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REVIEW

Non-traditional flours: frontiers between ancestral heritage and innovation

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Renewed interest in under-utilized plant species that can be used for obtaining flour mainly arises from the finding and promotion of nutritionally relevant attributes. These products can also gain value as functional foods and ingredients. Although they are often presented as new crops and raw materials, they have been used by local populations in traditional ways for many centuries. Their innovation is rather related to the ways in which old and new uses are being readdressed. The present work summarizes recent information about production, chemical composition, nutritional and functional components and health benefits of non-traditional flours. Amongst the most representative groups, pseudocereals, roots and tubers, and leguminous flours are included. Since non-traditional flours or other derivatives could contain relatively high amounts of antinutritional factors that also have health implications, related information about this subject is included.

Introduction

The nutrition of humankind is mostly reliant on two dozen crops, with rice, wheat and maize contributing some 60% of the total caloric intake.[1] The production of these worldwide crops corresponds to economies of scale and implies the use of high yielding varieties, constantly improved agronomical practices, and post-harvest technologies, which lead to reducing production costs and the availability of less expensive foodstuffs.[1]

Cereal grains are at the head of this process of dietary sources concentration. The flour milling industry is the main destination of wheat and rye because these grains are the key cereals used for bread production. Maize, oat, barley and rice are used in flour production in relatively lesser quantities. Wheat flour – the most important product of wheat milling – is used in the baking and confectionary industries and for home cooking.[2] In 2007/2008

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the global flour trade reached a record high of 11.5 million tons on a wave of high cereal prices. World trade in wheat flour has accounted for 6–8% of total world wheat trade.[2]

The food supply relying on relatively few crops has eroded the competitiveness of minor or heritage crops, some of these being pushed into mere subsistence uses or even disappearing.[1] Interest in neglected and under-utilized species (NUS) arises from a variety of factors, including their contribution to agricultural diversification and improvement in the use of land, their economic potential and the opportunity that they provide for diet diversification.[3] NUS are often presented as new species though they have been used by local populations in traditional ways for many centuries. Their innovation is thus not related to their introduction to new areas but rather to the ways in which old and new uses are being readdressed.[3]

According to Hermann,[1] and Hermann & Heller,[4] recent years have seen interesting examples of plant foods re-gaining ground in production systems and markets, such as 'minor millets' in India, Andean grains, and Andean roots and tubers. Much of the new interest in NUS has been stimulated by the finding and promotion of nutritional relevant attributes.

In the development and formulation of new products, nutritional concerns have played an important role for the food industry, particularly in the expansion of the so-called "functional foods". Functional foods are commonly defined as foods or their ingredients that provide an extra physiological benefit further than their contribution to basic nutrition.[5] In keeping with this definition, even certain conventional foods, such as fruits and vegetables, can be considered functional products, since they are rich in fibre and bioactive phytochemicals.[5] The European Commission Concerted Action on Functional Food Science in Europe regards a food as functional if it is satisfactorily demonstrated to beneficially affect one or more target functions in the body, beyond adequate nutritional effects, in a way that is relevant to either an improved state of health and well-being and/or a reduction of risk of disease.[6] Functional foods include conventional, modified (*i.e.* fortified, enriched, or enhanced), medical foods, and foods for special dietary use.[6] Some selected examples for the last category include: infant, hypoallergenic (such as gluten-free, lactose-free) and weight-loss foods. A number of functional products are intended for people with specific health problems, such as cardiovascular disease, hypertension, diabetes, morbid obesity and gluten intolerance.[7]

Coeliac disease is estimated to affect approximately 1% of the population in Europe, North and South America, North Africa and the Indian subcontinent. Gliadins (part of the gluten proteins) trigger coeliac disease and are also the major allergens in wheat allergy. Coeliac disease is thus an important public health issue. Treatment of both coeliac disease and wheat allergy relies on avoidance of wheat, rye and barley proteins.

In order to develop gluten-free breads for coeliac patients, a number of alternative flour types to wheat flour, such as corn, cassava, rice, soybean and chickpea, have been used, as well as several formulations based on gluten-free starches and/or flours with some added hydrocolloids (*e.g.* pectins or guar gum) and enzymes, such as transglutaminase.[8] Likewise, attention must be paid to the long term dietary habits and foods choices of coeliac patients subjected to a strict gluten-free diet, since results from a number of studies indicate an unbalanced intake of carbohydrates, protein, and fat, as well as limited intake of certain essential nutrients in coeliac subjects compared with controls.[9] Thus, non-conventional flours are gaining protagonism in the production of bread for coeliac sprue-affected people beyond constituting ingredients in some traditional regional recipes.[10] A large number of non-traditional flours can be mentioned, varying in their botanical origin, dissemination of use and economic relevance. Amongst the most representative groups, pseudocereals, roots and tubers, and leguminous flours are included. Data related to the global production of the major raw materials are presented in Table 1.

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Pseudocereals flours

In botanical terms, amaranth, quinoa and buckwheat are dicotyledonous plants. They are referred to as *pseudocereals*, as their seeds resemble in function and composition those of the true cereals, which are monocotyledonous species.[9] According to Borneo & León,[11] the American Association of Cereal Chemists International Whole Grains Task Force broadened the definition of whole grains to include pseudocereals in 2006, since they have an overall macronutrient composition similar to that of cereals.

Table 1 World production (tonnes) in 2009 for major non-traditional flour raw materials. Source: FAOSTAT | © FAO Statistics Division 2011

Item	Production (tonnes)
Roots and Tubers (Total)	735 807 453
Potatoes	329 581 307
Cassava	233 795 973
Sweet Potatoes	102 297 894
Yams	49 183 219
Taro (cocoyam)	11 312 073
Buckwheat	1 787 547
Quinoa	69 020
Soybeans	223 184 884
Chickpeas	10 461 215
Lentils	3 917 923

Amaranth (*Amaranthus* sp.) is an ancient crop consumed as vegetable and grain during the Mayan and Aztec periods; the Spanish conquerors called amaranth "the Inca wheat".[12] Seeds more than 2000 years old have been found in ancient tombs.[13] Nowadays, there are three species of amaranth grown for grain production: *A. hypochondriacus*, *A. cruentus* and *A. caudatus*. Although the three species are native to America, they are also currently distributed in Asia and Africa. In the Americas, *A. hypocondriacus* is sited primarily in northern and central Mexico, *A. cruentus* in southern Mexico and Central America and *A. caudatus* in the Andes, though there are cultivated areas in countries such as Argentina.[12] Amaranth has gained interest as a potential functional food due to the cholesterol-lowering effect reported in laboratory animals.[14,15]

The chemical composition of amaranth cultivated species has been determined by various authors (Table 2). The main components correspond to carbohydrates followed by protein, fibre, lipids, and ash. In particular, the revalorization of this pseudocereal relies on its contents of protein and fat, which are relatively higher than those found in cereals (Table 2). Repo-Carrasco-Valencia *et al.*[13] pointed out that *A. caudatus* can be considered a very nutritive product when compared with wheat, barley and corn since it has a significant content of high-quality protein and constitutes a source of dietary fibre and other bioactive compounds, such as phenolics. Authors evaluated the protein digestibility *in vitro* of crude and extruded *A. caudatus* grains (varieties Oscar Blanco and Centenario). Results showed that Oscar Blanco had a higher value of digestibility *in vitro* than Centenario (80.1 and 78.8%, respectively) and both varieties had lower digestibility than casein, used as the reference material.[13]

Amongst amaranth carbohydrates, the major fraction is represented by starch. Mono and oligosaccharides correspond to only small quantities.[12] Repo-Carrasco-Valencia *et al.*[13] reported that *A. caudatus* starch showed 31.3–33.4% of digestibility *in vitro*.

