates C-terminal dipeptide from the lysate of the originator decapeptide angiotensin, which also deactivates vasodilator bradykinin. In alcalase-mediated digestion, bioactive peptides can be released from amaranth grain protein [25].

Diverse metabolic pathways produce radical species, including reactive oxygen species (ROS), such as O_2, HO_2, H_2O_2, and OH, and reactive nitrogen species (RNS). When free radicals are created in extra amount or when cellular defenses are lacking, biomolecules are damaged by a process called oxidative stress [26]. This process seems to be concerned with cellular aging and also in related diseases such as atherosis, cardiovascular disease, cancer, and neurological degenerative diseases [27] as well as in gastrointestinal disorders [28].

There are negative concerns to the oxidative processes and their inhibition, both inside the organism and in foods, and are of great importance. Some proteins have been described as nutritious proteins, and hydrohydrates have anti-oxide potential. This antioxidant activity is present in peptides from soy protein, casinos, soy milk, egg protein, butter protein, and others. Amaranth is mainly from the United States and is considered a pseudocereal. It has high nutritional value with high-protein material (15–17 g/100 g) and excellent amino acid balance.

There are also phytochemicals in amaranth seeds, whose effects on humans have been described.

Amaranthus mantegazzianus seeds include peptides and polypeptides that prevent the occurrence of natural free radicals and oxygen activity. Peptides presenting radical-scavenging capacity have been released in simulated gastrointestinal digestion from diverse food sources. The amaranth proteins released antioxidant peptides into the human body, which have the capacity to scavenge free radicals after gastrointestinal digestion [29].

The amount of total and soluble fiber has also been mentioned, and possibly the amino acid profile of its proteins may be involved in this mechanism as well. The presence of phytochemicals such as tocotrienols, phytosterols, tocopherols, and squalene have undoubtedly been proposed projecting a rather complex scenario, but this also suggests the participation of a set of components of a different chemical nature [9].

It was noticed that amaranth minimized the total cholesterol by 50% as compared to others. The mechanism suggested that the unsaturated fatty acid content of amaranth controls cholesterol [30].

An experiment was carried out on a variety of animals such as chicken, hamsters, rabbits, and rats. It was showed that when hypercholesterolemic rabbits were fed with amaranth flour, it minimizes the LDL and total cholesterol levels by 50%, as compared with other grains. It was also shown that amaranth oil was also not effective as an extruded amaranth [31].

A diet containing 20% of A. cruentus grains and totaling 5% amaranth oil decreased non-HDL cholesterol in hamsters. It was suggested that phytosterols and proteins of amaranth had hypocholesterolemic effects, which negated the effect that fatty acids, tocopherols, and tocotrienols had involved in lowering of non-HDL cholesterol level (Berger et al. [18]).

Amaranth oil decreases blood pressure, heart disease, and hypertension, when 18 ml was consumed per day. The hydrocarbon squalene and phytosterols were theorized to be involved in the mechanism of decreasing diseases [32].

There is a protein (MPI) in *Amaranthus mantegazzianus*, which is used in antitumor treatments. Four tumor cells, MC3T3E1, UMR106, Caco-2, and TC7, were tested in which UMR106 was inhibited by *A. mantegazzianus* grains. MPI prevented adhesion and induced apoptosis and necrosis in cell of UMR106, which shows that *A. mantegazzianus* grains are involved in antitumor mechanisms [33].

Feeding the rats with amaranth whole grain or with its oil effect on AST (aspartate aminotransferase) and ALT (alanine aminotransferase) enzymes and decrease its amount which are estimated to be the ferments-markers of hepatic cytolysis in liver and it has the symbols of erythrocytolysis and haemoglobin damage or disorder in system of conjugated bilirubin transmission from a hepatic cell into bile. Furthermore, there was a decrease in TBARS levels (thiobarbituric acid reactive substances, lipid peroxidation, and oxidative stress indexes) in liver cytosol.

The amaranth oil sustains antitoxic and antioxidant activity. Amaranth oil can be used for prophylaxis of toxic and drug-induced liver lesions and as important an element of functional foods and dietetics of different diseases [34].

Amaranth is a good source of many bioactive peptides which help control diseases like cancer and hypertension. Amaranth also contains a lunasin-like bioactive compound which acts as an anticancer compound. Lunasin has a high amount of aspartic acid. Lunasin is a unique 43 amino acid peptide. It acts as an anticancer compound and acts against chemical carcinogens and oncogenes and activates tumor suppressor proteins.

Amaranth also comprises a lunasin-like peptide. Lunasin comprises a slight amount of aspartic acid, while amaranth glutelin portions also have a comparatively high amount of aspartic acid, 10.6% of the total protein. It was considered to be only present in soy, barley, and, more recently, wheat. It is an anticancer bioactive compound. It is a matchless 43 amino acid peptide. The anticancer components of Amaranth have been proved in a mammalian cell culture models and in a skin cancer mouse model against chemical carcinogens, oncogenes, and in activators of tumor suppressor proteins. Amaranth seeds also contain globulins and glutelins. It is a good source of antihypertensive peptides [12].

But other scientists [35] argued that gluten causes an intestinal mucosa disease called celiac. This disease can be cured by the removal of gluten from the diet. Amaranth grain was used by patients because it does not cause allergies for intestinal mucosa. Therefore, another scientist [36] developed gluten-free cookies from whole amaranth flour, cornstarch, eggs, margarine, sugar, baking soda, potassium bitartrate, and butylhydroxytoluene, which contained high amounts of protein (5.7 g/100 g) and dietary fiber (1.1 g/100 g). These cookies are very useful for such kinds of diseases.

Amaranth grain is also used as a cure for anemia. Anemia is caused by the deficiency of essential amino acid such as iron; folic acid; vitamins B12, B6, and C; and proteins. Absence of iron is the main cause of anemia [37].

Amaranth also contains antioxidants. In modal systems of β-carotene/linoleic acid, two amaranth fractions *A. caudatus* and *A. paniculatus* showed antioxidant activity. The amount of phenolic compound of *A. caudatus* is 39.17 mg/100 g and 56.22 mg/100 g in *A. paniculatus* by Folin-Ciocalteu method [38].

Amaranth grain can also decrease the amount of IgE and increase cytokine Th1 production both in vitro and in vivo. Because of this, allergies decrease in particular antigens.

Water-soluble amaranth grains help in the growth of helper cell Type 1 (Th1) phenotypes, and amaranth extract decreases the production of IgE, which in turn stops allergy flow.

When mice were feed with both soluble amaranth grain and grain soluble extract, the mice showed no allergic symptoms. It can also be applied in the allergic diseases such as asthma and atopic dermatitis [39].

13.4 Effects of Processing on Availability

Amaranth is currently gaining popularity due to its excellent nutritional value. The grains have contents of 15 g/100 g of protein, 60 g/100 g starch, and 8 g/100 g fat in addition to being a source of thiamine, niacin, riboflavin, and folate and dietary minerals including calcium, iron, magnesium, phosphorus, zinc, copper, and manganese [40, 41].

From the grains of amaranth, bread, cakes, muffins, pancakes, cookies, dumplings, crepes, noodles, pastas, and crackers are made because it can be toasted and popped and it can be also milled into flour. The grain of amaranth contains more protein and essential amino acids compare to other grains. There is lysine in the protein of amaranth grain which is not commonly available in other cereals [42].

Heat processing effects the digestibility and bioavailability of carbohydrates, proteins, and amino acids and also brings change in the profile of all active substances. When amaranth grain is cooked, popped, toasted, and milled into flour, it affects the phenolic content of amaranth and reduces it to about 30%. Decreases were also observed in antioxidant activity of amaranth, in toasting. The inhibition of lipid oxidation was not changed by extrusion, toasting, or popping [43].

Low-cost extrusion of two amaranth grain verities Peruvian *A. caudatus* shows reduction in the amount total phenolics, antioxidant activity, and phytic acid [44].

When the varieties of amaranth were treated hydrothermally, there was loss in phenolics, phytic acid, and antioxidant activity. As compared to other cereals and legumes like finger millet, sunflower seeds, pumpkin seeds, ground nuts, and field beans, the losses were larger in amaranth with thermal processing [45].

Recently composited flours and other grains have greater nutritional value, and phenolic compounds have moderately replaced pasta products made from wheat semolina. Also, it is possible to make special nutritional pasta such as low glycemic index and gluten-free pasta. Pasta enriched with amaranth flour and amaranth leaves shows higher amounts of protein, lipids, and ash compared to pasta made from commercial wheat and organic brands as reported by [46].

