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Current trends in the use of unconventional raw materials for the development of gluten-free bakery and pastry products with high nutritional value: A review

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Abstract

Currently correcting and improving lifestyles, hence the "style" of food has become a priority and a constant concern, due to the many diseases that have developed as a consequence of the eaten food and its adjuvants. Globally the population is facing a rising epidemic of disorders related to the consumption of gluten-containing foods such as celiac disease, allergies and gluten sensitivity. Even when not reaching constituted morbid entities, the act of eating can generate simple functional disturbances. A gluten-free diet is essential for the management of any signs and symptoms of celiac disease and for any other medical conditions associated with gluten. This paper presents an overview of the most recent scientific results, approaches and investigations concerning other unconventional raw materials (chestnuts, almond, coconut, acorn, teff, tapioca, etc), in order to identify and exploit their potential, whether technological, biological, chemical or physical, to meet the needs and demands of consumers. Introducing new, innovative products using unconventional raw materials to the market would help improve and increase the diversity of functional flour products.

Keywords: Celiac disease, gluten-free flour, unconventional raw materials, nutritional quality

1. Introduction

In recent decades, nutrition has had an impact on the whole of human existence, determining the health and working capacity of each individual. In this regard, current research is concentrated and focused on nutritional sciences and food technologies that result in providing national, regional and global markets with innovative food products with high nutritional potential. These products, together with recommended changes in dietary regimes and lifestyles, have a positive impact on public health and quality of life. All experts agree on one thing: a healthy diet is the best way to prevent disease and live a peaceful life [1, 2, 3].

Also, food and medical research carried out in different countries of the world, including our country, has shown that it is necessary to improve the concept of food quality, in the sense that it must meet the four mandatory requirements: psycho-sensory value, energy value, biological value and hygienic value [4, 5].

In recent years, the food industry has turned to new raw materials capable of meeting consumer demands. Consumers are much more informed about the food they eat than in past generations. This increase in knowledge proportionately increases the demand for more nutritious, high quality and tasty food. Consumers are more aware of food issues and are monitoring and adjusting what they consume as they have become more concerned about improving their overall health through their daily diet. There has been a progressive increase in consumer demand for natural products, free of synthetic food additives, but to be replaced by safe alternatives, thus functional products are becoming increasingly sought after and appreciated [6, 7]. The food pyramid shows the nutritional recommendations, amounts and types of food that should be eaten daily to maintain good health and reduce the risk of

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developing various diet-related diseases. The most important foods that make up the food pyramid are grains, vegetables and fruits as the foundation of a balanced diet, calling them the "foundation" for proper nutrition and health [3, 8].

Cereals and cereal products are the basic element in ensuring food security for the population. Cereal crops are the world's largest crop area, with 55% of the world's agricultural land, or about 730 billion hectares, devoted to cereal crops [9].

In recent decades, although nutritional trends have shifted towards whole grains, very often refined grains, especially white flour and white bread varieties are preferred over whole grains. This trend is due to the general desire of consumers to consume products with superior technological characteristics, which has led to the selection of wheat varieties with increased gluten content to obtain voluminous products with high porosity and longer shelf life. Consequently, today we are facing a rising epidemic of gluten-related disorders such as celiac disease, allergy and gluten sensitivity [7, 10].

The number of people with gluten intolerance is constantly increasing, and the area of spread is also increasing, with the globalization of celiac disease. Thanks to better diagnostic methods, more and more people are being identified with celiac disease. According to data provided by the Italian Celiac Association, the prevalence of the disease is over 1% of the global population, with lows of 0.5% and highs of 1.26% of the population of North America and Europe [8, 11, 12]. In Romania, the number of patients with celiac disease has increased 5-10 times compared to what it was 10 years ago, being between 250,000 and 1,000,000 due to the increase in the rate of diagnosis but also due to the increase in autoimmune diseases in general [13].

Celiac disease is a chronic autoimmune small bowel disease (your own immune system causes the condition), which occurs in people with a certain genetic predisposition, and can manifest itself at any age, starting as early as childhood. The pathogenic process is caused by intolerance to gluten - the protein present in cereals such as wheat, barley, rye and oats. This implies that when the gluten intolerant person consumes products containing gluten (food, nutritional supplements or medication), the host immune system is self-activated and synthesizes "anti-gliadin" antibodies that are secreted in the intestine (the immune system attacks through antibodies), causing an inflammatory reaction in the mucosa [14, 15]. The exact cause of coeliac disease is unknown, but medical research in recent years has identified certain genes that define an increased predisposition to the disease, which is more prevalent in Europe. Environmental factors as well as viral or bacterial infections can trigger various changes in the small intestine in genetically predisposed individuals. The ingestion of gluten-containing foods then triggers various immune reactions, which cause the intestinal lesions characteristic of the disease (maldigestion, malabsorption). People with celiac disease often have other conditions such as dermatitis herpetiformis (more common in adults, but can also occur in children), type I diabetes (insulin-dependent diabetes), autoimmune thyroiditis, Down syndrome, Sjogren's syndrome, selective antibody deficiency (immunoglobulin A deficiency) [16].