About 90% of amaranth total lipids corresponds to triglycerides and complex lipids (phospholipids and glycolipids). Amaranth lipids contain a high proportion of unsaturated fatty acids (70% oleic and linoleic acids, 1% α-linolenic acid) and a low fraction of saturated fatty acids (20% stearic acid), which is desirable from a nutritional point of view. In the three cultivated species of amaranth the ratio of saturated to unsaturated fatty acids is in the range 0.26–0.31.The quality of the fat is more important than the amount of the intake. In that sense, saturated fat and *trans* fat are involved in the atherogenic risk, so in the design of a healthy diet these nutrients must be replaced by complex carbohydrates or unsaturated fats, keeping the consumption of saturated fat below 10% of the total caloric intake.[16]

Marcone *et al.*[17] analysed four commonly available amaranth varieties (Amaranthus K343, RRC1011, K433, K432) and they reported the presence of three major phytosterols (μ-sitosterol, campesterol, stigmasterol) with a total sterol content (543–834 μg per 100 g) several folds higher than those found in cottonseed, peanut, olive and soybean oils. Phytosterols have been used as blood cholesterol–lowering agents for more than 50 years.[18] They have been shown to be effective and safe although several questions have arisen concerning their safety. However, at the present time and at the current level of usage, no undesirable effects have been observed.[18]

Concerning amaranth proteins, albumin, globulin and glutelin fractions were referred as the most abundant, with prolamin as the minor fraction (1.5–11%).[12] Albumins and globulins contain less glutamic acid and proline and more lysine than prolamins.[9] The amino acid composition of amaranth and the other pseudocereals proteins is well balanced, with a high content of essential amino acids (Table 3).

In the latest years the role of proteins as bioactive components has been recognized, either directly or after hydrolysis *in vivo* or *in vitro*. Fritz *et al.*[19] reported the existence of encrypted peptides

Table 2 The chemical composition of conventional and non-conventional flours

Main group	Botanical source	Moisture (%, db)[a]	Carbohydrates (%, db)	Proteins (%, db)	Lipids (%, db)	Fibre (%, db)	Ash (%, db)	References
Cereal	**Wheat**	14.2 ± 0.3	77.3 ± 1.1	11.5 ± 0.7	0.7 ± 0.1	2.2 ± 0.1	0.5 ± 0.1	43
	Corn	nd	87.6–92.5	5.18–7.82	1.56–2.42	0.42–0.62	0.19–1.63	134
	Oat	12.0 ± 0.3	62.0 ± 0.8	12.6 ± 0.8	12.3 ± 0.6	11.4 ± 0.6	1.9 ± 0.1	43
	Rice	11.9 ± 0.3	80.1 ± 1.2	5.9 ± 0.9	1.4 ± 0.1	2.4 ± 0.2	0.6 ± 0.2	43
	Rye	9.8 ± 0.3	77.5 ± 1.5	9.4 ± 0.6	1.7 ± 0.1	14.6 ± 0.6	1.5 ± 0.1	43
Pseudocereals	**Amaranth**	9.8 ± 0.2	66.2 ± 1.0	14.4 ± 0.6	5.7–7.0	9.3–20.6	3.0 ± 0.3	9,15,43
	Quinoa	9.3 ± 0.1	68.9 ± 1.2	13.0 ± 0.9	5.2–5.8	5.9 ± 0.3	0.6 ± 0.1	9,43
	Buckwheat	11.1 ± 0.4	70.6 ± 1.1	10.6–12.6	2.1–3.1	10.0 ± 0.7	1.8–2.5	9,30,43
Leguminous	**Soybean**	8.2 ± 0.1	30.4 ± 0.7	37.6 ± 0.9	18.6 ± 0.9	4.2 ± 0.3	4.2 ± 0.1	43
	Chickpea	10.6 ± 0.4	48.0 ± 0.7	26.0 ± 0.8	6.0 ± 0.1	11.0 ± 0.6	2.4 ± 0.1	43
	Cowpea	9.7 ± 0.1	61.8 ± 0.3	23.7 ± 0.35	1.3 ± 0.02	nd[b]	3.5 ± 0.06	135
	Split pea	nd	nd	261.4 ± 0.4	2.5 ± 0.09	13.4	2.9 ± 0.02	136
	Faba bean	nd	nd	29.0 ± 0.8	2.5 ± 0.09	7.3	3.4 ± 0.02	136
Tubers and roots	**Cassava**	4.24–13.03	81.23	1.41–4.59	0.1–0.72	0.81–2.31	1.00–2.49	51,55,137
	Ahipa	nd	88.1 ± 0.4	9.0 ± 0.4	0.39 ± 0.01	5.9 ± 0.5	2.51 ± 0.01	59
	Potato	7.2	nd	6.7	0.3	nd	2.2	138
	Sweet potato	8.67	83.94	3.48	1.27	5.26	3.45	70,72
	Yam	4.32–4.73	nd	10.2–11.3	0.3–0.29	1.44–1.49	4.68–4.92	139
	Taro	nd	36.4–77.8	2.7–5.4	0.3–0.6	0.4–1.2	4.5–5.7	79

[a] db: dry basis. [b] nd: not determined.

Table 3 The relevant contributions of amino acids of conventional and non-conventional flours

Main group	Botanical source	Relevant contribution of amino acids (μmol g^{-1}) Three major essential	Three major non-essential	References
Cereal	**Wheat**	Ile = 72; Phe + Tyr = 80; Val = 47[a]	Glu = 195.1; Arg = 83.4; Asp = 94	140,141
	Corn	Leu = 13; Phe = 4.8; Thr = 4.3	Glu = 22.6; Asp = 9.4; Ala = 8.5	142
	Oat	Leu = 76; Val = 55; Phe = 52	nd	143
	Rice	Ile = 86; Phe + Tyr = 91; Val = 58	Glu = 20.8; Asp = 10.7; Arg = 8.2	140,142
	Barley	Leu = 98.2; Phe = 56.1; Val = 49	Glu = 261.2; Asp = 62.5; Arg = 50.1	141
Pseudocereals	**Amaranth**	Phe + Tyr = 73; Leu = 57; Lys = 55	nd	144
	Quinoa	Leu = 59.5; Lys = 54.2; Val = 42.1	Glu = 132.1; Asp = 80.3; Arg = 77.3	141
	Buckwheat	Leu = 6.92; Lys = 5.84; Val = 5.23	Glu = 17.6; Asp = 10.2; Arg = 9.91	30
Leguminous	**Soybean**	Leu = 7.9; Lys = 6.3; Phe = 5.3	Glu = 151; Asp = 136.3; Arg = 69.5	141,145
	Pea	Leu = 4.76; Lys = 4.31; Val = 2.98[a]	Glu = 10.3; Asp = 3.28; Ala = 3.26[a]	146
	Cowpea	Leu = 1.84; Lys = 1.66; Phe = 1.38[b]	Glu = 4.29; Asp = 2.76; Arg = 1.69[b]	135
Tubers and roots	**Cassava**	Lys = 56; Leu = 44	nd	147
	P. erosus	Hys = 2.58; Leu = 2.13; Ile = 1.75	Glu = 13.6; Gly = 4.15; Ser = 2.13	64
	Potato	Val = 9.45; Leu = 7.15; Tyr = 6.23	Asp = 15.16; Glu = 13.6; Ala = 7.56	64
	Sweet potato	Val = 11.25; Leu = 10.15; Ile = 6.75	Asp = 23.25; Glu = 10.95; Ala = 10.5	64

[a] =expressed as g per 100 g protein. [b] =expressed as g per 100 g sample.

showing antihypertensive activity in *Amaranthus mantegazzianus* proteins. Authors pointed out that hydrolysates with hydrolysis degrees of 45% and 65% (IC50 0.12 mg ml^{-1}, equivalent to 300–600 μM) exhibited an angiotensin-I converting enzyme 1 (ACE) inhibitory activity equal or higher than the potential inhibitory of the common antihypertensive peptides registered in the BIOPEP database and of semi-purified *Amaranthus hypochondriacus* albumin and globulin protein fractions.

Likewise, Orsini Delgado *et al.*[20] found that antioxidant activity increased significantly after simulated gastrointestinal digestion of amaranth proteins. Authors stated that both the protein isolates and the alcalase-hydrolysates showed potential capacity to scavenge free radicals, appearing as promising ingredients to formulate functional foods with antioxidant activity.

Referring to the cholesterol-lowering effect of amaranth protein, Mendonça[21] introduced amaranth protein isolate in the diet of hamsters with their cholesterol blood level previously increased. Protein isolate induced 30% (used as supplementation) and 51% (used as substitution) of cholesterol reduction with respect to the control (casein) that showed only a 7% reduction.