The mean amount of b-carotene (BC) in leaves of cowpea is 806.0 lg/g DM, amaranth is 599.0 lg/g DM, and white cabbage is 105.0 lg/g DM. The level of b-carotene in cowpeas decreased up to 77.6%, and the amaranth level of b-carotene decreased 76% after cooking. In sun drying, the level of b-carotene in leaves of cowpea decreased up to 70.1%, and amaranth leaves BC decreased to a level of 66%. Cowpeas have less decrease in b-carotene (BC) while cooking, because of higher fiber content [47].

Heat processing effects the digestibility and bioavailability of carbohydrates, proteins, and amino acids and also brings changes in the profile of all active substances. When varieties of amaranth were treated hydrothermally, there was a loss in phenolic, phytic acid, and antioxidant activity. As compared to other cereals and legumes like finger millet, sunflower seeds, pumpkin seeds, ground nuts, and field beans, the losses were larger in amaranth with thermal processing (Kunyanga et al. [45]).

Amaranth leaves were stored inside or without polythene bags in the refrigerator or at 30 °C with polythene bags for 24–48 h. The decrease occurred in both of the situations, but the leaves stored at 30 °C showed more losses in ascorbic acid content. This loss may be due to the high temperature because ascorbic acid content is sensitive to heat. In oven drying, the rate of losses was also high. Amaranth ascorbic acid content decreased by 83.4–822.5% at 30 °C.

Fresh leaves have more ascorbic acid than sun- or oven-dried leaves. The loss is due to high temperatures extended periods. Decreases of ascorbic acid were also noted in blanched leaves. If leaves are blanched for 5–15 min, ascorbic acid decreases 52–93%. As the time of blanching increased, the decrease in ascorbic acid content also increased. Cooked amaranth leaves have less ascorbic acid than fresh leaves. The losses of ascorbic acid in amaranth leaves are high in open pan cooking as compared to cooking in a pressure cooker. Ascorbic acid is sensitive to heat, light, oxidizing agents, blanching, drying, and cooking involved in heat treatment, so the loss of ascorbic acid is a must. Decreases in β-carotene are higher in sun-dried than oven-dried leaves. Decreases of β-carotene also occurred during blanching and cooking of the leaves. The highest loss was observed in blanching [48].

When whole flour (WAF) is used in different percentages in bread making, it will increase mineral content in bread. Adding amaranth flour increases the nutritional value of the bread. Bread is a staple food and used all over the world. White bread does not contain much Fe; thus by adding amaranth flour, the amount of Fe and other micronutrients increases. Bread with 40% amaranth flour also adds high amounts of dietary fiber, lipids, and proteins [49].

Pastas made from amaranth flour and leaves have high amounts of essential amino acids, minerals, vitamins, and phenolic compounds. Amaranth is a Mexican crop with high nutritional value. Pastas made from amaranth flour and dried amaranth leaves have low cooking time as compared to the control pasta. Cooking losses will be high with large amount of amaranth flour, and pastas made with more dried amaranth leaves have faster cooking time. Pastas made from amaranth flour and dried amaranth leaves show high amount of crude fiber, protein, potassium, magnesium, zinc, and iron. Cooking decreases antioxidant activity, but pasta with dried amaranth leaves and amaranth flour has high antioxidant activity after cooking. Pasta with amaranth flour and dried amaranth leaves has high functional benefits [50].

The comparison between pale and black seed of amaranth shows less starch in black amaranth seed than pale amaranth seed, while the amounts of protein, ash, and dietary fiber of black amaranth seed are higher than the pale seed of amaranth. In the heating process, starch is reduced, and dietary fiber increases in pale amaranth seeds. In toasting, fiber and ash are reduced, while the starch remains high in black seeds. Glycine and serine are abundant in black seed, while the amount of lysine is scarce. While in pale amaranth seeds, lysine is abundant. Amino acid composition was not affected by flaking, but the amount of lysine was decreased up to 83% by popping of different varieties of raw seeds. In black seeds, amino acids decreased while toasting [51].

13.5 Possible Approach to Enhance Health Benefits of Amaranth Bioactive

Humans need different daily nutrition depending on the sex, size, age, and activity level. The reference intake (RI) refers to the suggested amount of daily intake of food for an average individual to get a healthy, balanced diet and activate and keep weight loss or weight gain. Due to a lack of minerals and vitamins, more than 2 billion people have become susceptible to malnutrition worldwide. In pregnant women and children, mineral deficiency is more prominent. Therefore, dietary fortification in processed food to supplement micronutrients is necessary. This is the easiest way to get micronutrients. These are long-term and short-term benefits because they interface with public health management.

Wheat bread and other foods are fortified to improve the nutritional value with some plant products. Amaranth seed is used in bakery additives. The amaranth plant is selected for fortification because it contains a large amount of lysine which is deficient in other cereals. Amaranth also contains high amounts of minerals, mainly magnesium, calcium, dietary fiber, and unsaturated oils.

Tocotrienols are an uncommon form of vitamin E, which is found in amaranth oil, and hinder the enzyme that controls cholesterol biosynthesis. Squalene is also present in amaranth oil, more so than in other vegetable oils. Squalene carries oxygen to various cells of the body and thus increases the immune system by maintaining LDL (maintaining low-density lipoprotein) in the blood cholesterol and inhibits cancer-like diseases [52].

Leaves of amaranth contain great amount of protein, vitamins, minerals, and dietary fiber. Amaranth is a safe component for people suffering from celiac disease because its protein contains less prolamins. Its peptides also have antihypertensive and anti-inflammatory abilities. For a healthy breakfast, popped amaranth can be eaten with fruits and milk. It can also be used for breakfast cereals, and soup can be made from it. It can be cooked whole to make breakfast salty or spicy "polenta." Extract of amaranth leaves has anticancer effects on liver, breast, and colon cancer cell. The vegetable part also has antitumor properties [13].

Amaranth has high nutritive properties. Thus it should be of more biological value in processed foods, which are as follows:

- It can be used in pastes and salad dressing. It can also be used in combination with wheat in bakery foods.
- It can be used in preparing bread with wheat without disturbing sensory value.
- To increase taste, water absorption, and appearance of bread, amaranth acts as a gelatinizer of starch.
- The starch of amaranth is used for sauces, as a fat remover, in gravies, and in thickening of soup and muffins.
- Jollof or fried rice can be made by boiling grinded amaranth grain with rice and vegetables.
- Ogi, a local paste, can be made from amaranth.
- Candies and molasses can be made from popped amaranth seeds.
- In Peru bells are made by mixing popped seeds of amaranth with syrup.
- Snack cakes can be made with popped amaranth seed and honey [52].

In health benefits, amaranth grain can play an important role in the human body. Amaranth usage for CVD and hypertension has been confirmed. This traditional vegetables can be grown in someone's garden with little cost and little struggle. It can be used as a cereal or its constituent. Amaranth oil is advantageous for health aspects. Amaranth flour can be used in place of wheat, rye and barley because, which contain gluten, while the amaranth flour is free of gluten. Its flours can also be used in many products. It is recommended that wherever it can be possibly grown, it should be cultivated.

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Chapter 14
Other Typical Pseudo-cereals in Diet

Kalekristos Yohannes Woldemariam

14.1 Adlay

14.1.1 Introduction

Adlay, the seeds of *Coix lachryma-jobi L. var. ma-yuen Stapf* is a perennial grass crop belonging to the family of Gramineae. Four species of adlay are commonly used as food and medicine. These are *Taichung No. 1*, *Okayama zairai*, *Hatohikari* and *Hatomusume* [1]. Adlay has synonymous names like *Coix agrestis Lour.*, *Coix arundinacea Lam.*, *Coix exaltata Jacq. ex Spreng.*, *Coix ouwehandii Koord.*, *Coix palustris Koord.*, *Coix pumila Roxb.*, *Coix stigmatosa K. Koch* and *C. D. Bouché.*

Adlay is called by different local names, including Job's tears, yi yi, coix seeds, Chinese pearl barley, semen coicis, yokuinin, yi yi ren, soft-shelled Jobs tears and yi mi [2]. This crop is in the South of Asia mostly flowering between July and September and reaches a height of 100 to 180 cm at full maturation [2]. It is widely planted in Asian countries including but not limited to China, Taiwan and Japan [3]. Adlay is native to South Asian countries (Andaman Is., Assam, Bangladesh, Borneo, Cambodia, China South-Central, China Southeast, East Himalaya, Hainan, India, Laos, Malaya, Myanmar, Nepal, Nicobar Is., Sri Lanka, Taiwan, Thailand, Vietnam, West Himalaya) [4].

14.1.1.1 Adlay Cereal Parts

The polished adlay seed consists of four major parts including the hull, testate, bran and endosperm [2].