It is now estimated that many people suffer from celiac disease, but many of the symptoms overlap with other diseases. Constipation, diarrhoea, flatulence, bloating, joint pain and fatigue cited as the most common manifestations of coeliac disease can occur in dozens of diseases and conditions. The most accurate way to identify and diagnose symptoms of gluten intolerance is to use a strict diet from which gluten-containing foods are eliminated for a significant period of time. During this time, the symptoms from the previous period and the period of food elimination should be observed and compared [17]. The practical implementation of the gluten-free diet requires the observance of two major principles: the total exclusion of gluten-containing foods and the compensation of deficits thus created with permitted foods. It is necessary to ensure a sufficient caloric ration, adapted to the needs of each subject, a complete diet that includes all the food principles and the avoidance of food monotony by using the most varied and attractive ways of preparation and presentation [18, 19].

People suffering from coeliac disease should eliminate products made from wheat, rye, barley and their derivatives from their diet and replace them with foods made from natural ingredients enriched with biologically active elements that reduce the symptoms of the condition and offer the potential for a healthy life. The exclusion of gluten-containing foods, however, raises a problem of nutritional compensation for the deficits created by restricting the range of foods [18]. Modern nutrition for people with celiac disease aims to remove these

deficiencies and ensure a complete diet in terms of calories and nutrients. The following nutritional imbalances are corrected: hypocalcaemia, hypomagnesaemia, hypokalaemia, hypoalbuminaemia, iron deficiency, vitamin B12, folic acid, vitamin K, etc.). In the development of gluten-free flour products, account is also taken of the not inconsiderable intolerances to lactose and fat. The diet must be designed in such a way as to please the patient who consumes it [19].

Gluten-free products, as well as those aimed at a healthy diet, are growing worldwide, due to the large number of people diagnosed with coeliac disease and people who want to change their diet [20, 21].

Producing bakery and pastry products from gluten-free cereals that do not harm these people is a big challenge for bakers and scientists. The use of different gluten-free cereals and flours makes it necessary to find possibilities to take over the role of gluten from the other ingredients in the flour, by adding different components, on different treatments on flours and doughs, or by changing the baking method [10, 22].

Gluten is the component of the wheat grain, its proteins are divided into two main classes according to their solubility in water: soluble gliadins and insoluble glutenin, collectively called prolamins. It allows the formation of elastic doughs that can be stretched easily, which is very difficult to achieve with doughs made from flours other than wheat. When they come into contact with liquids, the two gluten components form a sticky, elastic mass, which makes the dough elastic and increases its stretching qualities. In short, gluten is responsible for the technological characteristics of doughs used to make bakery products [13, 23].

The absence of gluten often results in a dough that is more liquid rather than pre-baked, which can lead to a baked product with a crumbly texture, poor colour and other post-baking quality defects. Gluten-free bread doughs can only retain gas if another gel replaces the gluten. Preparation of gluten-free doughs is difficult because gluten contributes to a strong protein network, which prevents the dough from dissolving during baking [24]. The development of new technologies and the use of gluten-free flour, starches, hydrocolloids and new food ingredients will make it possible to find alternatives to traditional bakery products. Modification of gas binding capacity and stabilization of starch gel during baking are the most important aspect [25].

In 2013, EU Regulation 609 laid down rules on the requirements, composition and labelling of gluten-free products, giving people with gluten intolerance clear and reliable information about the difference between products that naturally contain gluten and those processed to reduce gluten content. Gluten-free labelled products must not contain more than 20 mg/kg gluten, according to European Commission Regulation (EU) No 828/2014. The global gluten-free product market is estimated at $ 4.48 billion in 2018 and is expected to grow by 7.6% in the coming years to $ 6.47 billion in 2023. This strong growth is driven by good identification and understanding of celiac disease and other diseases that include gluten intolerance, as well as trends in gluten-free diets [21]. In recent years, in Romania too, there has been a growing interest in gluten-free flour products, an interest that is based on satisfying the preferences, needs and, last but not least, the increasing demands of consumers. Optimising recipes and the technological process for gluten-free flour products is a great challenge, especially for improving the sensory characteristics of the product. Numerous ingredients are commonly used for the purpose of substituting gluten functionality. Apart from the gluten- free flours obtained from cereals and pseudocereals such as rice, oats, buckwheat, maize, millet, quinoa, amaranth, sorghum, flax, hulls, soya and lentils with which we are becoming increasingly familiar, there are other unconventional raw materials that can be used to obtain various gluten-free bakery and pastry doughs, such as: chestnut flour, almond flour, coconut flour, acorn flour, teff flour, tapioca flour, etc.

Unconventional raw materials

The category of unconventional raw materials includes *chestnut flour, almond flour, coconut flour, acorn flour, teff flour, tapioca flour* which are gluten-free and an important source of nutrients, especially fiber and protein, contain no *trans* fatty acids and have a low glycemic index.