The positive effects of amaranth grains on cholesterolemia might be explained by several mechanisms, such as a diminution in the intestinal absorption of cholesterol and/or bile acids, a raise in plasma cholesterol clearance in association with enhanced hepatic LDL receptor activity, and modifications in the hepatic transformation of cholesterol.[14]

Quinoa (*Chenopodium quinoa* Willd.) is also an indigenous plant from the Andean region, cultivated by the Incas who called it "the mother grain" and considered it a sacred food. Quinoa dates from more than 5000 years ago. This seed was one of the main crops of the pre-Columbian cultures in Latin America. Quinoa is mainly produced in Bolivia although it has recently been introduced on small scale in other regions (South America, USA, Denmark).[22] Quinoa seeds represent an interesting foodstuff, owing to their high protein content (with most essential amino acids) and lack of gluten.[22,23] Quinoa chemical composition is shown in Table 2.

Compared to cereal grains, the total protein content of quinoa seeds is higher than that of barley, rice, and corn, and it is similar to that of wheat.[24] As well as in amaranth, quinoa proteins are mainly composed of albumins and globulins (chenopodin), with very little or no storage prolamin proteins, which are the toxic proteins in coeliac disease.[9,24]

Abugoch *et al.*[25] have studied some physicochemical and functional properties of quinoa protein isolates that were prepared from quinoa seeds by alkaline solubilization at pH 9 (Q9), and pH 11 (Q11) followed by isoelectric precipitation and spray drying. Authors have pointed out that Q9 and Q11 can be used as a valuable supplement for infants and children. Q9 might be used as an ingredient in nutritive beverages, and Q11 as a component in sauces, sausages, and soups.[25]

The quinoa essential amino acid range is wider than in cereals and legumes. Its proteins are principally high in lysine (5.1–6.4%), the limiting amino acid in most cereal grains[24] (Table 3).

Aluko and Monu[26] obtained active biopeptides by enzymatic hydrolysis from quinoa seed flour protein concentrate and reported that membrane fractionation of the protein hydrolysate into lower-molecular-weight peptides improved radical scavenging activity and inhibition of the angiotensin-converting enzyme activity. Functional and bioactive properties were dependent on the molecular size of peptides in the quinoa protein hydrolysates.

According to Alvarez-Jubete *et al.*,[9] quinoa lipids are characterized by a high degree of unsaturation. Linoleic acid is the predominant fatty acid (50.7–54.3% of the total) followed by oleic (20.8–24.9%) and palmitic acid (8.3–8.9%).[27] Likewise, a high α-linolenic acid (C18:3) content is found in quinoa seeds (7.7–8.4%) from the cultivars 407, Apelawa, and Pison.[27] This feature is valuable, since ω-3 polyunsaturated fatty acids (PUFAs) significantly lowered blood pressure in observational, epidemiological, and some small prospective clinical trials.[28]

With regards to the vitamins of the group B, quinoa is a good source of riboflavin, thiamine and folic acid[9,29] (Table 4). Vitamin E content in foods is relevant since it acts as an antioxidant at the cell membrane domain, protecting fatty acids of the biological

Table 4 The relevant contribution of vitamins of conventional and non-conventional flours

		Vitamin (mg per 100 g)[a]						
Main group	Botanical source	Ascorbic acid	Pyridoxine	Niacin	Thiamine	Riboflavin	Folic acid	References
Cereal	**Wheat**	nd[b]	nd	0.7	0.3	0.03	0.0135	34,147
	Corn	nd	0.332	1.8	0.3	0.1		147,148
	Oat	nd	0.119	0.961	0.763	0.139	0.056	141
	Rice	nd	0.043	1.5	0.043	0.028		147,148
	Barley	nd	0.26	4.604	0.191	0.114	0.023	141
Pseudocereals	**Amaranth**	2.8–3	nd	1–1.15	0.14–0.25	0.29–0.32	0.0706	12,34
	Quinoa	nd	0.487	1.24–1.52	0.29–0.36	0.3–0.32	0.132–0.184	34,141
	Buckwheat	nd	0.15	nd	0.28	0.14	0.0247	30,34
Leguminous	**Soybean**		0.53	nd	0.711	0.395	nd	148
	Split pea	nd	0.15	3.1	0.83	0.14	0.025	136
	Faba bean	nd	0.23	2.5	0.66	0.2	0.145	136
Tubers and roots	**Cassava**	34	nd	0.8	0.04	0.04	nd	45,149
	P. erosus	14	0.25	0.2	0.05	0.02	0.001	64
	Potato	16.28	0.35	1.56	0.03	0.048	0.005	64
	Sweet potato	28.75	0.45	0.95	0.075		0.007	64

[a] db: dry basis. [b] nd: non determined.

membranes against damage caused by free radicals content. α-Tocopherol (vitamin E) content in quinoa seeds has been reported to be 2.6–5.4 mg per 100 g dry weight.[29]

Buckwheat (*Fagopyrum esculentum* Moench) was originated in Asia and it is believed to have been cultivated in China during the fifth and sixth centuries. After some 800–900 years, it was introduced into Europe and in the XVII century buckwheat arrived in North America.[9] Two types of buckwheat are used worldwide: the common buckwheat (*F. esculentum*) and the tartary buckwheat (*F. tataricum*), distributed in different regions. According to Bonafaccia *et al.*,[30] common buckwheat is usually grown in Europe, USA, Canada, Brazil, South Africa, Australia, Japan, Korea, central and northern China. Tartary buckwheat can be found in the mountainous regions of southwest China, most frequently grown in rough climatic conditions.[30] The major buckwheat worldwide producers in 2007 were Russia (1 004 850 tonnes) and China (800 000 tonnes).[9] Buckwheat global production in 2009 is indicated in Table 1.

Sedej *et al.*[31] have pointed out that buckwheat is a highly nutritious pseudocereal, a dietary source of protein with a desirable amino acid composition (especially rich in essential amino acids) and vitamins, starch, and dietary fibre (DF).

The chemical composition (% dry-weight basis) of common buckwheat flour is shown in Table 2. Bonafaccia *et al.*[30] pointed out that the main carbohydrate fractions were: 78.4% starch; 6.77% total DF and 0.88% soluble DF. Authors have also quantified thiamine, riboflavin, and pyridoxine content (Table 4).

Krkošková and Mrázová[32] have remarked that together with high-quality protein levels, buckwheat seeds contain several components showing health impact: flavonoids, phytosterols, fagopyrins (naphthodianthrones) and thiamin-binding proteins.

Phenolic compounds are found in abundance in buckwheat, including rutin, orientin, vitexin, quercetin, isovitexin, kaempferol-3-rutinoside, isoorientin, and catechins.[33]

Schoenlechner *et al.*,[34] have analysed pseudocereals' wholemeal flour and pointed out that they had high total folate contents, except for buckwheat, which had an amount of 24.7 mg per 100 g dm total folate. Total folate values ranged from 52–70 mg per 100 g dm in the amaranth species to 132.7 mg per 100 g dm in quinoa (Table 4).

From the technological point of view, pseudocereals may have texture and nutritional features which make them suitable for replacing, at least in part, traditional cereal-based products. In particular, buckwheat has a high concentration of DF,[35] amaranth is a source of technologically useful proteins which also have an antifungal effect,[36] and quinoa contains high nutritional quality fatty acids.[35] Pseudocereal flours have some nutritional and functional features preferable to cereal flours.[26,37,38]

Since pseudocereals are rich in minerals, DF and show antioxidant, antinflammatory, and anticarcinogenic activities,[39] their flours were used for baked goods or pastamaking[40] and in the manufacture of gluten-free foods.[35,41] Some studies[35,42] demonstrated the successful replacement of wheat flour with quinoa or amaranth flours for processing baked goods. Besides, Coda *et al.*[43] reported that the use of a blend of buckwheat, amaranth, chickpea and quinoa flours subjected to sourdough fermentation by selected γ-aminobutyric acid producing strains allowed the manufacture of bread and should be considered as a promising possibility for enhancing nutritional, functional, sensory, and technological properties of bread. Chillo *et al.*[44] developed spaghetti of amaranthus wholemeal flour enriched with quinoa, chick pea and broad bean flour and stressed that the cooking resistance of amaranthus based spaghetti was equal or inferior to those of semolina, while the instrumental stickiness has been visibly lower. The sensory analysis did not demonstrate relevant differences among the spaghetti samples.

