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Review Article

Functional Properties of Polyphenols in Grains and Effects of Physicochemical Processing on Polyphenols

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Phenolic compounds are important products of secondary metabolism in plants. They cannot be synthesized in the human body and are mainly taken from food. Cereals, especially whole grains, are important sources of dietary polyphenols. Compared with vegetables and fruits, the content and biological activities of polyphenols in cereals have long been underestimated. Polyphenols in whole grains are non-nutritive compounds, which are distributed in all structural areas of cereal substances, mainly phenolic acids, flavonoids, and lignans. In recent years, the health effects of whole grains are closely related to their phenolic compounds and their antioxidant activities. Now, different physicochemical processing treatments and their effects have been summarized in order to provide the basis for promoting the development and utilization of food. The various functions of whole grains are closely related to the antioxidant effect of polyphenols. As the basic research on evaluating the antioxidant effect of active substances, in vitro antioxidant tests are faster and more convenient.

1. Introduction

Natural polyphenols are mostly found in plants which are a kind of compounds with phenolic hydroxyl structure widely existing in nature [1]. Polyphenols mainly include flavonoid, phenolic acid, tannin, and other substances and have strong antioxidation performance, which eliminates free radicals generated by the human body, and the effect of preventing cardiocerebral syndrome and deferring decrepitude. Polyphenols not only have a strong antioxidation characteristic [2] but also have anticancer [3], bacteriostatic [4], liver-protecting [5], anti-infection [6], cholesterol lowering [7], and immunity enhancement [8] properties, and they also prevent various biological activities such as type 2 diabetes [9, 10]. As far as their formation mechanism is concerned, most polyphenols are the secondary metabolites of the phenylpropanoid biosynthesis pathway, which are also known as phenyl propane compounds [11]. Polyphenols and polyphenol-enriched by-products have been widely used in bakery foods because of their nutraceutical properties. While their use in pharmaceutical and cosmetic industries is largely documented, several environmental conditions (e.g., light, temperature, or oxygen) may affect the physicochemical stability of polyphenols. To overcome these limitations, the loading of polyphenols into nanoparticles has been proposed [12].

Although polyphenols cannot provide nutrition for growth and development, they can play a role as defense compounds, such as plant antitoxin as pollinators, prevention of pathogenic bacteria and parasitic bacteria, prevention of ultraviolet rays, and giving color to plants. The existing whole grains mainly include rice, wheat, corn, sorghum, millet, oat, barley, and buck. The process of converting the whole ingredient into one product is referred to as whole grain utilization and the processed food product is referred to as whole grain food [13]. Common whole grain foods are brown rice flour, oatmeal, whole meal flour, whole meal bread, whole meal noodle, cornflakes, and popcorn. The phenolic content of different grains is also different, of which corn has the highest polyphenol content (15.55 μg/g), followed by wheat (7.99 μg/g), oats (6.53 μg/g), and rice (5.56 μg/g) [14]. As shown in Figure 1, whole grains contain more phenols than the processed grains. For example, brown rice contains more ferulic acid than polished rice because

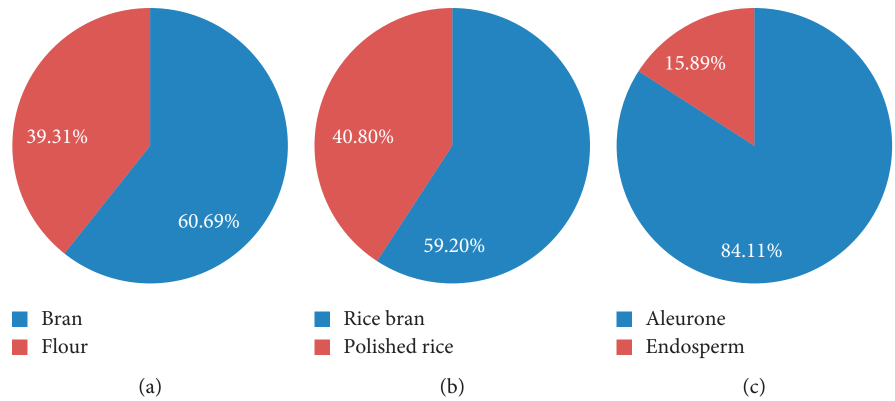

Figure 1: Distribution of phenolic compounds in different tissue parts of whole grains. (a) Wheat. (b) Brown Rice. (c) Corn.