Chestnut flour is a gluten-free, sweet, light brown flour that is naturally prepared by freeze-drying or bleaching and dehydrating. The quality of the flour depends on the drying method applied, the temperature used, the drying time, the speed of air as drying agent, etc [26]. Chestnut flour contains high quality proteins with essential amino acids (4-7

g/100 g), a relatively high amount of sugars (20-30 g/100 g), starch (50-60 g/100 g), dietary fiber (4-10 g/100 g) and low amount of fat (2-4 g/100 g), mostly unsaturated, vitamin B1 (0.2-0.4 mg/100 g), vitamin B2 (0.1-0.4 mg/100 g) vitamin B3 (0.1-0.3 mg/100 g), vitamin A (11-12 mg/100 g), vitamin C (15-43 mg/100 g) and minerals such as potassium (723-738 mg/100 g), phosphorus (94-131 mg/100 g), magnesium (48-110 mg/100 g), calcium (56-136 mg/100 g), zinc (1-5 mg/100 g) and iron (1-3 mg/100 g). The humidity of the chestnut flour is between 10 to 14 g/100g product. In addition, it is a good source of phenolic compounds (flavonoids: rutin, quercetin and apigenin), pholates, gallic and ellagic acid [27, 28, 29]. Due to its nutritional properties and lack of gluten, chestnut flour can be used by patients suffering from celiac disease. There are studies recommending the use of chestnut flour as an alternative to cow's milk in the preparation of desserts and soups suitable for children, as it does not contain lactose, which is the cause of some food allergies [26]. In another study, aiming gluten-free bread production, chestnut flour was used and some physical and chemical properties were investigated during storage. Using chestnut flour (in proportion of 10% and 20%) in bread samples prepared using gluten-free flours, decreased the volume, and caused hardness inside of the bread but hardly enough in the bread's crust. Moreover, chestnut flour provides more stability during the storage protecting the color property of the bread [30]. Chestnut flour can be used as a functional food additive with a distinct flavour in snacks and similar products [31]. Chestnut flour has great potential to be used in food manufacturing as it is a good source of starch and can be used to modify many characteristics such as texture, rheology, gelatinisation, moisture retention, homogeneity of products, etc. The addition of chestnut flour to food products increases their nutritional value by increasing the content of fiber, lysine and B-complex vitamins, etc. [27]. In bakery products, chestnut flour should be mixed with other types of flour, the most recommended being rice flour, to prevent a number of defects (low volume, stiff structure, unpleasant flavor and a dark colour) of the products. The best results in terms of colour, hardness, texture and flavour of the finished products were obtained when the ratio of chestnut flour to rice flour was 30:70 with the addition of xanthan gum and emulsifiers. In addition, chestnut flour added to bakery products (gluten-free cake, bread and cookies in different proportions 20%, 40%, 80% and 100%), besides improving colour and flavour, led to a delay in the ageing process [29]. Chestnut flour can be successfully used in the production of gluten-free cookies, setting the maximum optimum proportion of 20-40% of the total ingredients used in the manufacturing recipes and leading to the desired quality characteristics. Partial replacement of rice flour with chestnut flour resulted in decreased hardness of the cookie samples, obtaining cookies with a representative dietary fiber content, lower glycemic index than products without chestnut flour and increased shelf life [31].

Chestnut flour can be stored at room temperature for several months or at 4°C for a longer period of time. In some European countries, especially Italy, chestnut flour is used on an industrial scale in the production of cookies, breakfast cereals, muffins, cakes, flakes, pasta, pudding with milk, bread, soups and sauces instead of wheat flour is used or added chestnut flour in various proportions. Thus, interest in chestnuts and chestnut products is growing by the day due to their potential effects in terms of nutritional quality and health [29-34]. Due to the high content of vitamins and minerals, the consumption of chestnut flour has numerous benefits for the human body, such as: improving the immune system, through the high intake of vitamin C and other antioxidant compounds; improving brain functions, supporting the development of neurological functions and supporting the health of the nervous system; increasing bone mineral density, through the intake of copper and magnesium, thus preventing diseases such as osteoporosis; improving heart health, by balancing cholesterol, reducing inflammation, reducing blood pressure, lowering the risk of stroke, heart attack and coronary heart disease [35, 36].

Almond flour does not contain gluten, it is a product that can be obtained by grinding peeled and cleaned almonds, it has a strong flavour but does not influence the final taste of the product [37]. Specialists have found that almonds contain particularly valuable proteins (16-22 g/100 g) for the human body, fats (45-60 g/100 g), saturated acids (3-4 g/100 g), monounsaturated acids (30-35 g/100 g), dietary fiber (8-14 g/100 g), phenolic compounds (270-340 mg/100 g), vitamins B2 (1-1.1 mg/100 g), vitamin E (25-27 mg/100 g) and minerals: iron (3-5 mg/100 g), zinc (3-4 mg/100 g), magnesium (232-270 mg/100 g), calcium (269-300 mg/100 g), potassium (704-733 mg/100 g), phosphorus (445-480 mg/100 g), manganese (1.2-