Roots and tubers (R&T) flours

R&T constitute an important part of the food system and are consumed all around the world. However, certain species play a greater role in some regions than others. According to Opara,[45] three groups of R&T can be distinguished: a) those that are grown and utilized in large quantities in all parts of the world, such as potatoes; b) tropical crops that are staple foods in many parts of the developing regions (*e.g.* cassava, aroids, and yams); and c) several lesser-known crops such as the Andean R&T or some specialty vegetables (*e.g.* Chinese water chestnut *Eleocharis dulcis* and the Trin and New Zealand yam, *Oxalis tuberosa*). Except for potatoes, R&T are grown in warmer areas of the world. They correspond to storage organs and most of them constitute sources of carbohydrate intake.[46] R&T crops demand large storage capacity, thus processing into flour would be a suitable alternative.

Potato. Potato flour can be considered the oldest commercial processed potato product and is widely used in the baking industry. Potato flour has long been associated with the baking of bread. Small amounts of added potato solids help to retain the freshness of bread, to impart a distinctive flavour and to improve the toasting qualities.[47] Potato flour composition is shown in Table 2.

The starch content of potato flour corresponds to 63.8%, meanwhile the protein content ranges from 6–12%, which is similar to that present in common cereals.[48] Potato flour is a nourishing food but an increase in its protein content could be desirable for use in combination with other protein rich sources. Gahlawat and Sehgal[48] reported that the *in vitro* digestibility of potato flour protein was 73.3% and this value was significantly higher than that of raw potatoes. Likewise, starch digestibility of raw potato was 105.54 mg maltose released per gram, which significantly increased to 112.85 mg maltose released per gram in the developed potato flour.[48]

Potatoes are a rich source of free asparagine (2010–4250 mg kg^{-1})[49] and reducing sugars (97–2550 mg kg^{-1}).[50]

Cassava. Cassava (*Manihot esculenta* Crantz) is a relatively highly perishable, starchy root crop, which starts to deteriorate after harvest if not processed. Processing is undertaken primarily to detoxify the cassava product, to improve its palatability and to convert it into a storable form.[51]

Edible cassava flour is the product prepared from dried cassava chips or paste by a pounding, grinding or milling process, followed by sifting to separate the fibre from the flour. In the case of edible cassava flour prepared from bitter cassava (*Manihot utilissima* Pohl), detoxification is carried out by soaking the roots in water for a few days, before they undergo drying in the form of whole, pounded root (paste) or in small pieces.[52] Specific quality factors refers to moisture and hydrocyanic acid content. The specification states a maximum moisture content of 13% m/m although lower limits should be required for certain destinations in relation to the climate, duration of transport and storage. The total hydrocyanic acid content of edible cassava flour shall not exceed 10 mg kg^{-1}.[52] Cassava produces two cyanogenic glucosides, linamarin and a small amount of lotaustralin (methyl linamarin), and the enzyme linamarase that catalyses their breakdown to glucose and cyanohydrins. The cyanohydrins are decomposed spontaneously above pH 5 producing hydrogen cyanide (HCN) and a ketone.[53] In West Africa, cassava is processed predominantly by grating the peeled roots and allowing fermentation for about 3 days, followed by expression of the cyanogenic liquid and heating with stirring to give a granular, roasted product called *gari.*[53]

The amount of remaining cyanide in the flour amounts to 25–33% of that initially present for the dried product, and 12.5–16.5% for the fermented one.[54] However, if flour is wetted and left in a thin layer for 5 h at about 30 °C to allow HCN gas to escape, the total cyanide content can be reduced 3–6-fold.[53,54]

Cassava flour is mainly used in baking and confectionery products to substitute wheat flour at different levels. Other food uses include application in the manufacture of weaning foods and pasta, and the production of starch used by the food, pharmaceutical, and chemical industries.[55]

According to Shittu *et al.*,[55] starch, sugar, amylase, and the pH of cassava flour differed significantly among cassava clones. The ash, sugar, and protein contents varied slightly between 1.5–3.6%, 1.2–2.2%, and 0.8–1.9% (dry basis), respectively. The cyanogenic potential (CNP) of the flours also ranged between 0 and 38 mg kg^{-1} (dry basis). Only one clone (92/0326) gave a CNP value above the maximum level recommended for edible cassava flour.[52] The starch and amylose contents showed the highest variation, ranging from 65–88% and 13–23% (dry basis), respectively.[55]

Referring to technological aspects, cassava flour is widely used in the formulation of products, especially oriented to coeliac patients; nevertheless, the very low protein content (1.0% dry basis) and absence of gluten are considered disadvantageous for its exclusive use in food formulations, especially in those uses where elasticity of the dough is essential for product quality. Efforts have been made worldwide by the researchers, to overcome this inconvenience through the use of composite flours.[56,57] Jisha and coworkers[58] improved the nutritional and functional attributes of cassava flour through fortification with cereal (whole wheat) and/or legume flours (chick pea), bran sources (wheat and rice), and through pre-treatment with enzymes to improve the functionality and reduce the energy content. The study led to the development of cassava based composite flours with low starch digestibility, high protein content and low energy content which could be effectively utilized for developing foods for obese and diabetic people. Enhanced digestibility of pregelatinized malted flours from cassava finds potential application for the development of foods for geriatric and convalescent people.

The functionality and nutritional attributes of cassava flour could be favourably modified through pre-treatment with amylases, pregelatinization and composite flour technology incorporating cereals, legumes and bran sources. Pre-treatment with termamyl (commercial enzyme) was more effective than green gram amylase in reducing the viscosity. Significant enhancement in digestibility was achieved through pre-gelatinization. Bran sources reduced the *in vitro* starch digestibility considerably, indicating the possible use in nutrition therapy for prophylactic use in the case of obese or diabetic people and also suggesting diets for people suffering constipation.

***Pachyrhizus* spp.** Some leguminous plants from the genus *Pachyrhizus* (yam beans) produce tuberous roots. This genus is native to southern and central America. Main cultivated species of this genus are: *Pachyrhizus tuberosus*, the "Amazonian yam bean", mainly grown in Bolivia, Peru, Ecuador and Brazil; *Pachyrhizus erosus*, the "jacatupe" or "Mexican yam bean", found in Central America and the Caribbean; and *Pachyrhizus* *ahipa*, the "ahipa" or "Andean yam bean", from the Andes of Bolivia and northern Argentina.[59–62]

According to Morales-Arellano *et al.*,[63] the scarce information on many basic aspects of underutilized crops hinders their development and their rational utilization and this is the case of the yam bean plants, which were cultivated by the ancient Mayans and Aztecs several centuries ago. The Mexican jícama (*Pachyrhizus erosus*) has been rediscovered as a root crop of great economic significance. Mexican jícama tuberous roots have, on a dry weight basis, 3–5 times the protein content of other root crops, such as potato. However, these roots have been used mostly for their carbohydrate content.[63] *P. erosus* roots are used as human food and for feeding livestock and they have been judged to be of good nutritional value.[64] *P. erosus* originated in Mexico and Central America and is cultivated in Mexico, Guatemala, El Salvador, and Honduras. Its cultivation has also been introduced to different pan-tropical zones, with outstanding success in southeast Asia. Tubers are consumed raw by the local people, being considered rich in energy and easily digestible. They have a high water content, considerable amounts of carbohydrate, crude fibre and protein, and negligible lipid levels.[64]

Cantwell *et al.*[46] have analysed the phenolic compounds present in jícama (*P. erosus*) tissue, finding that the main phenolics were catechin-like compounds since their UV spectra were similar to those of (+)-catechin and (−)-epicatechin, although no simple catechins were found. When roots were transferred from 10 to 20 °C, chill-induced changes of phenolic concentrations were greatly enhanced in jícama.[46]

Nutrient analysis revealed that *P. erosus* tubers can supply potassium, sodium, phosphorus, calcium, and magnesium, together with a significant amount of ascorbic acid. Other vitamins, such as thiamine, riboflavin, pyridoxine, niacin and folic acid, were also present. Antinutrient components were detected, although their content was practically negligible.[64]

Referring to *P. ahipa*, this plant was cultivated in the past by the Incan civilisation. Ahipa production and use declined significantly since the collapse of the aboriginal cultures following the Conquest of America. Currently, ahipa production remains relatively low.[65] Ahipa flour can be considered an alternative gluten-free product, suitable for people with specific nutritional needs. Compared to other R&T, ahipa flour has a more balanced composition from a nutritional point of view, providing protein, fibre and minerals, such as potassium, calcium and iron[59] (Tables 2 and 5).