phenols are mainly found on the cortical layer of rice grains. Smaller grains contain more ferulic acid than larger grains, such as rye, oats, and millet than rice, because ferulic acid is associated with total fiber and insoluble dietary fiber content, and the higher the fiber content, the higher the ferulic acid content [15]. After germination, the content of polyphenols is much higher than that before germination [16]. The content of polyphenols in grains is equal to that of fruits and vegetables, and even some highly active phenolic compounds only exist in whole grains. Whole grain polyphenols are a general term for phenolic substances distributed in the structure of grains.

2. Main Constituents of Grains

Polyphenols in whole grains are non-nutritive compounds, which are distributed in all structural areas of cereal substances, mainly phenolic acids, flavonoids, and lignans. Phenolic acid is mainly found on the cortical layer of grains, in which ferulic acid is higher, followed by oxalic acid, p-coumaric acid, and caffeic acid. It has a strong antioxidant effect and can prevent the tissues inside the cortex from oxidation [17, 18]. It also has antimutagenic effects on toxic substances such as nitrosamine and mycotoxins in the environment. Flavonoids are widely distributed in plants, mainly in the cortex and green leaves of plants. Lignans are the primitive substances that make up the cell wall component of lignins in cereal cells [19]. Grain food is the most important source of lignins in human food. The grain content is 2–7 mg/kg, lower than that in flaxseeds, but much higher than that in vegetables. It not only affects the metabolism and biological activity of endogenous hormones, but also affects the synthesis of enzymes and proteins in cells as well as cell proliferation and differentiation. As shown in Table 1 and Figure 2, polyphenols in cereals exist in free form, soluble binding form, or insoluble binding form. The vast majority of them exist in the binding form. Free-form polyphenols mainly include ferulic acid, parabiosanoic acid, protocatechuic acid, gallic acid, coffee acid, and erucic acid can also be detected. The polyphenols in the binding form are made up of ferulic acid, vanillic acid, coffee acid, and syringic acid [36–38].

3. Whole Grain Phenolics Antioxidant Activity

Modern epidemiological studies show that whole grain foods can prevent chronic diseases such as type 2 diabetes, coronary heart disease, and bowel cancer [39–44]. Although the mechanisms underlying these effects are not fully understood, they are likely to be closely related to the antioxidant activity of whole grains [45, 46]. The bioactivity of whole grains is closely related to the natural antioxidants, and polyphenol is the important one.

Polyphenols are very important secondary metabolites in plants. They are synthesized in plants mainly through shikimic acid and malonic acid [47]. In humans, polyphenols in the diet can also enhance the immune defense ability of the body, reduce the incidence of chronic diseases, and have significant effects such as antiallergy, antiarterial atherosclerosis, anti-inflammation, antioxidation, antibacterial, antithrombotic, and protecting heart and blood vessels [48]. The health benefits of polyphenols on the human body are mainly due to their oxidation resistance. Polyphenols in grains have a stronger antioxidant effect in the body through the synergistic effect of multiple bioactive compounds than the single active ingredient and can eliminate too many oxidation free radicals in the body as antioxidants or after the intestinal digestion. The free-form polyphenols are absorbed into the mouth and the protein in the mouth which is rich in protic acid, which is absorbed by the body in the stomach or in the small intestine. Free polyphenols are more easily digested in the upper digestive tract than in the combined state [49]. Due to the combination of the combined polyphenols in the more difficult digested cell walls, the digestion and absorption process mainly occurs in the large intestine. Binding polyphenols in the large intestine are released from the cell wall in the form of glycosidic ligand through the action of microorganisms or related enzymes and then reformed into glucoside, which is used by the human body through the glucose transporter in the cell. Furthermore, the intestinal microbial environment was effectively improved by the interaction of binding polyphenols with microorganisms in the large intestine, and the risk of colon cancer was significantly reduced [14].