1.7 mg/100 g) in amounts much higher than in peanuts, all this energizing and providing vitamins and minerals for human body [37, 38, 39]. Almond flour contains high amounts of phenolic compounds, including benzoic and cinnamic acid derivatives (vanillic, caffeic, p-coumaric and ferulic acids), flavonols (quercetin, kaempferol and isoramnetin), anthocyanidins (delphinidin and cyanidin) and procyanidins (B2 and B3) [39]. Also, in the almond composition can be found a substance called amygdalin, also known as vitamin B17, which plays an important role in the fight against cancer and successfully prevents the occurrence of the disease by removing the cancer cells [40]. Amygdalin is known for thousands of years in China, Egypt, Greece and Rome, is extracted from bitter almonds and since then is used in the treatment of skin tumors. Several studies have associated higher vitamin E intake with lower rates of heart disease and Alzheimer's disease [41]. The consistency of almond flour is similar to wheat flour, except that almond flour is much richer in vitamin E, mineral salts and has a high natural fibre content, is low in carbohydrates, and has a low glycemic index. It can be used as a substitute for wheat flour even in 100% ratio but also in combination with other unconventional flours [39]. Almond flour is an assortment of flour suitable for use in making bakery and pastry products. In most manufacturing recipes, ordinary wheat flour is replaced by almond flour, but the finished products obtained are low in volume and dense, characteristics less appreciated by consumers. The best results in terms of texture, sensory acceptance, pleasant nutty aroma and sweet taste of cookies were obtained when wheat flour was substituted up to 45% with almond flour. Cookies have a high degree of sensory acceptance (over 70% of acceptance by potential consumers), a considerable content of protein and lipids and are sources of iron. The data suggests a possible commercial exploration of the cookies produced, so that the number of these types of products to increase on the market, offering new nutritional options for consumption for people intolerant to gluten [42]. Also, in bakery (bread in different proportions of 10%, 30% and 50%) products, almond flour should be mixed with other flours, the most recommended being rice flour, to prevent a number of defects (low volume, low porosity, unpleasant flavour and a dark colour) of the products [37]. Chestnut flour can also be used in the production of gluten-free muffins, establishing the optimal substitution ratio of 60% rice flour with 40% almond flour, resulting in products that are nutritionally valuable (representative content of protein, fat and fibre) as well as in terms of quality requirements (texture, volume, colour corresponding to quality requirements, pleasant taste and smell) [38]. Other studies recommend the use of 60% rice flour, 20% almond flour and 20% arrowroot flour for the preparation of cake, resulting in nutritionally (high protein, fiber and fat content) and technologically (texture, aroma, sensory acceptance, colour corresponding to quality requirements, pleasant taste and smell) valuable products [43]. Cookies, cakes and biscuits made with almond flour are very popular all over the world, with names specific to each region, e.g. *macaroon cookies* (USA or UK), *speculaasjes* (Netherlands), *mandelkuchen* (Germany), *kourabiethes* (Greece), *macarons* and *amandes* (France), *polvorones* and *perrunillas* (Spain), *amaretti* (Italy). Almond flour is stored in a cool, dark place in airtight containers for up to one year [38]. Almond flour can also be used in the preparation of other confectionery and pas

try products, pasta, extruded products, pizza topping, pancakes, culinary products, shakes, other non-alcoholic and alcoholic beverages, etc [37-40]. This type of flour contains polyunsaturated fatty acids, which provide a certain amount of omega-3 fatty acids, which are used by nerve cells, but also help protect the heart and reduce the risk of stroke. Almonds and almond flour are an important source of magnesium, a mineral that supports the activities of the nervous system, which helps in cases of insomnia or depression but also for those suffering from fatigue or stress. Almond flour has a role in the proper management of diabetes and maintaining body weight while controlling the level of triglycerides in the blood, cancer [41].

Coconut flour contains no gluten, is a soft flour, and the production process involves first scraping the kernel (pulp) from the inside of the nuts and extracting the existing milk, which is dried in the oven at a low temperature and then ground to a fine powder. Coconut flour also falls into the category of alternative flours, as it is gluten-free and is an important source of nutrients, especially fiber and protein, contains no trans fatty acids and has a low glycemic index. Coconut flour contains 61% fiber, which is the highest percentage of dietary fiber found in any flour [44, 45] and can play an important role in controlling cholesterol and blood sugar levels, and prevent colon cancer.

Coconut flour is made from coconut which is classified as a "functional food" because it provides many health benefits beyond its nutritional content [46]. The chemical composition of coconut flour varies depending on the extraction methods that are applied to obtain coconut oil, this significantly affects the retention of components such as the amount of fat remaining in the final product. The proteins contained in coconut are classified into three fractions, namely albumins, globulins, and glutelins, with globulin being the major fraction [47]. Coconut presents high quality proteins (3-6 g/100 g), fats (36-60 g/100 g), saturated acids (36-60 g/100 g), dietary fibre (7-14 g/100 g), carbohydrates (3-11 g/100 g), vitamin B1 (0.1-1.4 mg/100 g), vitamin B2 (0.1-1.2 mg/100 g) vitamin B3 (0.3-0.6 mg/100 g), vitamin B6 (0.2-0.3 mg/100 g), vitamin C (1.5-1.7 mg/100 g) minerals such as potassium (530-542 mg/100 g), phosphorus (180-206 mg/100 g), magnesium (55-90 mg/100 g), calcium (16-26 mg/100 g), zinc (1-2 mg/100 g) and iron (1-3 mg/100 g). Through the process, most of the coconut's nutrients are found in the flour. On average, coconut flour contains 3.6% water, 3.1% minerals, 10.9% fat, 12.1% protein and 60.9% dietary fibre [45-48]. Coconut flour can be successfully used in the production of gluten-free cookies, setting the maximum optimum proportion of 45% of the total flour used in the manufacturing recipes. The obtained results indicate that the incorporation of up to a level of 45% coconut flour in the gluten-free cookies formula resulted in products with improved sensory (taste, aroma and overall acceptability) and functional properties (are rich in fiber, minerals, fats and proteins) compared to the control sample. The sensory quality is based on the taste, aroma, crispiness, appearance and overall acceptability. The overall acceptability shows sample whit 45% coconut flour was preferred among the cookies. The results obtained could be very valuable for local industries to substitute wheat partially or completely in production of snacks [48]. The use of coconut flour in products such as muffins, cakes, bread can be done by partially substituting wheat flour or rice flour up to a maximum of 50%, the products obtained having superior nutritional characteristics (high protein content, fiber), improved sensory characteristics (taste, smell, color, general acceptability) and technological characteristics: volume, porosity, elasticity, texture lower but in accordance with quality standards [45, 46, 47]. According to other studies [46], the addition of up to 20% coconut flour as a substitute for wheat flour in the manufacture of noodles did not cause significant changes in their sensory characteristics, but improved the protein and fiber content of the finished products [46]. Also, partial substitution of wheat flour with coconut flour in different proportions (10%, 20%, 30%) in the bread recipe resulted in changes in sensory and rheological characteristics, but bread with the addition of up to 20% coconut flour was accepted sensory and rheologically by the evaluators [47]. The main characteristic of coconut flour is its high degree of absorption, which makes it necessary to store coconut flour in airtight covered containers in moisture-free spaces. Because it is naturally gluten-free, coconut flour is often used in culinary preparations, but also for other pastry and confectionery products, pasta, extruded products, shakes, non-alcoholic and alcoholic beverages [49]. Coconut flour may play a role in controlling cholesterol and sugar levels in blood and prevention of colon cancer. The dietary fibers present in coconut flour are described as plant materials that produce large amounts of butyric acid, beneficial in inhibiting tumor formation in the stomach. Foods in which coconut flour is incorporated have a low glycemic index, with a role in the proper management of diabetes mellitus and maintenance of body weight while controlling blood triglyceride levels. The application of coconut flour as a functional food in food products may prevent the prevailing chronic diseases, and also inspire the food industry to produce value-added products from coconut flour. Coconut flour can also be used as fillers for emulsified products such as sausages, meat loaf and burger patties. This will lead to increment in the production of coconut and promotion of the coconut industry [46].