From a technological point of view, Doporto *et al.*[59] described different procedures for obtaining ahipa flour, the slicing one being selected due its simplicity and that the resulting product showed the advantages of a higher content of potassium, magnesium, calcium and protein than in the case of ahipa flour obtained by grating and pressing. The water holding capacity of ahipa flour was high, this functional property being relevant to many food applications. An additional technological advantage of ahipa flour was its low gelatinization temperature, which would be related to its low protein content with associated high melting points. The differences observed for flours obtained by different procedures in terms of α-amylase activity and swelling power (measured at temperatures above the gelatinization one) must be taken into account in relation to the specific applications.

Yacon. Yacon is a member of the Asteraceae, now recognised as *Smallanthus sonchifolius* [Poepp.& Endl.] H. Robinson. It is cultivated as a root crop in the Andes from Colombia to northwestern Argentina at altitudes between 1000 and 3500 m above sea level.

Lobo *et al.*[66] have pointed out that yacon has also been cultivated in south-eastern Brazil. The yacon underground system consists of two different types of reserve organs: the tuberous roots, *i.e.* the commercialized product; and the rhizophores, the organs of vegetative reproduction.[66] The complete system accumulates fructans and other soluble carbohydrates, such as fructose, glucose and sucrose. The tuberous roots, which are eaten either raw or cooked, are sweet and crispy. Yacon roots can also be exposed to the sun for several days, a process known as 'sunning' ('soleado' in Spanish); this treatment is intended to increase the sweetness of the roots. Alternatively, yacon roots can be dehydrated and processed into a range of convenience products. Likewise, yacon roots have been used in the development of beverages and bakery products according to their physicochemical properties.[66,67]

The storage roots contain 10–14% dry matter, mostly represented by carbohydrates. Yacon tuberous roots do not contain starch. The major proportion of carbohydrates is represented by sugar in the form of oligofructans or fructo-oligosaccharides (FOS), which are short polymers of fructose with a polymerisation degree of 3–10 fructans.

According to Graefe *et al.*,[68] the β-(2→1) bonds prevent FOS from being digested in the colon, since humans do not have the enzymes needed for their hydrolysis. Another health benefit attributed to FOS is their bifidogenic character leading to the improvement of beneficial microflora (bifidobacteria) in the colon. FOS have been considered prebiotic ingredients since they are selectively fermented by the microflora in the large intestine, modulating the composition of the natural ecosystem.[66] According to different studies carried out in animals and humans, fructans may indirectly affect the immunological function, as well as carbohydrate, lipid, and mineral metabolism due to their gastrointestinal effects.[66]

Lobo *et al.*[66] reported that caecal histology changed noticeably in rats fed with yacon flour, in association to an increase in the depth and number of total and bifurcated crypts. Likewise, yacon flour consumption significantly resulted in a positive Ca and Mg balance, leading to higher values of bone mineral retention and biomechanical properties (peak load and stiffness) when compared to the control group. Likewise, the increased number of bifurcating crypts might be related to a higher mineral absorption caused by the enlargement of the absorbing surface in the large intestine of the assayed animals.[66]

Also, hypoglycaemic properties have been reported for yacon roots and leaves.[68,69] However, these properties demand exhaustive research in order to evaluate the safety of prolonged oral consumption of yacon. In this sense, de Oliveira *et al.*[69] have studied the repeated-dose toxicity of three extracts from yacon leaves: an aqueous extract prepared as a tea infusion; an extract rich in sesquiterpene lactones; and a polar extract rich in chlorogenic acids. The authors have reported that the renal damage observed in Wistar rats was associated with increased blood glucose levels after prolonged oral administration of the yacon aqueous extract, pointing out the evidence that the

Table 5 Relevant contribution of minerals of conventional and non-conventional flours

		Significant mineral content (mg per 100 g)									
		Macro-mineral elements					Micro-mineral elements				
Main group	Botanical source	K	Na	Ca	Mg	P	Fe	Zn	Cu	Se	References
Cereal	**Wheat**	132.4	nd	28–34.8	45.5–96.4	139	1.53–3.3	0.84–1.2	nd	nd	9,150
	Corn	nd	nd	10	nd	nd	2.5	nd	nd	nd	147
	Oat	566	4	58	235	734	5.4	3.11	0.4	nd	141
	Rice	nd	nd	4	nd	nd	0.5	nd	nd	nd	147
	Barley	280	9	29	79	221	2.5	2.1	0.4	nd	141
Pseudocereals	**Amaranth**	563	23	180–244	279–342	600	9.2–53	1.6	nd	nd	9,12
	Quinoa	714–855	2.7–93	70–86	161–232	22–462	2.6–6.3	3.2–3.8	0.7–7.6	nd	141
	Buckwheat	399.4	nd	19.4	234.9	460.6	2.72	2.09	nd	nd	150
Leguminous	**Soybean**	240–246	nd	200–400	290–310	600–700	nd	nd	nd	nd	147
	Split pea	nd	nd	nd	115	495	5.4	nd	nd	nd	136
	Faba bean	nd	nd	nd	124	630	6	nd	nd	nd	136
Roots and tubers	**Cassava**	49.8	43.8	61.6	43.4	134.1	26	13.1	0.15	nd	151,152
	P. ahipa	619	20.6	109.8	42	435	4	nd	nd	nd	59
	P. erosus	172	35	16	12.9	18	1.4	0.16	0.048	0.7	64
	Potato	560	4	27	51	31	1.08	0.21	0.14	0.5	64
	Sweet potato	232	7	32	95	50	1.52	0.11	0.17	0.7	64

sesquiterpene lactones are the main toxic compounds in yacon leaves.

Sweet potato. Sweet potato (*Ipomoea batatas* Lam) is a highly nutritious vegetable, rich in calories and phytochemicals, such as β-carotene, polyphenols, ascorbic acid and dietary fibre.[70,71] Sweet potatoes are highly perishable and difficult to store and transport, especially in developing countries. Dehydrated sweet potatoes can be used for baked products (*i.e.* pancakes, cakes, flat breads, cookies, fritters), or to partially replace wheat flour in bread making.[71] Although sweet potatoes are starch sources cheaper than other crops, their preparation has several disadvantages. Discolouration is a major quality problem and arises from the enzymatic brown discolouration caused by the oxidase reaction of polyphenol groups and the non-enzymatic browning that occurs when reducing sugars condense with amino groups at high temperatures.[72,73] When sweet potatoes are processed into flour, the resulting product is more stable than the perishable fresh roots. Several uses are reported for this flour: as a thickener in soup, for the manufacture of snacks and bakery products, for the enhancing of food products through colour, flavour, natural sweetness, and nutrients.[72]

According to Ahmed *et al.*,[72] the chemical composition of sweet potato flour (on a dry basis) was as follows: moisture 6.2–8.7%, ash 3.4–3.9%, and fat content 0.6–1.3% (Table 2). The protein content in sweet potato flour is rather low, being in the range 3.3–3.7%.[72] On the other hand, this flour might make a contribution of total sugars, which can be in the range of 3.0–3.6%. Ahmed *et al.*[72] have pointed out that carbohydrate, total dietary fibre, and starch content of sweet potato flour ranged from 83.89–85.90%, 5.26–7.14% and 64.81–65.81%, respectively.

β–Carotene is a tetraterpenoid that acts as pro-vitamin A. Although its content in sweet potato varies depending mainly on cultivars and phenological stage, Ahmed *et al.*,[72] have reported β-carotene content in sweet potato flour ranging from 2.68–3.43 mg per 100 g (wet weight basis), together with the total phenolic levels from 4.03–4.59 mg per 100 g (wet weight basis). Ahmed *et al.*,[72] have pointed out that flour from unpeeled sweet potatoes had a higher total phenolic content than flour obtained from peeled sweet potatoes, related to the fact that peels are known to be high in phenolic content.