Table 1: Composition and existing forms of phenolic acids in whole grains.

Cereal species	Free phenolic acid	Combined with phenolic acid	References
Wheat	Gallic acid, protocatechuic acid, chlorogenic acid, coffee acid, syringic acid, ferulic acid, vanillic acid, p-coumaric acid, p-hydroxybenzoic acid	Gallic acid, syringic acid, ferulic acid, vanillic acid, p-coumaric acid, isoferulic acid	[20–23]
Brown rice	Ferulic acid, coffee acid, syringic acid, protocatechuic acid, chlorogenic acid, coumaric acid, salicylic acid, o-coumaric acid, syringol, 2-4-dihydroxybenzaldehyde, sinapic acid, 2-hydroxycinnamic acid	Ferulic acid, chlorogenic acid, coffee acid, syringic acid, vanillic acid, p-coumaric acid, p-hydroxybenzoic acid, syringol, protocatechuic acid, o-coumaric acid, 2-4-dihydroxybenzaldehyde, sinapic acid,	[24–28]
Corn	Ferulic acid, coffee acid, gallic acid, p-coumaric acid, o-coumaric acid,	Ferulic acid, coffee acid, p-coumaric acid, p-hydroxybenzoic acid, syringic acid, protocatechuic acid,	[29–32]
Oats	Chlorogenic acid, coffee acid, syringic acid, vanillic acid, p-coumaric acid, p-hydroxybenzoic acid, 2-4-dihydroxybenzaldehyde, sinapic acid, chlorogenic, ferulic acid	Coffee acid, syringic acid, vanillic acid, p-coumaric acid, p-hydroxybenzoic acid, 2-4-dihydroxybenzaldehyde, sinapic acid, chlorogenic, ferulic acid	[33–35]

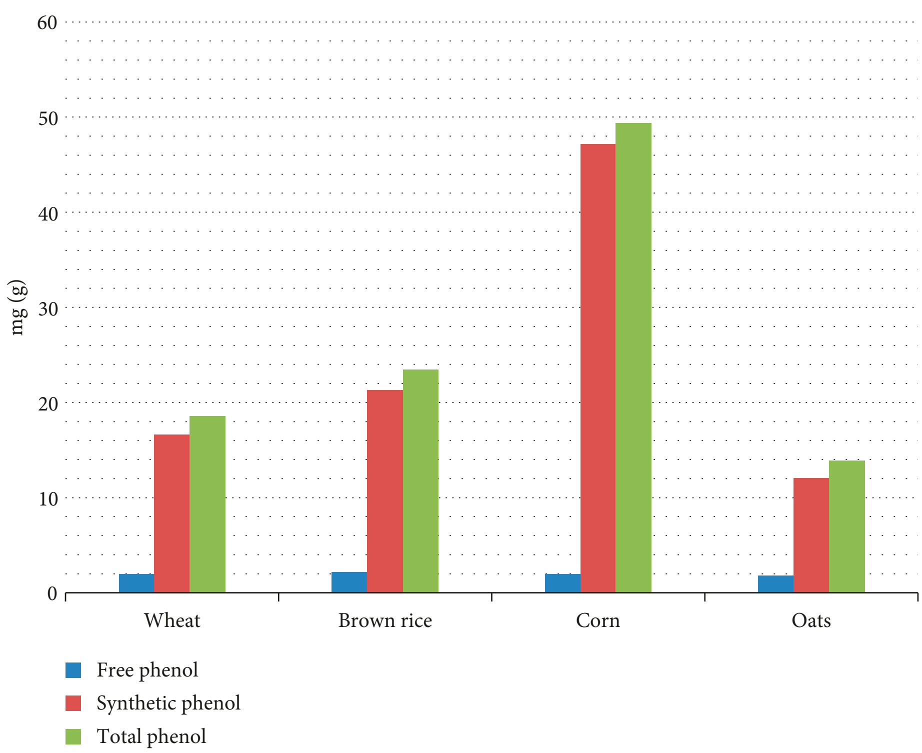

Figure 2: Total phenolic content of whole grains (mg/g) [36, 37].