Acorn flour is also a gluten-free flour, obtained from the fruit of Quercus sp. by drying, maturing, milling and de-tinning. Acorns are made up of compounds comparable to that of cereals and are a rich source of carbohydrates, mainly starch (31-51 g/100 g), proteins (2-8 g/100g) and fats (0.7-9 g/100 g). The chemical composition of acorn flour varies depending on several factors, such as oak species, acorn maturity and related differences in metabolic processes. Due to their high starch content, acorns are mainly used for flour production, and acorn flour is considered as a replacement for cereal flour in a wide range of applications in food production [50]. The basic composition of acorn flour, compared with conventional cereal flours, is

distinctive primarily due to the low proportion of protein (4.3-7.5 g/100 g) and a high proportion of fat (8.5-30 g/100 g), dietary fiber (11-18 g/100 g), and ash (1.7-2.1 g/100 g),

carbohydrates (75-84 g/100 g), vitamin B1 (0.02-0.15 mg/100 g), vitamin B2 (0.13-0.15 mg/100 g) vitamin B3 (1.5-2.3 mg/100 g), vitamin B6 (0.03-0.7 mg/100 g) and minerals such as calcium (42-160 mg/100 g), phosphorus (90-102 mg/100 g), potassium (379-710 mg/100 g), magnesium (54-110 mg/100 g), zinc (0.64-0.83 mg/100 g), manganese (1.7-3.4 mg/100 g) and iron (1.2-18 mg/100 g), tannins (7.5-11 mg/100 g) [50 - 52]. In the process of obtaining acorn flour, Ozcan *et. al.* (2006) [53] identified all eight essential amino acids, including leucine (245 mg/100 g d.m.) and lysine (208 mg/100 g d.m.) occurring in the largest amounts. Among nonessential amino acids identified: histidine - 0.208 g/100 g, alanine - 0.427 g/100 g, glycine - 0.348 g/100 g, serine - 0.318 g/100 g, leucine - 0.596 g/100 g, the highest amounts were found for asparagine(696 mg/100 g) and glutamine (518 mg/100 g). The benefits resulting from the introduction of acorn flour into baking products include an increase in their nutritional value, especially observed in gluten-free products. Products made of acorn flour are characterized by a higher content of dietary fiber and mineral compounds as well as the content of total phenolic compounds and the resulting increased antioxidant activity [54, 55]. Unconventional flours are an alternative to flours traditionally used in the baking and pastry industries. Acorn flour offers various benefits, including a lack of gluten proteins, high fiber and mineral content, and antioxidant properties. However, research to date indicates a negative effect of acorn flour on the rheological characteristics of dough and the physical properties of products made with it. Therefore, in bread and pastry production, it is advisable to mix acorn flour in different proportions of 15% to 20% with wheat flour or rice flour [56], the products obtained having superior nutritional characteristics (high protein content, fibre), improved sensory characteristics (taste, odour, colour, general acceptability) and technological characteristics: lower volume, porosity, elasticity, texture but in compliance with quality standards [57]. The addition of acorn flour to gluten-free bread had a positive effect on product acceptance. The results of sensory evaluation were also dependent on the level of substitution of conventional flours with acorn flour. Most of researchers suggest that acorn flour incorporation up to 15% substantially enhance the nutritional qualities of the bakery products without significant affecting their sensory and quality properties [57]. The literature data indicates that acorn flour substitution for pastry production depends on the product type and ranges from 10 to even 60% [50, 56, 57]. Acorn flour can be used in the manufacture of various bakery products, beverages, confectionery, pasta, cookies, as a coffee substitute, etc. For example, the use of acorn flour in bakery products has led to increased shelf life [54]. Acorn flour cookies showed significantly higher content of phenolics compounds, antioxidant activity and oxidative stability than control cookies, prepared with out acorn flour. These features improved as the level of acorn flour increased. As for appearance, the acorn flour cookies were darker, larger, and more friable than control cookies. Higher levels of fermentative alcohols and esters, as well as Maillard reaction volatile compounds (particularly furans), were observed in the acorn flour cookies [58].