Edible aroids

Amongst tropical R&T crops are the edible aroids (taro and tannia). They are extensively grown as a staple food in many parts of Africa, America, Asia, and the Pacific Islands. These crops show especial advantages in the humid and subhumid tropics, where cereal production is not favoured.[74]

Taro (*Colocasia esculenta* L. Schott) produces underground corms that accumulate 70–80% starch with the distinctive characteristic of its small and highly digestible granules.[75] Taro corms are also rich in mucilage, reaching up to 9.1% of crude mucilage. In the Pacific, precooked taro flour is prepared by boiling slices to a soft texture, followed by drying and grinding into flour.[76]

Olajide *et al.*,[77] have performed the proximal analysis of raw and processed taro corms, finding that crude protein ranged between 6.13–7.44%; crude fibre: 3.45–3.90%; ash content: 2.63–2.93%; ether extract: 0.75–1.10%; and nitrogen free extract: 73.43–75.46%. In this work, processing consisted of soaking, cooking and fermentation. Njintang and Mbofung[78] have pointed out that taro flour had a moisture content varying from 3.5–9.9 g per 100 g on a fresh weight basis. In this case, the average protein content was 4.8 g per 100 g dry weight, slightly below the above mentioned. Total fat content was rather low, indicating that, according to the authors, taro is not a rich source of fat or fat-soluble vitamins. Conversely, the carbohydrate content of the different samples analysed was 33.4 g per 100 g. Mean ash content was 4.4 g per 100 g.

According to Njintang *et al.*,[79] taro flour can be used for the preparation of *achu*, a usually consumed paste prepared by cooking and pounding fresh taro corms. Some taro varieties with positive characteristics, such as fast cooking and low browning tendency, have been identified.[78,79]

Yams. Yams (Greater yam, *Dioscorea alata* and white yam, *D. rotundata*) are major crops of the sub-Saharan Africa. They are usually processed into pounded yam 'fufu'. Alternatively, they are used to get flour, being previously peeled, sliced and blanched in hot water, followed by sun drying and milling.[80,81] Yam crops are gaining importance in view of the health contributing phytopharmaceuticals in the roots.[81–85]

Krishnan *et al.*,[81] evaluated the effect of pre-soaking treatments on the nutritional profile and browning index of yam flours. In that work, control greater yam and white yam flour had 72.5% and 76.3% starch, respectively. Total sugars ranged from 4.59–5.43% and reducing sugar level from 1.84–3.77%. The total phenol content was 107 and 281 mg per 100 g in white and greater yam flour, respectively. Total free amino acid level was higher in greater yam (88 mg per 100 g) than in white yam flour (38 mg per 100 g). The authors have concluded that browning related to the processing of yams could be reduced using certain soaking treatments of the slices, before sun-drying and powdering for obtaining flour. In this sense, sodium metabisulfite, citric acid and acetic acid yielded greater yam and white yam flours with low browning indices.

Leguminous flours

Grain legumes include those species belonging to the family *Fabaceae* or *Leguminosae*, whose primary use is as seeds. This group includes chickpeas (*Cicer arietinum*), lentils (*Lens culinaris*), common or dry beans (*Phaseolus vulgaris*), horse, field, fava or broad beans (*Vicia faba*) and peas (*Pisum sativum*). Soybean (*Glycine max L. Merr.*) and peanuts (*Arachis hypogaea*) are also important and are characterized by their high fat content (Table 2). Due to its high worldwide production, soybean and its flour derivative will be consider separately.

With regard to chemical composition, legume flours are an important source of proteins, and their contents varied significantly with the botanical origin of the flours (Table 2). Legume flours are good supplements for cereal-based products since both legume and cereal proteins are complementary in essential amino acids.[86] Cereals are deficient in the essential amino acid lysine, while legumes have a high content. On the other hand, cereal proteins complement legume proteins in the essential amino acid methionine[12,87] (Table 3).

Starch from legume flour is more slowly digested than that from cereals and its ingestion produces less abrupt changes in plasma glucose and insulin.[88] Legume seeds are also valuable sources of dietary fibre, vitamins – including folate, thiamine and riboflavin – and minerals (Table 4). Thus, they are important components of a healthy diet. However, their nutritional quality is limited by the presence of heat labile and heat-stable antinutritional factors (ANF) that exhibit undesirable physiological effects.[89]

Several studies about the industrial process of dehydration after soaking and cooking treatments have been carried out[90] in order to eliminate ANFs and improve protein digestibility from legume flours. Besides, these flours could be considered ready-to-use for special meals to specific groups of populations with mastication and/or swallowing problems. Consumption of pulses has been associated with many health benefits, including the reduction of the risk of type 2 diabetes and cardiovascular disease, as well as the prevention of the onset of various cancers.[91,92] However, legume flours remain underexploited, partially due to the presence of undesirable beany flavors.[93]

On the other hand, soybean (*Glycine max*), a legume native to Asia, has been a widely used crop for human consumption for 2000 years.[94] Modern processing includes the removal of oil by solvent extraction and the high quality residual cake is used for human and animal consumption. The grinding and sieving of the dry cake produced non defatted flour while removing the residual oils could be obtained from the defatted one, for obtaining protein concentrates and isolates.

Soy proteins are classified, based on their solubility, in albumins (water soluble) and globulins (soluble in saline solutions). The globulin fraction represents 80% of total protein. Globulins are soluble at pH > 8 and precipitate at pH 4.5 (pI). The fraction is composed of 7S and 11S globulin.[95,96] The nutritional value of soybeans and their products is given by the nutrient content and is reduced by the presence of anti-nutrients, which decrease their use. Soybean flour has a high content of lysine, compared with cereals (Table 3); however, it is limited in the sulfur amino acids cysteine and methionine. Besides, soybean flour is characterized by its significant contribution of minerals, such as Ca, Mg and P, compared to other flour sources (Table 5).

The carbohydrates present in soybeans and their derivatives are classified into soluble and insoluble. The former are mainly oligosaccharides, such as sucrose, raffinose, stachyose and verbascose and soluble polysaccharides, including FD (mainly pectin). The oligosaccharides are responsible for flatulence, and are absent in the protein concentrates and isolates. However, they can act as prebiotics, compounds that alter the balance of intestinal microflora, stimulating the growth and/or activity of beneficial microorganisms in the colon.[97] These include the disaccharides (lactulose, lactitol), oligosaccharides (galacto or fructooligosaccharides) and polysaccharides (inulin and hydrolyzed starch).

Heat treatment of soybeans and their derivatives, such as flour, increase their digestibility due not only to inactivation of antiproteases and other heat-labile anti-nutrients, but also to distortion, which make them more susceptible to digestive proteases action.[12]

The World Health Organization[98] categorizes foods that contain soy as a possible factor in decreasing the risk for cardiovascular disease. Their consumption would exert this effect through the action of some components on the metabolism of lipids, like cholesterol and triglycerides. Rosell *et al.*,[99] found that moderate consumption of soy is associated with a decrease in plasma cholesterol. Soy flour is rich in isoflavones, which are a phytochemical group of intense interest due to their association with a variety of health protective effects, including the reduction in the risk of cardiovascular disease, lowering rates of prostate, breast and colon cancers, and improving bone health among many other claims.[100] There are around 12 chemical forms of isoflavones in soybeans and soy foods. Genistein, daidzein and glycitein, which belong to the phytoestrogens, are the aglucons with three possible glucoside forms. The concentrations of these forms will vary in soy foods depending upon the type of processing that has occurred.[101,102]

Regarding some technological aspects, addition of legume flours to baked product formulations improves nutritional quality[103] increasing protein content and quality due to its high biological value; however, it affects dough characteristics and final product quality. Bloksma and Bushuk[104] attributed the observed changes to the weakening of gluten network in dough due to exogenous proteins incorporation. Likewise, Singh *et al.*[105] stressed that both proteins of legumes and cereals competed for binding water molecules, which would also affect the dough behavior.

The addition of pulses results in increased proteolytic enzyme content, affecting the rheology of pastes. Chickpea flour pastes exhibited lower peak viscosity, holding strength, breakdown, final viscosity and total setback than the wheat flour; this is likely due to their lower carbohydrate content (Table 2), and also their different protein content could affect the viscometric parameters.[106]

Likewise, wheat flour could be totally or partially substituted by chickpea flour, in the formulation of different types of cakes, resulting in softer crumb products.[107] However, in general when the substitution percentage of wheat flour by chickpea flour increased a decrease in batter density, cake volume and symmetry is observed, and thus, texture became firmer, more gummy and less cohesive.