According to the antioxidant mechanism of polyphenols, free radical-scavenging and chelating transition metal ions were used to determine the antioxidant capacity of grain in vitro [50, 51]. The method of in vitro antioxidant experiment is simple, and as a basic research to evaluate the antioxidant activity of active substances, it is faster and more convenient. Previous studies showed the correlation between the content of combined total phenol and the content of total phenolic acid in wheat, corn, oat, and other grains and DPPH free radical-scavenging capacity and found that the former two have significant correlation with the latter and the antioxidant can be used as the evaluation index of functional food. The antioxidative activity of the whole grain is the same as that of the polyphenol, and it is in close relationship with the variety, tissue, form, and content [52]. It is reported that the antioxidant ABTS values of 24 kinds of whole grains was analysed and found that sorghum had higher antioxidant activity compared with brown rice, wheat, corn, and other whole grains [53]. Choi compared the antioxidant DPPH values of 9 whole grains and reached a similar conclusion [54].

At present, the rapid screening method is the most used to evaluate the antioxidant activity of the phenols in cereals (DPPH, ORAC, HO, and ABTS).The advantage is simple operation and can rapid screening of whole grain varieties that are rich in polyphenols and areas of polyphenol concentration. However, the results of these in vitro experiments cannot reflect the real antioxidant effect of polyphenols in vivo, so it is necessary to introduce the method of in vivo experiments into the evaluation of the antioxidant activity of phenols in whole grains.

4. Application of Grain Polyphenols

At present, the extraction and product development of polyphenols in grains mainly focus on the research of the outer seed coat of grains, but the research on the extraction of polyphenols in grains and their antioxidant activity is less. With the development of social economy and the progress of grain processing technology, consumers are chasing taste and delicacy. As grain processing becomes more and more refined, it is required to be able to control it more skillfully under various conditions.

4.1. Physical Treatment

4.1.1. Effects of Grinding on Polyphenols in Grain. Milling is the main process of grain physical processing, which is divided into dry grinding and wet grinding [55]. Dry grinding is the separation of outer fibers and germs, while wet grinding is considered the best way to produce cereal endosperm products. Dry grinding consists of two parts: grinding and screening. Screening mainly refers to removing impurities, pest-infested grain, bacterial discolored grain, weeds, and foreign substances [56]. Tylewicz found that overmilling destroys the nutrients in the grains [57]. Compared with dry grinding, wet grinding is the process of soaking grains in water and then separating starch, protein, and fiber components [58]. However, due to the high content of pentosan and poor formation capacity of gluten, it is difficult to realize the industrial wet milling process. The bran layer and protein cortex are difficult to completely separate, and the high content of glucan leads to increased viscosity, which makes it difficult to pass screening and centrifugation [59].

Through milling, the taste and flavor of grains can be greatly improved, and the digestibility can also be improved to a certain extent. However, the nutritional value of grains is greatly reduced. This is because the bran and germ, which are rich in vitamins, minerals, and biologically active ingredients, are removed by milling. As the antioxidant components of whole grains are mainly located in the cortex, aleurone layer, and germ part, the milling process inevitably has adverse effects on the polyphenols and their antioxidant activities. With the improvement of processing accuracy, the total phenol content of both japonica brown rice and indica brown rice decreased significantly, and the free phenol content of both types of brown rice showed a downward trend, and the reduction of combined phenol content was more significant than that of free phenol. The free and combined phenolic acid composition of brown rice with different milling degrees is basically the same, while the phenolic acid content is significantly different. Under the influence of milling treatment, the antioxidant activity of brown rice decreased significantly. After 30 s milling (up to the national first-grade rice quality standard), the total phenol and cellular antioxidant activity (CAA) value of brown rice decreased by 55.50% and 92.85%, respectively [60]. It is mainly caused by the removal of the skin rich in polyphenols and the thermal effect caused by grinding, which leads to the oxidation of polyphenols. The results showed that the polyphenols content of sorghum and millet and their antioxidant effects were similar. In the process of milling, the flavor and nutritive value should be taken into consideration [61, 62].