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14.1.1.2 Adlay Cereal Nutritional Composition

Its nutritional value makes adlay a good source of nutrients. The nutritional composition of the adlay cereal may differ based on the variety and source of the crop. Based on a study conducted by the Wu et al. [5], polished adlay samples from four countries (Thailand, Vietnam, Taiwan and Laos) contained 10.59–12.38% moisture, 6.20–7.22% crude fat, 12.1–14.2% protein, 1.78–2.43% crude fibre and 1.62–2.30% crude ash.

14.1.2 Bioactives in Adlay

The different parts of the adlay crop contain a different level of the phytosterols. Naturally occurring antioxidant components including ascorbic acid, tocopherols and total phenols were found in methanolic extracts from various adlay products. Some of the phytochemicals of adlay reported in the literature include benzoxazinones, lignan, phenolic acids, phenolic alcohols, phenolic aldehydes, phenolic glycerides, phenolic ketones, flavonoids (naringenin, tricin), phytin, polysaccharides (coixan A, B, C and glucan), diol lipid (coixenolide), fatty acids, phospholipids (phosphatidylcholine, phosphatidylinositol, phosphatidylserine), sphingolipid (cerebrosides) and steroids (campestanol, campesterol, bsitosterol, stigmasterol) [5]. Included in the bran extract of adlay are p-hydroxybenzoic acid, p-coumaric acid and quercetin and also the most abundant phenolic components like tangeretin, nobiletin and p-hydroxybenzoic acid [6]. The different composition of these phenolic compounds in adlay makes it a valuable crop.

14.1.2.1 Food and Pharmaceutical Application

The different parts of the adlay cereal have different applications as a cereal-based food, functional food, traditional and modern medication, cosmetics, ornamental and joularies and for animal feed.

Besides its application as food, this crop has been used as a traditional herbal medicine in different parts of the world, especially in China. Some of the types of adlay foods consumed includes adlay milk, which is a well-known and popular local snack in Taiwan and other parts of Southern Asia. It is produced by cooking adlay in water and usually mixing the solution with green beans [3]. The other food applications are in the form of cooked dehulled mature seeds mixed together with cooked rice. It can also be prepared to make a cooling drink by polishing and milling flour and mixing it with water and is consumed like barley or flour water. In some places it can also be pounded to flour and used for the production of brewing of beer especially in the Garo, Karbi and Naga tribes [7].

The application of adlay in traditional treatment of inflammatory, skin, neuralgia, wart and rheumatism disease is most common in China. Besides, the traditional application adlay has a role in antiphologistic, diuretic, antispasmodic, antitumour, anodynic effect and in increase digestion [2]. It is reported to have various effects, such as anticancer, anti-inflammatory and anti-allergic. One of the experiments conducted by the Hong Jhang shows that adlay bran extract can potentially be used as a functional food aiding in the treatment of allergic responses [8].

In general, adlay cereal can be used as food, animal feed, medicine, and ornament and as a process ingredient substitute and many applications as a traditional medicine and supplementary medicinal food.

14.1.3 Molecular Mechanisms of Bioactives in Adlay

The functional food and medical application of adlay can be as antioxidant/free radical scavenging, anti-inflammatory, antimutagenic, antitumour, anti-allergic, hypolipidemic, hypocholesterolemic, hypoglycaemic, antiobesity, antiulcer, prebiotic activity, abortifacient, hormonal modulating, osteoporosis preventing and antimicrobial [2].

14.1.3.1 Cancer Chemoprevention by Blocking Using

Adlay has the potential to block cancer through cancer chemoprevention by four mechanisms. These include scavenging electrophiles and reactive oxygen species, anti-mutagenicity, enhanced Nrf2-mediated detoxification and antioxidant effect, and by altering carcinogen metabolism. This can be seen from Fig. 14.1.

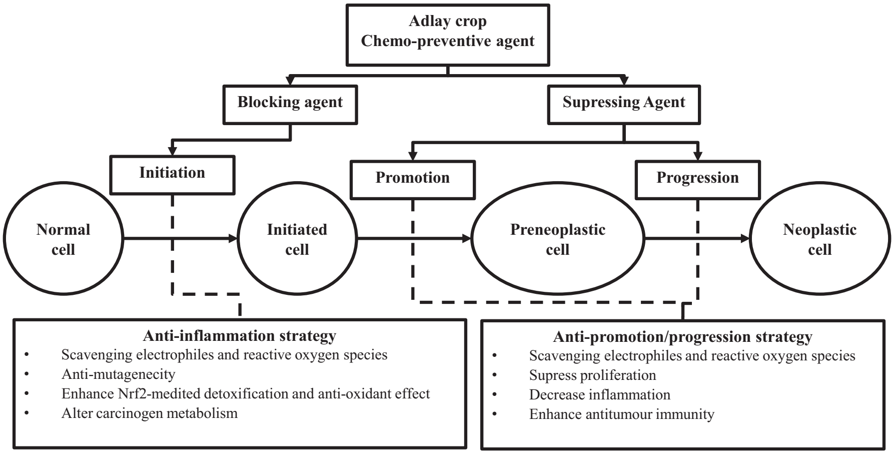

Fig. 14.1 Multistage carcinogenesis and strategies for cancer chemoprevention. (Adopted and modified from Ref. [2])

The cell damage by the oxidative stress from the different sources (endogenous and exogenous) can be prevented by the adlay because adlay contains chemopreventive agents. This chemopreventive agent eliminates the reactive oxygen and electrophiles the reactive oxygen to prevent its development. The development of cancer cell starts with a single mutational episode and then goes to the multiple stage. This mutagenic activity can be prevented using the adlay acetone extract. This acetone has an antimutagenic activity against 2-amino-3-methylimidazo [4, 5-f] quinoline (IQ), 4 nitroquinoline-N-oxide (NQNO) and benzo pyrene (BP) in the salmonella typhimurium TA98 [2].

The extracts of adlay containing 4-ketopinoresinol, trans-coniferylaldehyde and sinapaldehyde induce Nrf2/ARE-driven luciferase activity which is a cytoprotective gene which neutralizes the reactive oxygen stimulators or carcinogens. Besides the neutralization of the carcinogens, it contributes to the cellular defence mechanism by using the 4-ketopinoresinol to induce OH-1 and prevent hydrogen-peroxide induced cell injury [2].

The extract of adlay bran (ABE) has a potential to supress the cytochrome P450 enzymes like CYP1A1 and CYP1A2. These cytochrome P450 enzymes have been indicated in the metabolic activity of carcinogens such as benzo () pyrene, N-nitroso dimethylamine and aflatoxin B1. Adlay bran extract may have chemopreventive effect against colon carcinogenesis in the initiation stage. In addition, other research groups have revealed that dehulled adlay reduced the risk of colorectal carcinogenesis through the modulation of COX-2 expressions in a rat model [9].

14.1.3.2 Cancer Chemoprevention by Suppressing

Adlay bran extract is also a good source of the coixenolide, which is a good suppressing agent. It suppresses proliferation, decreases inflammation and enhances antitumour immunity. This can be used to treat breast, stomach, lung, colon and cervical cancers. Adlay contains high amount of coixenolide about 473 ppm.

It reported that the methanolic extract of the adlay seed inhibited NO formation. It was also reported that the anti-inflammation guided fractionation with high phenolic and flavonoid content from the ethanol extracts of adlay bran suppressed LPS-stimulated IL-6 and TNF-α secretions in RAW 264.7 cells. Flavonoids are the major components responsible for the anti-inflammatory activities. Adlay bran is also a source of natural inflammatory inhibitors and is beneficial to the health of consumers [10].

Moreover, adlay seeds have the potential to increase peripheral cytotoxic lymphocytes, which increases the antitumor immunity and effective on viral infection, through the enhancement of cytotoxic activity [2].

14.1.4 Effect of Processing on Availability of Bioactives

Adlay has different parts including the hull, testa, bran and endosperm. The most common for food consumption is the polished adlay or the endosperm of the adlay. Unfortunately, adlay extracts lose much of their bioactive compounds through the process of extraction and purification [9].

14.1.4.1 Adlay Starch Production

Adlay starch is usually isolated using the alkaline steeping. Grains first steeped in excess water for 18 h at room temperature, ground in a blender (wet milling) and filtered stepwise through 50-, 100-, and 200-mesh sieves. Starch was isolated from the filtrate by centrifugation at 4410 g for 10 min. The supernatant discarded, and the top, yellowish layer of protein removed. The starch slurry was then neutralized by repeated washing and dried at room temperature [11]. The extraction of starch leaves all the nutrients out, which obviously affects the bioactives in the adlay crop.