Soy flour and its derivatives are widely used as supplements in the form of isolated protein and for the preparation of processed foods because of their high nutritional value (they are only deficient in sulfur amino acids) and good physicochemical and functional properties, *e.g.* emulsification capacity and formation of gels and foams.[94–96] Besides, soy flours have been widely used for coeliac product formulations due to its protein input, especially combined with cassava starch as well as rice starch.[108] Bread formulations containing up to 40% soy protein isolates had more protein (88%) and fat than wheat bread and showed satisfactory baking characteristics and sensorial attributes.[108]

Finally, proteins present in leguminous flours, such as legumins and vicilins, are responsible for their technological properties exhibiting emulsifying and foaming properties, as well as water and oil holding capacity.[109] In the case of pea, the heat-induced gelation property is attributed to the vicilins presents in the protein fraction. Besides, antimicrobial, antifungal and antiviral activities has been reported for vicilins of different beans.[110,111]

Antinutrients

Antinutrient or anti-nutritional factor (ANF) is the general name given to any natural or synthetic compound that interferes with the absorption of a nutrient.[112]

Most of the anti-nutritional factors known are plant secondary metabolites, which act as natural pesticides protecting plants from herbivores and pathogenic microorganisms.[113] ANFs are usually consumed in small amounts to produce severe or lethal effects, but their effects may be more acute in people whose diets are rich in vegetables or have deficient intake of some particular nutrient (especially micronutrients). In some specific cases, ANFs can also lead to life-threatening toxic reactions. Cyanogenic glycosides, for example, act as antinutrients in low doses, but in higher amounts, the cyanide released could produce fast lethal effects. Severe and fatal intoxications have been reported with bitter almond and cassava.[114–116] On the other hand, many substances considered antinutrients can also produce health benefits. In some instances, the negative effect observed in persons with restricted consumption of some nutrients may give positive results to people with overconsumption or low digestibility of these substances. In other cases ANFs are detrimental to some aspects of health and beneficial to others.

Antinutrients could be classified into three major groups:[117]

1) Antiproteins, which interfere with the utilization of proteins or aminoacids; 2) antiminerals, which impede or reduce the absorption of minerals; and 3) antivitamins, which hydrolyze or diminish the availability of vitamins.

The antiproteins most commonly found in foods are lectins and protease inhibitors. Lectins are glycoproteins capable of bounding carbohydrates with high specificity. This feature often gives them the ability to agglutinate erythrocytes of a particular human blood group, which leads them to be commonly known as "phytohemagglutins".[118]

Lectins are unaffected by the proteases present in the gastrointestinal tract of consumers thus they can bind to the glycosyl groups of the epithelial cells of the digestive tract resulting in harmful local and systemic reactions and, besides other adverse effects, interfering with nutrients absorption. Systemically, they can disrupt lipid, carbohydrate and protein metabolism.[119]

Protease inhibitors are proteins capable of interfering with the activity of some digestive proteases by binding to their active sites. Protease inhibitors can be divided into two main categories: those with high molecular weight (20–25 kDa) interfering principally with trypsin activity and those with low molecular weight (6–10 kDa) inhibiting chymotrypsin as well as trypsin at independent binding sites.[118] Trypsin inhibitors can induce pancreatic hypertrophy/hyperplasia and growth depression. Some protease inhibitors, such as those present in soybeans, kidney beans and potatoes, can also inhibit elastase, a pancreatic enzyme acting on elastin, an insoluble protein in meat.[117]

Cyanogenic glycosides can be included in the antiprotein group. Their hydrolysis leads to the production of HCN, which interferes with the respiratory chain by inhibiting cytochrome oxidase, making it a very potent poison.

Plants avoid self-poisoning by storing cyanogenic glycosides in vacuoles while the glycosidase, which catalyzes the hydrolysis of the glycoside, is present in the cytosol. If the cell is wounded the compartmentation is disrupted and the glycosidase comes into contact with the cyanogenic glycoside.[118]

At sub-lethal concentrations, chronic problems, such as a goiter, may appear as a result of a long-term consumption of cyanide.[118]

The group of antiminerals comprises phytic acid, oxalic acid, dietary fibre and gossypol. These compounds act as cation binders thus reducing the bioavailability of many minerals and essential trace elements, but they rarely have severe consequences on the health of consumers with well-balanced diets. Nevertheless, in some developing countries where the diet is rich in grains and vegetables, more acute effects could appear as response to the ingestion of large amounts of antiminerals.

Phytate, the anion released from phytic acid dissociation, is typically related to the reduction of iron availability. In the acidic condition of the stomach, phytate forms an insoluble complex with iron, impeding its combination with gastroferrium, an iron-binding protein secreted in the stomach. Iron is released in the alkaline conditions of the intestine as ferric hydroxide, which is not a bioavailable form of iron, and consequently prevents its absorption. Phytate is also involved in the precipitation of other elements, such as magnesium, zinc, copper, calcium and manganese. An important factor in the precipitation of phytates is the synergistic effect of two or more different cations, which can act together to increase the quantity of phytate that precipitates.[117] Phytate, on the other hand, has proved to have anticarcinogenic activity in cell culture and animal model assays.[120]

Oxalic acid (HOOC–COOH) can induce toxic as well as antinutritive effects, but the oxalic acid levels usually found in food, however, are no cause for concern. Besides reducing the bioavailability of calcium, the insoluble complexes of oxalate with this cation can also produce blockage of the renal tubules and development of urinary calculi.[121,122]

Negative effects of oxalic acid on calcium absorption can be predicted from the oxalate/calcium ratio of foods, so a food with an oxalate/Ca^{2+} ratio of 1 would not be a good calcium source, although it is rich in calcium. Calcium and vitamin D intake should be enhanced if large quantities of foods rich in oxalate are consumed.[117]

Dietary fibre (DF) forms the third group of antiminerals. DF is a collective term for all food components derived from plant cell walls not hydrolyzed by the human digestive tract enzymes. Although DF has well known beneficial effects on the regulation of the intestinal function, prevention of colonic disorders, and regulation of some metabolic diseases, the consumption of high amounts of DF also brings antinutritional effects. The various types of dietary fibre components have many reactive groups to which metals, amino acids, proteins, and even sugars can be bound. Diets rich in fibre can disturb Ca, Mg, Zn and P balances and considerably reduce nitrogen absorption. Carrageenans, which are highly indigestible, can decrease nitrogen absorption in about 16%.[117]

The interaction of dietary fibre with sugars does not result in a reduction of sugar absorption, but in a slow release of sugars into the bloodstream.[117]

Gossypols are antinutrients present in cotton plants, mainly in the seeds. As cottonseeds are recently gaining importance as a dietary oil and protein source, especially in tropical and subtropical countries, gossypol is gaining increasing significance as a food hazard, producing antimineral as well as antiprotein effects. It forms insoluble chelates with many essential metals, such as iron, and binds to amino acid moieties in proteins, especially to lysine. The protein binding suggests that gossypol can reduce the availability of food proteins and inactivate important enzymes.[117]

The third group of antinutrients, called antivitamins, includes the ascorbic acid oxidase, antithiamine factors and antipyridoxine factors.

Ascorbic acid oxidase mediates the oxidation of free ascorbic acid first to dehydroascorbic acid and next to diketogulonic acid, oxalic acid, and other oxidation products.[117]

Ascorbic acid oxidase occurs in many fruits and vegetables, such as pumpkins, bananas, and potatoes. The enzyme and the substrate are located in different compartments inside the plant cell. When the vegetable is cut, the compartmentalization is removed and the vitamin C content is gradually reduced. Ascorbic acid oxidase can be inhibited effectively with heat treatment.[117]

A second group of antivitamins is the antithiamine factors. They interact with vitamin B1, also known as thiamine, reducing its availability which can lead to serious neurotoxic effects. Normally, antithiamine factors are only hazardous to people whose diet is already low in thiamine. Antithiamine factors can be distinguished as thiaminases, tannins, and catechols.[117] Tannins are the most widespread antithiamine factor from vegetable origin. They are believed to be responsible for inhibition of growth in animals, and for inhibition of digestive enzymes. A study in volunteers on the effects of tannins on thiamine has shown that the tannins were responsible for thiamine destruction.[117] Besides their antinutritive activity, tannins can also reduce food palatability by the astringency associated with their interaction with salivary proteins. On the other side, condensed tannins have also been described as beneficial for health by reducing the risk of coronary diseases.[123,124]

Anti-vitamin E has been detected in isolated soy protein, and unheated soybean flour has been found to not only be deficient in Vitamin B12, but also contains a heat-labile factor that increases the requirement for this vitamin.[125,126]

Some ANFs can be classified into more than one category of antinutritive activity. Lectins, for example, besides interfering with protein absorption, reduces the assimilation of minerals and vitamins, consequently they also belong to the antimineral and antivitamin groups.[117] Tannins, as well, reduce vitamin B bioavaliability but also precipitate proteins. Other ANFs cannot be included in this classification as they have specific activities on some particular nutrients. Such is the case of saponins, since they could be considered antiproteins as they have been reported to inhibit various digestive enzymes, including trypsin and chymotrypsin, and are also known to inhibit protein degradation by forming saponin-protein complexes,[118] but their main antinutritional activity is by interaction with cholesterol, which causes hypocholesterolaemia and affects the permeability of the small intestinal mucosal cells, interfering with the active nutrient transport.[118] They also cause haemolysis of red blood cells and are toxic to rats.[127] Additionally, some particular saponins have also been demonstrated to have anti-spermal effects on human spermatozoa.[128,129] Furthermore, saponins are characterised by a bitter taste and foaming properties, which can produce undesirable characteristics in the flavour and texture of foods. Quinoa seeds contain bitter tasting saponins but they can be removed either by washing the seeds or by mechanical dehulling, since the outer seed layer shows the highest saponin content.[22] As with phytate, dietary fibre and tannins, saponins can also be beneficial, especially for persons with high levels of cholesterol in blood.