4.1.2. Effect of Heat Treatment on Polyphenols in Grains. Grains are digested and absorbed by the body before they are assimilated. Grains are usually cured by heat treatment type. Common heat treatment methods include baking, boiling, steaming, etc. The effects of different heat treatment on polyphenols in different grains were studied [63, 64]. Therefore, it is important to clarify the composition, content, and properties of polyphenols after different processing of grains to study the quality of polyphenols assimilated by the human body and its value in the human body.

The effects of the curing process on nutrition and processing quality of oat traditional food were studied. It was found that the physical and chemical indexes of protein, starch, fat, and wech-glucan content of oat were significantly improved after being processed, and the processing characteristics and flavor were greatly affected by them. The effects of evaporation treatment on the properties of oat starch were most significant. However, compared with other treatments, the effect of scalding on oat was minimal [65]. At present, in China, there are few studies on the change in polyphenol characteristics after heat treatment [66].

The effects of various commercial hydrothermal processes (steaming, autoclaving, and drum drying) on levels of selected oat antioxidants were investigated. Steaming and flaking of dehulled oat groats resulted in moderate losses of tocotrienols, caffeic acid, and avenanthramide Bp (N-(4′-hydroxy)-(E)-cinnamoyl-5-hydroxy-anthranilic acid), while ferulic acid and vanillin increased. The tocopherols and the avenanthramides Bc (N-(3′,4′-dihydroxy-(E)-cinnamoyl-5-hydroxy-anthranilic acid) and Bf (N-(4′-hydroxy-3′-methoxy)-(E)-cinnamoyl-5-hydroxy-anthranilic acid) were not affected by steaming [67]. The content of free polyphenols in wheat and sorghum was significantly increased after baking, while the content of total flavonoids was significantly decreased [68]. What is more, the effects of different heat treatments on polyphenols were also different. Compared with baking treatment, free polyphenol content in wheat and sorghum significantly decreased after high-pressure and atmospheric-pressure cooking. In addition, variety is also an important factor affecting the content of polyphenols after heat treatment or high-pressure steam treatment of purple waxy corn [69]. However, Harakotr et al. [70] carried out high-pressure steaming on sweet corn and found that free ferulic acid and total phenol content were significantly increased, and the content showed an upward trend with the extension of heat treatment time and the increase of temperature, but the content of combined ferulic acid and total phenol decreased, the total antioxidant capacity was consistent with the variation trend of total phenol content. It is found that the research about the influence of traditional heat treatment on the composition and properties of free and combined polyphenols in oat is not comprehensive [71].

4.1.3. Effects of Extrusion on Polyphenols in Grain. Extrusion is a new technology which combines heating, cooking, and extrusion molding. Short-term high temperature and high pressure can change the texture of food, change the composition of food, and even promote the interaction effect between food components. Similarly, extrusion treatment may also affect the polyphenols content and their antioxidant activity of whole grains [18]. The research in China is limited to the taste of processed grains and the determination of the changes of protein, starch, oil, and other components [72]. It was reported that the content of 5 kinds of sorghum total phenol (free phenol) decreased by 33.33%, 56.60%, 69.54%, 70.09%, and 78.37% and 81.82%, 76.92%, 86.63%, 84.90%, and 87.59%, respectively, after the extrusion treatment through a friction-type Maddox single screw extruder [73].