14.1.4.2 Saponification Process

One major compound in adlay is policosanols, located mainly in the adlay bran. Utilizing this compound as a commercial source of policosanols is achieved by not needing a saponification process during the extraction of the oil. Moreover, obtaining policosanols from adlay adds value to an underutilized by-product [5].

14.1.4.3 Extrusion of Flour

The extrusion process of different types of adlay shows that the extrudate mainly depends on the adlay variety and the physicochemical properties of these varieties give a different result. The high temperature application results in the loss of heat sensitive bioactive compounds. It involves high temperature and pressure processing which results in the change of the physicochemical properties of the adlay and also the nutritional composition. The effect of extrusion on bioactive compounds of adlay still needs further research and investigation.

14.1.4.4 Oil Extraction by Mechanical, Chemical and Super Fluid Extraction

Normally adlay oil is obtained using mechanical or chemical processes. Mechanical processes often produce low yields, while chemical extraction methods often involve the use of organic solvents, which can be harmful to human health and environment. Supercritical fluid extraction (SFE) is one of the newly emerging clean and environmentally friendly technologies for food and pharmaceutical products and now used for extraction of adlay oil [12].

14.1.4.5 Ultrasound Application in Oil Extraction

Ultrasound, a kind of elastic mechanical wave, can produce thermal effects, mechanical fluctuant effects and cavitation effects. Cavitation effects cause formation, growth, compression and explosion of bubbles in the solution, which can lead to the dispersion of solid particles. The mass transfer rate can also be improved by allowing more contact area between particles and extracting solvent. The ultrasound can effectively increase the extraction rate and speed up the extraction process. Though it increases the extraction of oil, its relationship with the extraction and the bioactive compounds still need further research [12].

14.2 Fonio

14.2.1 Introduction

Fonio (*Digitaria exilis* and *Digitaria iburua*) is a cereal belongs to the genus *Digitaria*. The Genus *Digitaria* consists of about 230 species of millets. Fonio mostly cultivated in West Africa. The *D. exilis* and *D. iburua* varieties are the most common ones as per the [13]. Different literature asserts that fonio was domesticated near the headwaters of the Niger River, at around 4500 B.C. The use of fonio as a food was most during the early stages of development in Africa. Fonio is one of the basic foods in the western Sudanic region of Africa, and also the local people have cultivated fonio and sold it as a grain crop in Mali as early as 1353–1354 in Ibn Batula [13].

There are actually two species of fonio. One, *Digitaria exilis* is commonly known as fonio, white fonio, true fonio or hungry rice. It is usually stands 30–75 cm tall. Its finger-shaped panicle has 2–5 slender racemes up to 15 cm long. This type of the fonio is highly cultivated and used as food due to its white colour and easy processing [13]. The other species of fonio, *Digitaria iburua,* is dark in colour. It is taller and may reach 1.4 m. It has 2–11 sub-digitate racemes up to 13 cm long [14].

Fonio cereal crop known by different names with respect to the country of origin and language and regions has diverse uses, applications, living statuses and parameters, seen in Table 14.1.

14.2.1.1 Fonio Cereal Parts

Fonio grains are very small and weigh 0.5 g per 1000grain. The length of the grain is 1.5 mm and width of 0.9 mm. The grain has a shiny pericarp appearance after threshing. The colour of fonio ranges in the white, yellow and purple colours

Table 14.1 Name of fonio in different countries and languages

Language	Name for fonio
English	Hungry rice, hungry millet, hungry koos, fonio and fundi millet
French	Fonio, petit mil (a name also used for other crops)
Fulani	Serémé, foinye, fonyo, fundenyo
Bambara	Fini
Mali	Fani, feni, foundé
Nigeria	Acha (*Digitaria exilis*, Hausa); iburu (*Digitaria iburua*, Hausa); aburo
Senegal	Eboniaye, efoleb, findi, fundi
The Gambia	Findo (Mandinka)
Togo	(Digitaria iburua); afio-warun (Lamba); ipoga (Somba, Sampkarba); fonio ga (black fonio); ova (Akposso)
Burkina Faso	Foni
Benin	Podgi
Ivory Coast	Pom, pohin
Guinea	Pende, kpendo, founié, pounié

Adopted and modified from Ref. [14]

depending on the variety. They have a hilum on one side and a relatively large germ, containing the fat reserves, on the other. The kernel (or albumen), which is the main storage organ, is made up of starch grains and a small protein reserve. It is the main element in whitened fonio**.** The husk and bran make up 23% and 9% of paddy grain, respectively.

14.2.1.2 Fonio Cereal Nutritional Composition

Cereals are good plant source of amino acids, next to pulse and legumes, especially for vegetarians. Fonio is probably one of the oldest cereals in this region of Africa, and it is often cultivated across the savannahs in West Africa. It is also very popular Mali [15]. Fonio proteins contain a higher amount of sulphur amino acids (methionine and cystine) and are less susceptible to denaturation, while its starch is composed of total starch (43.6%), resistant starch (2.1%) and digestible starch (41.4%) with a low glycaemic index [16]. The detail on the nutritional composition can be seen in Table 14.2.

14.2.2 Bioactives in Fonio

The bioactives in fonio are not well studied, and there is a big gap between what bioactive compounds it contains and the uses of these compounds. Though there is a gap, there are some studies which show the hidden value of this crop. Fonio is rich in high sulphur, containing methionine and cysteine amino acids. It is also an

Table 14.2 Nutritional composition of fonio from the Iporhouwan and Namba

Products	Moisture (%)	Carbohydrates (%)	Crude protein (%)	Crude lipid (%)	Crude fibre (%)	Total ash (%)	Iron (mg/g)	Zinc (mg/g)
De-husked	9.29–10.17b	91.68–89.98	5.80–7.04	1.29–1.35	0.57–0.63a	0.68–1.01	0.16–0.35	0.17–0.42
Milled	13.96–12.56	93.35–91.36c	4.85–6.21	0.91–1.13	0.50–0.67	0.40–0.64	0.07–0.12	0.12–0.11
Precooked	9.57–7.08	93.28–92.75	5.52–5.97	0.35–0.37	0.37–0.34	0.49–0.58	0.05–0.05	0.11–0.07
Roasted	2.32–2.33	92.46–91.83	5.63–5.63	1.11–1.97	0.46–0.15	0.35–0.43	0.11–0.14	0.08–0.05
Parboiling	5.37–5.15	91.42–89.51	6.06–7.24	0.89–1.45	0.64–0.67	1.00–1.14	0.2–0.23	0.34–0.21

Source modified from the Ballogou et al. [22] where the first number before the hash mark represents Iporhouwan and the second represents Namba sources of fonio types

important source of antioxidant phenolics, dietary fibre and cholesterol-lowering waxes and is capable of helping diabetic patients in West Africa [16].

14.2.2.1 Food and Pharmaceutical Application

Fonio is a common food staple in West Africa. This cereal accounted for 73% of the energy from plant foods and 74% of the protein in the Malian diet [15]. Similarities in the functional properties of fonio cereal with sorghum, millets, tef and other cereals and with increased quality of protein, vitamins, minerals and fibre give fonio great potential in product development.

Fonio consumption is mainly in the form of whole cereal, flour and further processed products like porridge, gruels, beverages, stew, and bread and also mixed with other cereals. As Carcea and Acquistucci [17] asserted, fonio can be consumed in the form of whole decorticated cereal, as flour in the form of gruel, porridge and in beverage forms. The most common food uses of white and dark fonio include in the production of biscuits, bread, alcoholic and non-alcoholic beverages, dumpling products and porridge [18].

Some of the recent developments in fonio include cakes, cookies and other snack foods. Wholemeal fonio flours can be used in the preparation of a number of biscuits and snacks, useful for individuals with gluten intolerance. From a functionality and health perspective, fonio can serve as ingredients in formulating bars, breakfast mueslis, ready-to-eat cereals, pasta, crackers, cookies and biscuits. Low-starch gelatinisation temperature and high beta-amylase activity show the brewing potential of fonio when partially substituted for barley malt [18]. It is also reported that the grain has high brewing and malting potentials [19]. The way of producing the malt from fonio cereal may differ, but there is great potential for the use of this crop in the production of alcoholic beverages, as it is still used in the traditional methods to produce alcoholic beverages.

Nutraceuticals are now saying it plays an important role in the prevention of diabetes. It is believed that fonio may have nutraceutical properties such as resistant starch, low sugar, fibre, phytochemicals, amino acids and other undiscovered benefits.

The presence of resistant starches in this cereal is believed to be related to diabetes. Resistant starches have shown promise in the management or prevention of certain diseases and health conditions. Fonio is a good source of starch, mainly resistant starches (Jideani and Jideani) [18]. The different functions of resistant starches in relation to insulin and glycaemic responses have been studied by different researchers. One piece of research was on the reduction of glycaemic and insulin responses. It showed that fonio can be used in preventing and managing prediabetes and type 2 diabetes. This is because fonio is a good source of the resistant starch.