Alkaloids cannot either be included in the previous classification, as over 10 000 alkaloids with different structures are known. Alkaloids are plant secondary metabolites, mainly related to plant defence against animals and microorganisms, which can produce a wide range of negative effects on human health, including gastrointestinal and neurological disorders.[118,126,130] Examples of these toxic compounds are the glycoalkaloids, solanine and chaconine, present in potato and other *Solanum* spp.[131] which produce haemolytic activity and have toxic effects.[126]

The occurrence of ecdysteroids in quinoa was also reported.[22] Ecdysteroids are plant secondary metabolites presenting various pharmacological effects on mammals and humans, rather beneficial to human health, such as diminution of glycaemia and cholesterolaemia, and possibly the prevention of osteoporosis.[22] Ecdysteroids shows certain anabolic effects related to the prompting in protein synthesis. Due to this effect, ecdysteroids were investigated as a supplement for sportsmen and bodybuilders.[22] Studies carried out on quinoa seeds showed the presence of significant amounts (450–1300 μg g^{-1} ecdysone equivalents) of ecdysteroids, the following compounds being identified in whole seeds: 20-hydroxyecdysone (30 μg g^{-1}) as the main one, and several minor compounds (3–9 μg g^{-1}) such as makisterone A, 24-*epi*-makisterone A, 24(28)-dehydro-makisterone A, and 20,26-dihydroxyecdysone. Referring to quinoa flour, Dini *et al.*[132] reported the presence of both 20-hydroxyecdysone and kancollosterone.[22]

Nsimba *et al.*,[133] reported the presence of three new phytoecdysteroids in Chenopodium quinoa seeds, identified as 20,26-dihydroxy, 28-methyl ecdysone, 20,26-dihydroxy, 24(28)-dehydro ecdysone, and 20-hydroxyecdysone 22-glycolate. Likewise, the authors pointed out that all isolated phytoecdysteroids demonstrated a high potency to inhibit calf skin collagenase (an enzyme involved in aging skin diseases) and to chelate the iron ion. Results suggest that ecdysteroids might be considered as potent chemical agents to prevent or delay both collagenase-related skin damages and oxidative stress.[133]

Some ANFs from commonly used and underutilized flours are presented in Table 6.

Final remarks

The number of investigations carried out on under-utilized plant species that can be used for flour production mainly arises from the finding and promotion of nutritionally relevant attributes. Non-traditional flours can also gain value as functional foods and ingredients. Although they are often presented as new products, they have been used by local populations for many centuries. Their innovation is rather related to the ways in which old and new uses are being readdressed and to the fact that they can meet the needs of individuals with specific nutritional requirements. Possibly the most obvious example is that of people who suffer from gluten intolerance.

Non-traditional flours have many common functional components with most generally used flours (*e.g.* cereal flours), such as dietary fibre, inulin, glucans, resistant starch, phenolics, carotenoids, vitamins. However, many times the proportion of these components is different and allows a better adjustment to the nutritional requirements (*e.g.* a more balanced supply of essential amino acids; high levels of specific vitamins). In some cases the presence of certain individual components gives the product specific properties related to innovative uses (*e.g.* the accumulation of fructans and other soluble carbohydrates in the underground organs of yacon).

Research carried out on non-traditional flours reveals that many of them represent a source of bioactive components that are responsible for antioxidant, antihypertensive, anti-inflammatory, anticarcinogenic activities, cholesterol-lowering effects and/or hypoglycemic properties. Some of these products are mentioned as a source of prebiotics (*e.g.* soybean flour).

Table 6 Antinutritional factors present in traditional and non-traditional flours.[a]

Main group	Botanical source	ANFs						References
Cereal flours	**Wheat**	PA: 8.5–22.2	O: 67 (w)					153–156
	Corn	PA: 10.78	T: nd	TIA: 3.6				153,154,157–159
	Oat	PA: 7.44–10.1	O: 21[b] (w)					153,154,160,161
	Rice	PA: 5.52–13.48	O: 37[c] (w)					153,154,156,162
	Rye	PA: 4.52–5.67	O: 51 (w)					153,154,156,163
	Millet	PA: 7.4	T: 270–2000					154,158,162,164
	Sorghum	PA: 3.7–10.12	T: 68–830	TIA: 26.3–29.9				153,154,162,165,166
	Barley	PA: 6.32–9.7	O: 56 (w)					153,154,156,160
Pseudocereal flours	**Amaranth**	PA: 5–22.4						167
	Quinoa	PA: ∼ 10	T: nd	TIA: nd	S: presence			168
	Buckwheat	PA: 14.2	O: 269 (w)					156,169
Legume flours	**Soybean**	PA: 11.64	O: 183 (w)	ID: 5.94	TIA: 41.5	HA: 77.4		156,170,171
	Chickpea	PA: 5.20–12.1	ID: 3.84	TIA: 6.4–18.8	S: 0.5	HA: 7.89		170,172
	Cowpea	PA: 7.61–14.0	ID: 4.28	TIA: 7.0–12.2	S: 12.8	HA: 2.0		170,172
	Lupin	PA: 8.17	ID: 5.61	TIA: 1.1–2.1	S: 0.8	CG: nd		170,173
	Lentil	PA: 6.2–8.1	ID: 3.74	TIA: 5.1	S: 5.6	HA: 14.6	T: 390	170,174
	Common bean	PA: 10.8	T: 670–3240					169,175
	Pea	PA: 6.3	HA: 3120					169,171
	Pigeon pea	PA: 5.94						120
Tubers and roots flours	**Cassava**	PA: 1.09	T: 200	CG: 3–149				151,152,176,177
	Ahipa	PA: 1.02–1.74	T: 150–200	CG: nd				unpublished data
	Sweet potato	PA: 10.8	T: 250	S: presence				178,179
	Yam	PA: 0.59–1.98						180
	Taro	PA: 1.39–1.69	O: 234–411					181

[a] (w): wet basis; nd: not detected; PA: phytic acid (mg g^{-1}); O: oxalate (mg per 100 g); T: tannins (mg per 100 g); ID: insoluble dietary fibre (%); HA: hemagglutinin activity (HU mg^{-1}); TIA: trypsin inhibitor activity (TIU mg^{-1}); CG: Cyanogenic glycosides (mg HCN kg^{-1}); S: saponins (HA g^{-1}). [b] From bran. [c] Brown rice.

However, the information on bioactive compounds and effects on the physiology and metabolism of some species is still scarce (e.g. *Pachyrhizus* spp.).

The incorporation of non traditional pseudocereal flours as well as legume or R&T flours into the diet allows varying textures and flavours of pastas and breads, particularly for persons with special diets, such as coeliacs, and also enables the incorporation of various nutrients and micronutrients.

However, special care must be taken in the incorporation of flours or other derivatives from underutilized crops into the diet, as those products may have not been subjected to genetic improvement and thus they could contain high amounts of antinutritional factors. Further research must be conducted related to this subject since it has relevant health implications. Considering that certain antinutrients show beneficial or deleterous effects on the organisms depending on their concentration and the quantity of the intake, the qualitative and quantitative study of these components could provide useful information to develop new innovative uses for non-traditional flours.

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