The extrusion treatment destroys the cell wall, promotes the transformation of binding polyphenols to free phenol, and also facilitates the extraction of free phenol. Compression heat inevitably leads to partial degradation of polyphenols and a certain degree of polymerization and changes in molecular structure. In addition, during extrusion, if the water content of the feed is too high (more than 18%), the polymerization of polyphenols will be promoted, and the extraction rate and antioxidant activity will be reduced. If the water content of the feed is too low (less than 15%), the depolymerization of condensed tannin will be accelerated and converted into oligomers with low molecular weight which can be extracted more easily. Extrusion treatment will produce or increase or decrease the content of total phenol and its monomer phenol in different parts of grain and then affect its antioxidant activity.

4.2. Chemical Treatment

4.2.1. Effects of Germination on Polyphenols in Grains. Germination is a complex physiological process. In the process of grain germination, a large number of endogenous enzymes are activated and released, which leads to the decomposition and recombination of the internal material components of grains, which may have a certain impact on the polyphenols of whole grains and their antioxidant activities. During germination, the biological, chemical, nutritional, and sensory properties of grains change significantly. Moreover, the relevant enzymes in the grains were activated, and the nutritive starch in the endosperm was decomposed into reducing sugars, the protein was degraded, and the content of soluble protein was increased. The embryo develops into roots and buds. Studies have shown that the germination process can significantly increase the content of polyphenols in grains such as millet and brown rice [74, 75].

The effects of germination on the nutritional quality of grains include high protein, low unsaturated fatty acids, low carbohydrates, mineral content, and vitamins. After 47 hours of germination treatment, the content of total phenol increased by 38.71% [74]. Similar reports have been reported [76, 77]. After the brown rice was germinated for 47 hours, the content of free phenol increased by 76.67% and binding phenol increased by 44.64%, respectively [78, 79]. The content of free phenol was obviously higher than that of the combined phenol. The composition of phenolic acid in free state and combined state of brown rice with different germination time is basically the same. However, the phenolic acid content is significantly different, which may be caused by the improved extraction rate of phenolic acid in germination or the concentration effect caused by the resynthesis and polymerization of tannin and hydrolysis of pentanine [80, 81]. The reduction of total phenol content in grains may be caused by the dissolution of some polyphenols from grains into the external water environment during the germination process or by the oxidation and decomposition of polyphenols by activated polyphenols oxidase and esterase.

4.2.2. Effects of Fermentation Treatment on Polyphenols in Grains. In the process of grain fermentation, many small molecules with physiological activity are produced while large molecules such as carbohydrates and proteins are consumed. Zhai et al. [82] used seven grains such as wheat, corn, brown rice, millet rice, oat, and sorghum in solid fermentation of agaricus matsutake and found that the content of total phenol (free phenol) of all grains except sorghum was significantly increased after the solid fermentation of agaricus matsutake. This may be related to the strong metabolism of agaricus matsutake to produce phenolic compounds. Except that, the content of total phenol (free phenol) in sorghum was negatively correlated with the fermentation time, the content of total phenol (free phenol) in other grains was positively correlated with the fermentation time, and the extension of fermentation time was beneficial to the improvement of total phenol (free phenol) content. Solid-state fermentation (5 d) can significantly increase the content of total phenol (free phenol) and antioxidant activity (ABTS) of corn, with an increase rate of 20.05% and 36.73% [83], respectively. Liquid fermentation also had significant effects on the content of total phenol (free phenol) and antioxidant activity (ABTS) of 5 kinds of sorghum (slurry and porridge) [71].

5. Conclusions

(1) Polyphenols exist in large quantities in grains and are an indispensable source of nutrition for the human body. When the research and application of polyphenols in grains are not common at the present stage, strengthening the research in this aspect is the most important task.

(2) Although the polyphenol contents in grains are high, the complex composition of polyphenols is mostly

located on the surface and outer shell of grains. It is of great help to the research of different kinds of grains and polyphenols to overcome some diseases.

(3) The various functions of whole grain foods are closely related to the antioxidant effect of polyphenols. As the basic research on evaluating the antioxidant effect of active substances, in vitro antioxidant tests are faster and more convenient.