The increasing concern about gluten and celiac disease makes fonio more attractive due to the lack of gluten in it. The consumption of fonio in Western Africa is more common among children and old people, who have difficulty of digesting foods. A study by Raji et al. [20] shows there is a high consumption of fonio by children, old people and celiac, diabetic and patients with stomach diseases.

The other advantages of fonio, besides its resistant starch, are that it contains low level of sugar. This is good for patients with diabetes. Research shows that diets from fonio have relatively low-sugar and glycaemic content, which makes it a part of an attractive diet for diabetic patients [20].

14.2.3 Molecular Mechanisms of Bioactives in Fonio

Though there is not enough research on the molecular mechanisms of fonio, the application and use of its bioactive compounds provide a plethora of benefits. Besides the bioactives, fonio is a good source of higher sulphur amino acid (methionine and cystine) content. Fonio has sulphur-containing amino acids which are crucial for proper heart function and nerve transmission [18]. In Western Africa it is also common to consume fonio after the consumption of the cassava, which has high cyanide content. This is mainly because it has detoxification properties due to high and cheap source of methionine. A study by Lumen et al. [21] shows that the proteins contributing to the unique amino acid profile of fonio are methionine and cysteine which are more than 4.8% and 2.5%, respectively [21].

14.2.4 Effect of Processing on Availability of Bioactive

Fonio is not yet processed on a large scale but local processing is common. The consumption and application of this cereal for different purpose start with the harvesting and storage of the cereal which results in the loss of the useful bioactive compounds.

The main processing of fonio starts with the harvesting of mature cereal, followed by storage. Storage method differs from place to place due to unequal technological development. The smaller size of the grain enables it to be stored compactly in silos and thus has good storage life while resisting insects. Then the cereal will be dehulled by traditional method resulting in the removal of the nutritious fibre and bioactive compounds. Even though there is a shortage of data on the effect of the dehulling, there is clearly a loss of nutritional compounds.

The next step is fonio flour production, which results in producing polished, dehulled and white flour. The milled grain (similar to polished rice) of fonio obtained after dehulling of the paddy is separated from bran, dust and sand using sieves of 850 and 600 mm and washed with water in two steps using the traditional sedimentation methods based on the principle of density difference. The product obtained from this process is called mid wet fonio (or ready-to-cook fonio) [23]. The major traditional processing steps in the preparation of fonio are shown in Fig. 14.2.

The flour of fonio cereal can be further processed, such as cooking, baking, roasting and boiling. All these thermal process can affect the nutritional composition of the fonio based on conditions, methods and time temperatures used. One study shows that the cooking of fonio results in a decrease in content of free phenolic acid along with an increase in the content of bound phenolic acid after cooking [24].

Even with temperature treatments, sulphur containing methionine and cysteine amino acids can withstand all the processes and can be used as a source of protein for vegetarians. In general there is a shortage of literature in the area of processing fonio and the effect of nutritional composition as well as the bioactive chemicals in fonio.

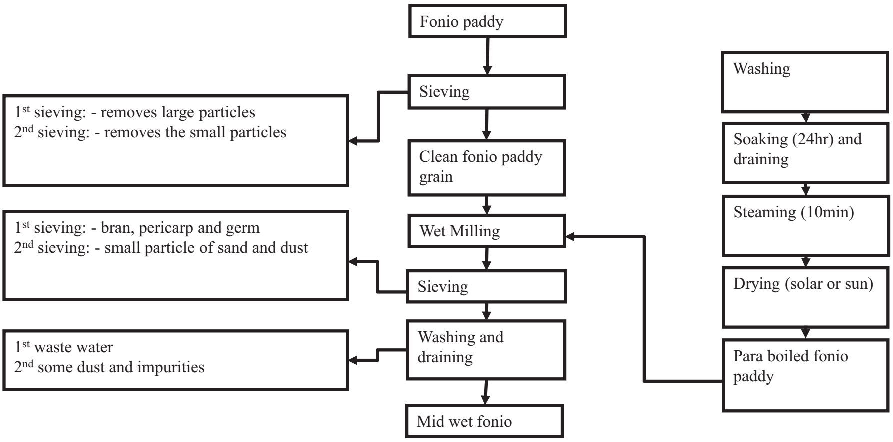

Fig. 14.2 The flow diagram for the processing of wet fonio. (Adopted from Ref. [23])

14.3 Hemp

14.3.1 Introduction

Hemp (*Cannabis sativa*) is an annual dicotyledonous angiosperm plant belonging to the Rosales order, suborder Rosidae and Cannabaceae family [25]. It is dioecious, with the staminate plants; contradicting this, some hemp cereal can sometimes be monoecious because of the short time period of cultivation [26].

A recent chemotaxonomic study by [27] confirms the common belief that Cannabis had its origin in Central Asia [28]. The history of hemp cultivation in China is as old as the civilization itself, and it can be dated back to at least 6000 years ago according to archaeological findings and ancient records [26]. According to Erodotus (484 B.C.), Scythians brought hemp to Europe from Asia during their migrations in 1500 B.C., while the Teutons played an important role in diffusing hemp cultivation throughout Europe [26, 29]. Even though it is an ancient crop, the cultivation of this plant decreased due to a lot of adverse factors of period.

The hemp plant has been prohibited for cultivation due to the content of tetrahydrocannabinol (THC). This is a chemical closely related to narcotics, especially during the secondary metabolite. The cultivation of hemp in Canada has been prohibited since 1938 due to the presence of the phytochemical drug component Δ-9-tetrahydrocannabinol (THC) [30].

Among the most types of hemp varieties, one containing Δ9-tetrahydrocannabinol (Δ9-THC) is a well-known natural psychotropic compound. Due to this, the only approved strains of hemp contain less than 0.2–0.3% of Δ9-THC and are officially allowed in Canada, the USA and many European countries [31]. Non-psychotropic cannabidiol (CBD) and its parent compound cannabidiolic acid (CBDA) were reported in various hemp cultivars as the major quantitatively cannabinoids grown for the purpose of food [31, 32]. The cultivation of hemp is now increasing widely because of its positive effect on health, high calorie value, a positive effect on the environment and other benefits.

The increasing demand for the cereal for different uses has resulted in a sharp increase in cultivation. [33] mentioned that the global market for hemp consists of more than 25,000 products and new applications of hemp products are continuously appearing [34].

14.3.1.1 Hemp Cereal Parts

The hemp plant consists of different parts including the fruit (seed), stem, leaf and root. Figure 14.3 shows the detail cross sectional view of the fruit and the stem.

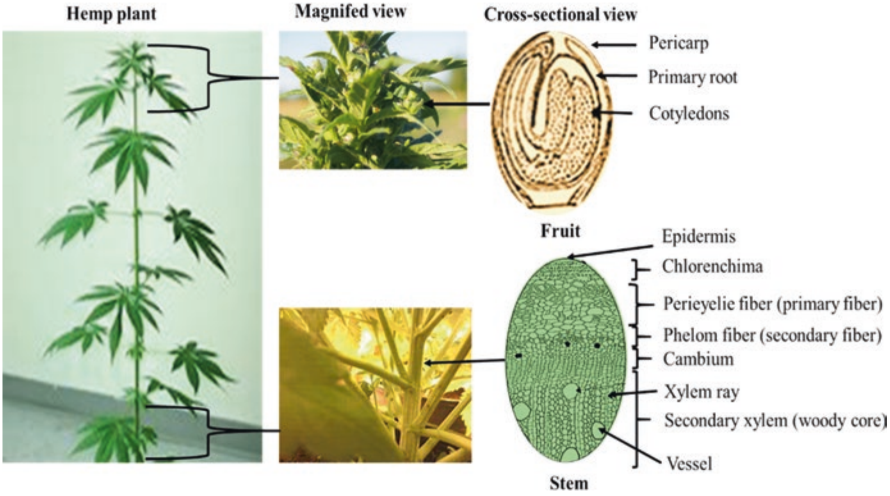

Fig. 14.3 From top to bottom, hempseed longitudinal section and stem section. (Adopted and modified from Ref. [26])

14.3.1.2 Hemp Cereal Nutritional Composition

The hempseed is the main source of chemicals and nutrients, used for food, nutrients, bioactive compounds, oil extraction and other uses. The seed contains 20–25% protein, 20–30% carbohydrates, 25–35% oil and 10–15% insoluble fibre and a rich array of minerals [30]. Even though this crop is rich in different nutrients, hemp cannot be used for the purpose of food. One of the most commonly applicable strains is *Cannabis sativa L.*, among the nondrug variety. The nondrug varieties of *C. sativa L.* for industrial use are also known as hemp. This variety of hempseed has been utilised as a source of folk food and an important source of nutrition in China for thousands of years [35].