Storage of acorn flour is done in a cool, dark place in airtight containers for up to one year [50]. Due to its high content of fiber, vitamins and minerals, consumption of acorn flour has numerous benefits for the human body, such as: skin care, improves digestion, prevents diabetes, regulates overall cholesterol levels and prevents obesity, atherosclerosis and other dangerous conditions that threaten heart health, regulates metabolism, has a tonic effect, has a regenerative effect and prevents cancer [59, 60].

Teff flour does not contain gluten and is obtained from grinding teff kernels, it has a pleasant, dense taste, similar to peanuts and millet. Teff (*Eragrostis teff* (Zucc.) Trotter) is a nutritious cereal indigenous to Ethiopia and Eritrea. Teff has naturally higher nutritional value when compared to many other grains and doesn't need to be fortified. Teff is most often consumed as a whole grain and products derived from teff are rich in carbohydrates, amino acids, including 8 essential amino acids: lysine - 3.7 g /16 g N, isoleucine - 4.1 g /16 g N, leucine – 8.5 g /16 g N, valine – 5.5 g /16 g N, phenylalanine – 5.7 g /16 g N, tyrosine - 3.8 g /16 g N, tryptophan – 1.3 g /16 g N, threonine – 4.3 g /16 g N and in fatty acids: linolenic acid 5 g/100 g and oleic acid 2.9 g/100 g. Phytic acid content in whole grain teff was 1544 mg/100 g (dry basis) [60]. Teff is a comparatively good source of essential fatty acids, fiber, minerals (especially calcium and iron),

and phytochemicals, such as polyphenols and phytates, is composed of complex carbohydrates with slowly digestible starch. Starch is the major component of teff grain and may amount up to over 70% of the dry weight [61]. Studies have confirmed the excellent nutrient composition of teff and have shown that by using enzymes, hydrocolloids, or dough fermentation, it is possible to overcome the food processing challenges it faces when using teff as an ingredient in its preparation bread [62]. Ferulic and gallic acids, quercetin, and catechin are the major bound phenolics in brown teff, whereas ferulic acid, rutin, catechin, and quercetin are the majority in white teff [63]. The chemical composition of teff is: moisture (9 -11 g/100 g), protein (8-13 g/100g), ash (2-3 g/100 g), fat (2-3 g/100 g), dietary fibre (2-6 g/100g), carbohydrates (65-73 g/100g) and minerals such as calcium (156-160 mg/100 g), phosphorus (348-366 mg/100 g), iron (18-59 mg/100 g) [64]. Teff is also valuable because of phenolic compounds with antioxidant activity, such as ferulic acid (285.9 µg/g), protocatechuic acid (25.5 µg/g), gentisic acid (15 µg/g), vanillic acid (54.8 µg/g), syringic acid (14.9 µg/g), coumaric acid (36.9 µg/g) and cinnamic acid (46 µg/g). The major component of teff grains is starch, which can account for up to 73% of the dry matter. Most of the fatty acids in the lipid composition are unsaturated (84%), with oleic acid (32.4%) and linoleic acids (23.8%) predominating, similar to those in maize, sorghum and quinoa. The proteins present in teff are the glytelins (44.55%) and albumins (36.6%), followed by prolamins (11.8%) and globulins (6.7%) [65]. Chemical composition of teff flours is: moisture (10 -11 g/100 g), protein (9-11g/100g), ash (2.6-3.5 g/100 g), fat (2.6-3.2 g/100 g), fibre (2-3 g/100g), carbohydrates (83-85 g/100g) and minerals such as calcium (154-156 mg/100 g), phosphorus (361-366 mg/100 g), iron (8-9 mg/100 g), potassium (379-382 mg/100 g), magnesium (168-170 mg/100 g), zinc (4-4.5 mg/100 g), manganese (3-4 mg/100 g), sodium (5-6 mg/100 g), copper (0.9-1 mg/100 g), chloride (46-48 mg/100 g), vitamin B1 (0.50-0.55 mg/100 g), vitamin B2 (<0.1 mg/100 g) vitamin B3 (0.8-1 mg/100 g), vitamin B6 (<0.1 mg/100 g), vitamin B9 (<0.02 mg/100 g), vitamin C (0.25-0.30 mg/100 g) [64 - 68]. Recently, the use of teff in food systems is gaining popularity as both a naturally gluten-free alternative to wheat products and a nutrient-rich ingredient in the baby food industry. Teff flour, despite it being gluten-free, has been reported to produce high-quality leavened flatbread that stales much slower than if made from other cereals, in particular sorghum, which is commonly used to produce gluten-free baked goods and traditional flatbreads [69]. As with the gluten-free flours presented in this study, teff flour must also be mixed with other types of traditional flours (e.g. wheat flour or rice flour) in order to be used in bakery and pastry recipes, thus preventing a number of defects (low volume, low porosity, unpleasant flavour, dark colour) of the finished products. Teff flour can be used to make gluten-free cookies in a proportion of up to 25% of the total ingredients used in the recipe compared to rice flour [70]. Compared to control cookies, cookies with teff flour exhibited decreased heights, weights and spreads. Texture analysis of the cookies done showed teff flour substitutions to have decreased hardness, and initial stiffness compared to control cookies. Sensory analysis showed no significant difference in flavor, taste, and appearance between the control and the teff flour cookies, control cookies and those with 25% teff flour were preferred [70]. Regarding the use of teff flour in the production of gluten-free muffins, a number of studies [71] have been carried out on some physical, textural and sensory measurements. The substitution ratios of rice flour with teff flour studied were: 100:0%, 75:25%, 50:50% and 25:75%. In terms of muffin sizes, a decrease in muffin height was observed as the percentage of added teff flour increased. Specific weight did not vary significantly in the teff flour samples, but compared to the control sample they were significantly lower. Texture measurements showed no significant differences between the 25% and 50% teff flour samples, but the 75% samples were noticeably harder. Elasticity was significantly lower in the teff flour muffins than in the 100% rice flour control sample, but there was no large variation in elasticity between them. In terms of sensory evaluation, it was observed that the highest degree of acceptance was for muffins with up to 50% added teff flour [71]. In another study [72] the physical (determination of water holding capacity, determination of stickiness, rheological properties of dough and size determination) and sensory characteristics of cookies made from teff flour and oat flour were studied in comparison with similar conventional products containing wheat. The water holding capacity was higher for cookies made with teff flour than for cookies made with wheat flour. Dough viscosity was much higher for the dough made from varying percentages of teff and oat flour compared to wheat flour.