(4) The effects of physical and chemical treatment on polyphenols in grains during food processing need to be further studied, and more effective treatment methods must be investigated to improve taste and flavor while preserving nutritional value.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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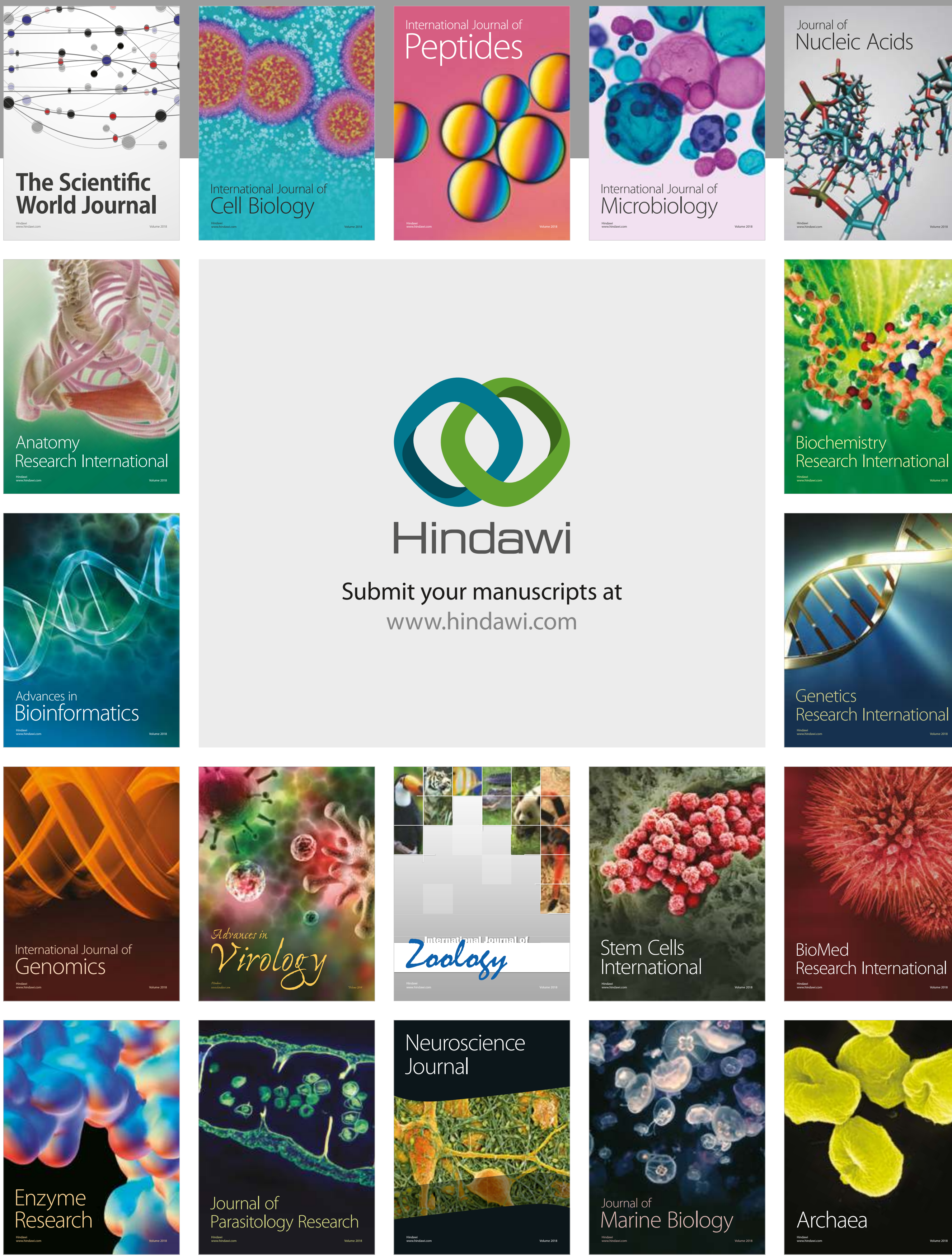
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