The hempseed is also the best source of certain vitamins such as tocopherol, which is an effective antioxidant and is also involved in the protection of DNA damage which can lead to cancer. In addition to its nutritional composition, which includes fatty acids and protein, hempseed is rich in lignanamides [36].

14.3.2 Bioactives in Hemp

An increased interest in the bioactive compounds has led to the investigation of different bioactives in hemp. Hemp contains specific phytochemicals in its leaf and seed. More than 70 biologically active and unique terpenophenolic compounds and phytocannabinoids have been found in hemp [31, 37].

Hemp is a rich source of phenolic compounds, a study conducted by [38] demonstrates that cold-pressed black caraway, cranberry, hemp, and carrot seed oils contain significant levels of antioxidants. Ten industrial hemp varieties contain an average phenolic content of 2224 mg/100 g gallic acid equivalence (GAE). The total phenolic concentrations per cultivar range between 1368 mg/100 g and 5160 mg/100 g GAE, and cold-pressed hempseed oil extract has 44.0 mg/100 g GAE [38, 39].

Even though hemp is rich in phytochemicals, the availability and accessibility of these compounds are limited. The separation and use of the non-narcotic phytocannabinoids like cannabidiol (CBD) and cannabigerol (CBG) and of lipophilic flavonoids (cannflavins) from hemp side products have the potential to complement the economy of hemp growing [40].

Most of the common bioactive compounds collected from different literatures through the comparison of NMR and MS data includes Cannabisin A, Cannabisin B, Cannabisin M, 3,3′-demethyl-grossamide, Cannabisin F, Cannabisin G, N-trans-caffeoyloctopamine, N-trans-coumaroyloctopamine, N-trans-coumaroyltyramine, N-trans-feryroyltyramine, N-trans-caffeoyltyramine, (S)-N-(2-(4-hydroxyphenyl)-2-methoxyethyl)cinnamamide, 4-[(E)-p-coumaroylamino]butan-1-ol, trans-ferulic acid-4-O-β-D-glucopyranoside, adenosine, sucrose, p-hydroxybenzaldehyde and 4-hydroxy-3-acid.

14.3.2.1 Food and Pharmaceutical Application

The different parts of the *Cannabis sativa L.* cereal can be used as a food, medicine, textiles and animal feed. Hempseeds are traditionally used in food and folk medicinal preparations or employed as a feed for birds and fish. Researchers assert that it has been an important source of food, fibre, oil and medicine (nondrug varieties) as well as a psychoactive drug since ancient times [41, 42].

A large number of studies have demonstrated health-promoting and medicinal properties of phytocannabinoids. CBD exerts modulating effects of the human endocannabinoid system, which have been associated with various beneficial medicinal and therapeutic properties such as analgesic, antibacterial, antidiabetic, antiemetic, antiepileptic, anti-inflammatory, proliferative, antipsychotic and antispasmodic effects. Studies reveal cannabinoids are as promising natural compounds in treating epilepsy, pain, depression, anorexia, cancer and other diseases and disorders [43].

Hempseed has also demonstrated positive health benefits, including the lowering of cholesterol and high blood pressure. It has been consumed in food preparations, folk medicine and as feed. Hempseed oil has a perfectly balanced polyunsaturated fatty acids of linoleic and linolenic acid in a ratio of 3:1. The oil, because of this and the presence of γ-linolenic acid, is an ideal ingredient for light body oils and lipid enrichment creams, known for their high penetration into the skin [30]. Recent studies have also reported that hempseed extracts displayed strong antioxidant and anti-aging effects as well as the potential to improve impaired learning and memory induced by chemical drugs in mice [44–46].

The multifunctionality of hemp is mainly due to its low density, specific mechanical property, high productivity and cellulose content. These traits make it convenient for the production of fibre-reinforced composites, energy and biofuel production [47].

14.3.2.2 Other Uses

In general, the *Cannabis sativa L.* was being cultivated previously mainly for its fibrous stem, being widely used in paper, textiles, construction, isolation, agriculture, composites, automotive, medicine, etc. These days this plant is cultivated for multipurpose applications in food, feed, medicine, agriculture, therapeutic value, cosmetics, fuel, and energy, isolation of bioactive and other applications like printer ink from polyunsaturated oil, wood preservative, and for detergents and soap production.

14.3.3 Molecular Mechanisms of Bioactives in Hemp

The application of the hempseed for food and functional uses has become more important. The details of the bioactives in hemp and their mechanisms in treating different problems have not been fully explored. Hempseed contains different phytochemicals, flavonoids and other nutritional components. One of the studies shows the potential of hempseed as a treatment against neurodegenerative diseases, which results in the inhibition of the NF-κB signalling pathway [48]. During the activation of microglia cells, NF-κB coordinates with other inflammatory-related channels to trigger a variety of signal cascades, which together regulate the inflammatory response [49, 50].

The other application of hemp is for use in antidiabetics as it contains the two novel α-glucosidase inhibitory oligopeptides with the sequences of Leu-Arg (287.2 Da) and Pro-Leu-Met-Leu-Pro (568.4 Da). These two antidiabetic peptide nutraceuticals have been isolated from hemp [51]. The purified fraction with higher α-GIA especially that which contains Leu, Pro, Met and Arg exhibits high application value, and two hydrophobic amino acids of Leu and Pro potentially contributed to α-GIA, in which they have antidiabetics potential [51]. The molecular mechanisms of the bioactive in hemp still lacks detailed information, but the application of this crop is becoming one of the most important areas of research in relation to treatment and prevention of different health problems.

14.3.4 Effect of Processing on Availability of Bioactive

The different applications of hemp result in the modification and use of different processing methods which further result in the effects of its bioactive content. Fibre bundles can be separated by using enzymatic, microbiological, chemical and physical methods. Still, the developed methods effect on the bioactive are not yet well studied [34].

The extraction of oil for the biofuel involves different processes, which has a direct and indirect impact on the nutritional and bioactive compounds. The conversion of lignocellulosic biomass in the hemp to biofuels usually happens in three steps: (i) pretreatment to open the rigid structure of plant cell walls, (ii) enzymatic saccharification to breakdown solid cellulose into sugars and (iii) fermentation to produce biofuels or chemicals [52]. Other processing parameters in the production of different end products result in loss of the bioactive compounds due to extensive processing and end-use objectives.

14.4 Linseed

14.4.1 Introduction

Linseed belongs to the family of *Linum usitatissimum* resembling the flaxseed. The golden yellow to reddish brown, small and flat seed of this crop has a blue flower during maturation. The resemblance of this crop with flax makes it difficult to differentiate, as even the crispy texture and nutty taste have a similarity with the flaxseed. The difference lies within its application as linseed is mostly used for the industrial application these days and flax is not mainly for the food use [53].

Linseed has been used as a food since ancient times. This crop is now cultivated for the purpose of fibre, oil, medicinal and nutritional applications [54]. The production of this crop is increasing in different countries due to its many applications in addition to the use of almost all parts of this crop plant. In the early time of production, the crop is mainly grown in India, China, the USA and Ethiopia, while with the importance of this crop being discovered, most countries start producing it as well [55].

Linseed is considered the best sources of oil, and it contains α-linoleic acid (ALA) of (55 to 60%) [56]. Due to this and other benefits of this cereal crop, it is considered as a potentially beneficial crop for human health, including reducing the risk of cardiovascular disease, promoting brain function and development as well as anti-inflammatory benefits [55].

14.4.1.1 Linseed Cereal Parts

The weight of linseed grain ranges from 5.4 to 14.0 g, and the whole plant is usually 45 to 80 cm tall. The generative part of the stem is about 1/3 of total plant length with a smaller root system. It is resistant to drought and flourishes in sunny and warm weather conditions [57]. The harvesting of linseed can be done after the seed is fully matured.

The different parts of the linseed are good sources of nutrients and phytochemicals. As investigated by the [58], the seed coat of flaxseed is rich in lignans, and the embryo is rich in oil with high omega-3 fatty acids [59].

14.4.1.2 Linseed Cereal Nutritional Composition

Linseed nutritional composition differs between variety growing environments. Depending on these factors, it contains approximately 40% lipids, 30% dietary fibre and 20% protein. The cotyledons contain 75% of the lipids, and 76% of protein is found in the seed. The endosperm contains only 23% of the lipids and 16% of protein [60].