A decrease in cookie size was observed for cookies made from teff flour blends compared to those made from wheat flour. Following this study it was determined that the optimal proportion of teff flour is 25% for the preparation of gluten-free cookies [72]. In order to determine the optimal proportion of teff flour to be used in the technology of making gluten-free bread, a series of studies were carried out [73]. The influence of the addition of teff flour (5, 10 and 20%) in different dry (from buckwheat or rice) or fresh (with *Lactobacillus helveticus*) doughs on the sensory quality of the bread samples obtained was studied. The combination of teff flour (10%) with cereal sourdough (rice or buckwheat) enhanced bread aroma. Bread sample with 20% teff flour and *Lactobacillus helveticus* showed a smaller volume. The appearance of the bread with 20% teff flour was highly appreciated by consumers, while the bread that combines 10% teff flour and rice dough was preferred in terms of flavor. The bitter taste of buckwheat dough was generally considered a negative attribute. This study highlights the great potential of teff flour (10% and 20% addition) and selected doughs to obtain gluten-free breads with targeted attributes and improved sensory profile. Gluten-free bread quality is dependent on ingredients and additives combination, but also processing can provide a way to improve bread quality. Nutritive value of the gluten-free breads must be always in mind when setting up recipes, for obtaining nutritionally balanced bread [73]. Teff flour can be used as a substitute for wheat flour and other cereals, works well in a range of recipes (bread and pasta to waffles and pizza), as well can be utilized in foods for people with celiac disease [65]. According to studies by Alaunyte *et.al.* (2012), in bread samples with 30% added teff flour, the iron content doubled [74]. Storage of teff flour must be done in a cool, dark place in airtight containers. Along with the possible health benefits in managing celiac disease, and a possible solution in preventing and controlling iron deficiency and diabetes, these all indicate the potential of teff to be a future global functional food for health promotion and disease prevention [60]. The dietary fiber in teff flour can help in the process of weight loss, good intestinal transit, detoxification, lowering blood sugar and cholesterol. Due to the bioavailability of iron in teff flour, it can be considered a very useful ingredient for patients suffering from celiac disease not only because of the lack of gluten, but also because of the increased iron content.

Teff flour contains omega-3 fatty acids that contribute to a healthy cardiovascular system. The group of B vitamins present in teff flour stimulates the metabolism to be as active as possible, helping the body to have energy and vitality [75]. Teff flour contains iron and calcium and can therefore have a positive effect on blood haemoglobin levels and bone health. Teff contains about 20 to 40% resistant starch and has a relatively low glycaemic index (GI), which can help diabetics better control their blood glucose levels. Like rice, millet and sorghum, teff can be consumed by those suffering from hypothyroidism [76, 77].

Tapioca flour does not contain gluten, is the starchy and fibrous food powder obtained from the roots of cassava plants after a wet and dry milling process, it is a very gentle flour for the intestines, it is also called cassava flour or tapioca starch. Tapioca (*Manihot esculenta*), also known as cassava, yucca or manioc, is a widely cultivated plant due to its adaptability to soil and water, and is the most important plant grown for its roots (tubers). Tapioca is the third most important food staple after rice and maize in tropical and subtropical countries. It is native to South America, in the Amazon region. Currently, Africa produces the largest quantity of tapioca in the world, in countries such as Nigeria (35% of the African continent's production and 19% of world production), Congo, Ghana, Tanzania, Zambia, Mozambique. Almost half of tapioca production is processed to obtain flour, the difference being used in animal feed [78, 79]. Tapioca should never be eaten raw because it can be toxic due to a very small amount of cyanides (cyanogenic glycosides) that can be found in the cassava root, but by boiling, this toxic potential disappears [80]. Tapioca does not contain saturated fat or protein and is not rich in vitamins, but it is particularly nutritious, and a 100 g of the product has 358 calories and a significant amount of iron (9% of the daily requirement), in addition to calcium, folic acid (vitamin B9), phosphorus, potassium, zinc or magnesium, adding omega-3 and omega-6 acids [81]. Tapioca flour has the following average chemical composition: moisture (7 -12 g/100 g), protein (0.60-2.6 g/100g), ash (0.55-2.4 g/100 g), fat (0.2-0.6 g/100 g), fibre (0.4-2.3 g/100g), carbohydrates (80-85 g/100g), vitamin C (20-25 mg/100 g), vitamin B9 (30-40 mg/100 g) and minerals such as calcium (12-50 mg/100 g), phosphorus (12-40 mg/100 g), iron (1-2 mg/100 g), potassium (20-25 mg/100 g) [80, 81, 82].