Linseed is a good source of alpha linolenic acid (ALA) which is an essential polyunsaturated fatty acid (PUFA). This PUFA has the potential for anti-inflammatory, antithrombotic and antiarrhythmic property. Linseed is also a good source for the dietary fibre, quality protein and phytoestrogens [61].

Linseed besides the main nutritional composition is also a good source of mineral like potassium, phosphorous, magnesium, calcium and low amount of sodium. The high amount of the potassium makes this seed more applicable in high blood pressure treatment, because it is related inversely to the blood platelet aggregation [62].

The vitamin content of linseed mainly consists of the fat soluble vitamins, such as vitamins A and E and vitamin C. Vitamin E content is the highest among all other vitamins as was reported by [55]. Flaxseed contains small amounts of water-soluble and fat-soluble vitamins mainly containing the fat-soluble vitamin E amounting to 39.5 mg/100 g.

14.4.2 Bioactives in Linseed

As it is mentioned in the introduction section of this section, linseed is a good source of omega-3 fatty acid called alpha-linolenic acid. It is also a good source of quality proteins, soluble fibres, flavonoids, lignans and other phenolic compounds. Some of the phenolic acids present in the defatted linseed include ferulic acid, chlorogenic acid and gallic acid which are present in a good amount. While low amounts of other phenolic acids include p-coumaric acid glucosides, hydroxycinnamic acid glucosides and 4-hydroxybenzoic acid also are present in linseed [59, 60, 63].

Linseed also is a good source of the flavonoids; the most common ones are flavone C and F glycosides. The content of the lignan in linseed mainly consists of secoisolariciresinol diglucoside (SDG), which results from the coupling of the 8 and 8′ C-atoms of the side chains of two coniferyl alcohol moieties [59].

14.4.2.1 Food and Pharmaceutical Application

The main use of linseed is for the production of oil and fibre. Besides these applications, it is also used in various edible forms like whole, milled, oil and roasted forms. Besides its direct uses, it can also be the main ingredient in many types of food preparation and production. It can be used together with baked products, barbecue and meat products, dairy products and cereal snacks.

Linseed is also potentially preventative of cancer as it contains nutrients to fight or reduce the cancer risk. Linseed is also a potential source of the nutrients which have the ability to reduce cancer cells; among these nutrients cysteine and methionine are the most common [60].

The biological activities of SDG and enterolactone of lignan components in the linseed have been shown to inhibit in vitro colon tumour cell growth and mammary tumourigenesis in rats and limit hypercholesterolemic atherosclerosis and pulmonary metastasis of melanoma cells in mice and delay the development of type 1 and type 2 diabetes [59].

14.4.2.2 Other Uses

Linseed, besides food and functional uses, is mainly applicable in the paint, gum, cosmetics and other products. The constituent of the different active compounds in the linseed like arabinose, galactose, rhamnose, xylose, fucose, glucose and galacturonic acid is a kind of anionic polysaccharide [64] that makes it more convenient for gum production also.

14.4.3 Molecular Mechanisms of Bioactives in Linseed

Linseed is a good source of vitamin E and this vitamin is present as γ-tocopherol. The protective effect of vitamin E against fat and cell protein oxidation is one function of the linseed; it also has a blood pressure lowering and prevention of the heart disease and Alzheimer [55]. The details of how the molecular mechanisms act this for the prevention, and curing of different diseases is still understudied and gaps in research abound.

14.4.4 Effect of Processing on Availability of Bioactive

Different processing steps in the production of linseed oil or other products result in loss of nutrients and some functional ingredients. While the defatting and de-husking of the linseed to get the meal results in the high protein content [65].

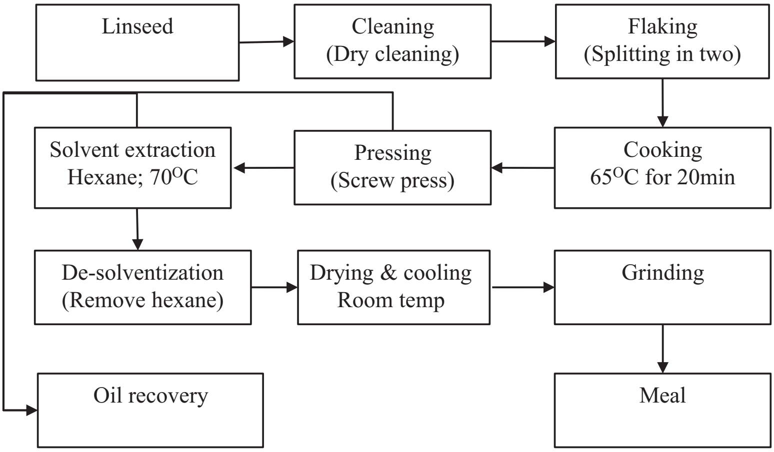

Fig. 14.4 Processing of linseed for the production of meal and oil. (Adopted and modified from Ref. [55])

Even though there is not enough data on the effects of different processes on the bioavailability of bioactive compounds, it is obvious that optimum processing results in an increase in the availability of the bioactive content. The effect of processing on the bioavailability of the ALA shows that it is more available in the oil form than in the milled seed [66]. The general processing for the extraction of linseed oil and meal can be seen from the Fig. 14.4. It can be seen that the application of different processing unit operations has a direct and indirect impact on the bioavailability of the compounds.

Processing also has a negative effect on the bioavailability of the functional ingredients. One example is the application of high temperature in food production. This treatment affects the composition of ALA and also some heat sensitive compositions. The bioavailability of the ALA is high in oil form, but still the high-temperature processing may affect this nutrient since it is heat sensitive [67].

The bioavailability of the functional ingredients in linseed is difficult to gauge because of it contains unsaturated fatty acid chains which oxidizes and gives an off-flavour. As indicated in the [68] study on linseed, linseed oil is susceptible to oxidation which contributes to the formations of undesirable off-flavours and potentially toxic substances due to the unsaturated bonds in the fatty acid chains.

The other main problem related to bioavailability is that the solubility of linseed in water is very low. This hydrophobic property makes complicates the absorption process. As it was described by [69], the solubility of linseed oil in water is extremely poor which decreases the absorption rate in the gastrointestinal tract, hence leading to low bioavailability [69, 70].

14.5 Teff

14.5.1 Introduction

Teff (*Eragrostis tef*) is a self-pollinated annual cereal crop. It has also been a staple food in East African countries like Ethiopia and Eritrea for over 2000 years. It is a small cereal grain, closely resembling millet and originated from widely grown cereal crops under cultivation in these countries [71]. The other parts of teff are used in other countries such as South Africa, India, Pakistan, Uganda, Kenya and Mozambique. These regions use the straw of the teff for livestock feed and are grown as a forage or pasture crop [72].

The finding of different literatures support Ethiopia is the centre of origin and diversity of teff cereal. In this country, teff remains the number one crop in terms of area coverage with an estimated annual acreage of more than 3 million ha [71].

The increasing interest in teff is due to its nutritional composition and lack of gluten proteins. This makes the cereal desirable by celiac patents and also for healthy food preparation [73].

14.5.1.1 Teff Cereal Parts

Teff cereal has different varieties, and these different varieties of cereal have a height ranging between 1 and 2 metres. The upper part of the teff or the shoot, which contains the seed, is thin, 1–4 mm in diameter, and during seed production it starts to bend. Teff possesses small (10–100 mm) and long (40–700 mm) leaf blades. Grains are approximately 0.5–1.7 mm long and 0.2–1.0 mm in diameter and have 1000-kernel weight of 0.25–0.5 grams. Grain colour varies between varieties, from plain white through dark yellow and bright red to dark brown [74].

14.5.1.2 Teff Cereal Nutritional Composition

Teff flour has been studied as a valuable ingredient to improve the quality of gluten-free and whole grain cereal products due to its superior nutritional quality. It is rich in carbohydrates and fibre and has a complete set of essential amino acids. Teff seed is also particularly high in iron and has more calcium, copper and zinc than other cereal grains [75].

The small size and the difficulty of removing the fibre of the teff crop make it to be used as a whole-milled flour. The whole-milled flour of teff is rich in fibre and has a high amount of bioactive compounds like polyphenols, which makes it to be given more attention these days [76].

It was estimated that an average daily allowance of 200 g of teff-enriched bread would contribute to Dietary Reference Intakes (DRIs) in the range of 42 to 81% for iron in females, 72 to138% for iron in males, 38 to 39% for protein in males, 46 to 48% for protein in females and 47 to 50% of fibre in adults [77].

The complexity of the proteins in teff flour is not comparable with that of the wheat but the more advantageous due to absence of the gluten. Protein fractions in teff are less complex than those of wheat, in terms of their apparent molecular size differences, and resemble more the pattern found in maize [78].