The predominant component in the dry matter of tapioca flour is starch (about 75% on average). The poorer baking behaviour of tapioca flour is due to its high starch but low protein content, absence of gluten and high water absorption capacity compared to wheat flour. Tapioca flour is a very valuable ingredient for modifying the rheology of food systems, both liquid and semi-solid. It performs a wide variety of functions based on its gelling, pasting and retrogradation properties [83]. Some food manufacturers prize tapioca for its weak flavor. Delicately flavored puddings, pastry fillings, and baby food products have traditionally been prepared with tapioca starch because of its flavor advantage. Tapioca is used in food industry to improve the taste and texture and to give consistency or stickiness to many products, including confectionary, yogurt, and noodles [78]. Other food applications generally make use of tapioca starch as a thickener and stabilizer, with special emphasis on its lack of flavor contribution to food systems, allowing full and immediate detection of the flavor of the food itself. Tapioca (cassava) is a basic source of low calories or a supplement to cereal [83]. According to studies conducted by Montes *et. al.* (2015) [84] tapioca flour can be used for the development of gluten-free cookie formulas in a proportion of up to 50% compared to rice flour of the total ingredients used in the manufacturing recipe. Five formulations were prepared: 100:0%, 75:25%, 50:50%, 25:75% and 0:100% to tapioca and rice flour respectively, with the addition of brown sugar, and analyses its technological, nutritional and sensory properties. The results indicate that cookies made of tapioca and rice flours with the addition of brown sugar have technological, physicochemical, and nutritional profiles within legal standards; however, the fiber contents were below recommendations. The sensory evaluation showed good acceptance of the cookies, with average scores above 7.0. Regarding specific volume, the value of the control sample was smaller and very close to 1, meaning there was a balance between weight and volume. The cookies made using tapioca and rice flours had higher values than the control, indicating a smaller weight and a larger increase in volume after baking. The elasticity and gumminess profiles did not differ significantly among the formulations. The cookies formulations displayed very similar hardness values. The sensory evaluation was conducted only for samples 75:25% and 50:50% because these formulations showed better technological profiles. For the scent, color, texture, flavor attributes and overall evaluation, the mean values of formulation 75:25% were significantly higher than those for formulation 50:50%. This predilection may be related to the sample 75:25% which has more tapioca flour (75%) than sample C (50%) and presentation more flavorful [84]. In another study [85] the physical characteristics (specific volume, weight loss percentage) and textural (firmness, elasticity and firmness recovery) were analyzed. The optimum bread selected, the bread with highest levels of fat and soybean flour and one egg, presented low values of firmness and elasticity (>65%) and the lowest variation of these parameters with storage. Overall acceptability of this bread was 84% for habitual consumers of wheat bread and 100% by celiac people. Therefore, tapioca starch-based breads with spongy crumb, high volume and a good sensory acceptance were obtained (sample bread with 80% tapioca starch and 20% corn flour). This study determined that the optimum proportion of tapioca starch is 80% for the preparation of gluten-free bread [85]. Tapioca flour is also used to make pastry and confectionery products, pasta, crisps, expanded and extruded products, sugar products, starch, ethyl alcohol, various beverages, and even dry yeast [86]. Tapioca flour has beneficial effects on the human body when consumed frequently and in balanced portions. Among the most important are the following: it gives energy and a prolonged feeling of satiety due to its high carbohydrate content, due to its high glycemic index it is recommended for daily consumption as part of a balanced diet for people with hypoglycemia, it is an easily digestible food, it can be a good adjuvant in the medical recovery of people who have undergone surgery, prolonged illness or have had nutritional disorders, it does not contain cholesterol, it facilitates blood circulation and reduces blood pressure, it has antibacterial and healing properties for the human body [87-90].

4. Conclusions

Gluten-free products are finding an increased demand since the incidence of celiac disease or other gluten-associated allergies. The replacement of gluten becomes a necessity to avoid the occurrence of any such disorder. Consumers, food manufacturers and health professionals are uniquely influenced by the growing popularity of the gluten-free diet.

Consumer expectations have urged the food industry to continuously adjust and improve the formulations and processing techniques used in gluten-free product manufacturing. Production of gluten-free products thus is possible by the application of functional ingredients like starches, alternatives flours, hydrocolloids, fibers, proteins, and enzymes, improving them nutritionally as well as functionally. Health experts have been interested in the nutritional adequacy of the diet, as well as its effectiveness in managing gluten-related disorders and other conditions. This review provides an overview of the latest advances in formulating gluten-free bakery and pastry products using unconventional raw materials new, as well as the technological and nutritional challenges in using these flours.

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