The mineral composition of teff is much better than most other cereals, and this makes it more advantageous than other cereal crops. A study by the [77] shows that the incorporation of teff significantly improved dietary iron levels as much as 30%. Teff breads contain more than double the amount of iron when compared to corresponding wheat bread (6 mg/100 g vs 2 mg/100 g).

14.5.2 Bioactives in Teff

Teff cereal is one which is getting a lot of attention these days because of its gluten-free advantages, fibre content and bioactive composition. Teff grain contains around 600 mg/100 of total phenolic content as catechin equivalent [79]. The different variety of this crop have a significant different their seed colour and especially in phytochemical composition. The brown colour teff is rich in TPC and TFC when it comes to the total phenolic content and the total flavonoid content [80].

The difference between the varieties of teff is one factor for the difference in the TPC and TFC, while the presence of the phenolic flavonoids in the teff also differ based on the way it exist in the cereal as bound or free phenols. The bound TPC and TFC are 226–376 mg GAE/100 g and 113–258 mg CE/100 g. While for the free TPC and TFC, it is 37–71 mg GAE/100 g and 36–64 mg CE/100 g [76]. The whole brown teff grain contains trans-p-coumaric, ferulic, gallic and protocatechuic acid as a major free phenolics and the white variety contains rutin, ferulic and protocatechuic acid [80].

The difference in the content TPC and TFC not only depends on the variety but also in the different parts of the cereal grains as the soluble and the insoluble part of the cereal is also another factor. The cell wall of the grain and the bran is a rich source of quercetin, luteolin, naringenin, naringenin-40-methoxy-7-ω-α-lrhamnoside and eriodictyol-30, 7-dimethoxy-40-ω-β-δ-glucoside as hydrolysed by alkaline solution [79, 81].

A study by [80] on the details of TFC shows that the free phenolics extract of teff ranged from 0.52 to 1.02 mg RE/g, and in bound phenolics extract, it ranges from 0.10 to 0.15 mg RE/g, and in this study it shows that the brown types of teff contained high amounts of trans-p-coumaric, ferulic, protocatechuic and gallic acid, whereas rutin, protocatechuic and ferulic acid were predominant in white teff. Total common free phenolics in teff ranged from 284.5 to 626.6 mg/g. Moreover, in this study, the trolox equivalent antioxidant capacity (TEAC) values of free phenolic extracts in teff varied from 1.70 to 4.37 mmol TEAC/g and for bound phenolic extracts from 0.69 to 1.62 mmol TEAC/g. Total antioxidant activity ranged from

2.86 to 5.99 mmol TEAC/g. It was also reported by Alaunyte et al. [77] that teff also significantly improved total antioxidant capacity from 1.4 mM to 2.4 mM/100 g based on the trolox equivalent antioxidant capacity.

14.5.2.1 Food and Pharmaceutical Application

Teff is used as staple crop in the eastern part of Africa. In Ethiopia and Eretria, this crop can be prepared in to different types of local food and beverages such as flat bread called injera; unleavened or unfermented bread called kitta and a fermented beverage called tella are the most common ones [73, 82]. The use of teff cereal as a food is now increasing throughout the world due to absence of the gluten protein and also the content of different phenolic and flavonoids. Besides this, it is a good source of fibre and has potential in the prevention of constipation. The availability of bioactive content also gives it antioxidant properties. The details on the production of the fermented flat bread (injera) are shown in Fig. 14.5.

Besides its use as a traditional food and beverage, there has been a recent development in using teff together with other cereals to develop new food products from the whole grain. Teff flour is rich in phytochemicals, while it is also free from gluten. This makes it lack a functional property to have a good bread, but by mixing it with wheat, this property can be improved, and also the end product gluten concentration can be lowered. The effect of different processing parameters on bioactives is not studied well, though the effect is on processing results in the reduction or improvement of the bioactives in teff cereal. The fermentation of teff for the production of local food injera will increase the composition of the bioactives, and it is well

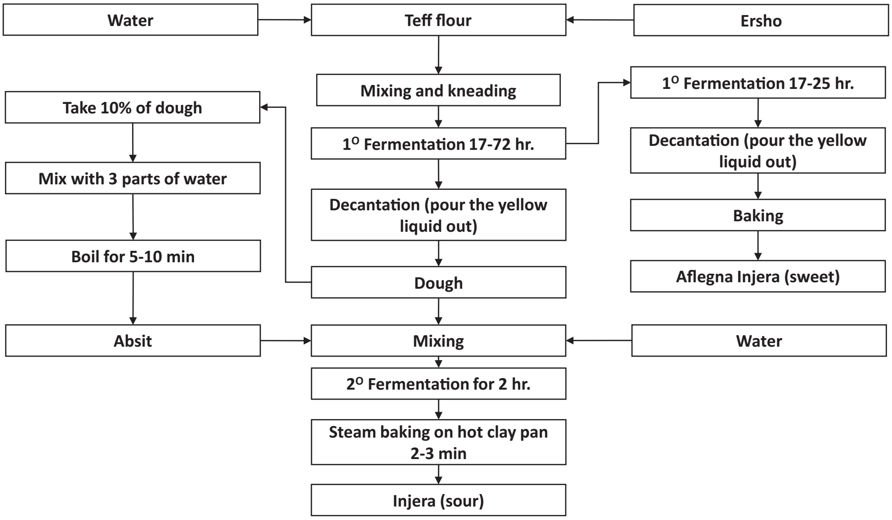

Fig. 14.5 General process flow chart for the production of Ethiopian injera (fermented flat bread) from teff flour

known that the fermentation will impart such advantages. The fermentation of the traditional brewing yeast *Saccharomyces cerevisiae* leads to satisfactory wort and beer quality attributes in both raw and malted teff trials [83].

The most common application of teff is as a food, but it can be used as a unique grain for its in vitro antioxidant activity, for improving the haemoglobin level in human body, to prevent malaria, and in an incidence of anaemia and diabetes [73, 81].

14.5.2.2 Other Uses

Besides the use of teff for food and other functional uses, the different parts of the cereal are very beneficial in animal feed and biofuel production. A large quantity of teff straw, which contains a high fraction of lignocellulosic compounds, is also being produced. More than 2 million tons of straw is reported as waste every year [84]. The application of lignocellulosic compounds in the production of biofuel is more advantageous and a good use of the straw and hay in fuel production in the future.

14.5.3 Molecular Mechanisms of Bioactives in Teff

Details on the molecular mechanisms of the bioactive in teff cereal are not yet fully explored. There is a need to conduct further investigations on the effects of its bioactive content, especially in relation to health mechanisms. In general, studies show that the use of teff in consumption in whole-grain cereals contributes to a reduced risk of cardiovascular ailments, type II diabetes, ischaemic stroke, obesity and cancers [85, 86].

14.5.4 Effect of Processing on Availability of Bioactive

The different functional and nutritional properties of teff have potential to be used in different foods, particularly in baked products, alcoholic beverages, weaning food and gluten-free products.

The application of different processes affects the physical and functional properties of teff flour. Different milling and grinding processes have been shown to produce different flours with different particle sizes and varying degrees of damage to starch granules in flour, depending on the mechanical forces and temperatures utilized during the grinding process [87]. Most of the processing parameters described in the production of Injera in Fig. 14.5 also results in the loss of most of the valuable bioactive and nutrients in teff.

The application of high temperature and time is one factor which affects the availability of the bioactive compounds in this cereal. An experiment in the production of pasta which involves high temperature over time shows that it is possible to produce pasta from teff flour and oat flour [88]. The application of high temperatures over time in the processing of teff affects heat-sensitive bioactives. Processing like extrusion requires the removal of the fiber, which results in a loss of its nutritional and functional quality. This can also affect the composition of bioactives in the fibre of this cereal.

The other main process is fermentation. Fermentation will increase the bioavailability of the bioactives in different fermented foods, but a detailed study on the effects of fermentation on teff is yet unexplored. In most research, the effects of fermentation on the physical, functional and textural properties are well studied. As per [89], the effect of fermentation by *L. plantarum* on the crumb hardness of different breads shows that there is a decrease in crumb hardness by 7% of teff sourdough as compared to whole wheat flour bread.

As indicated by [90], the physicochemical properties of teff indicate that there is great potential on a broad range of food applications. Teff flour has a high water absorption capacity, which results in a higher degree of swelling in the geling phase of teff starches and possibly the small and uniform size of teff starch granules, hence, providing larger surface area and higher water absorption.

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The book was inadvertently published with an incorrect spelling of the Author's name and this was updated globally in the book as RongTsao Cao whereas it should be Rong Tsao.

The updated version of the book can be found at https://doi.org/10.1007/978-981-13-6167-8

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