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Resistant starch as functional ingredient: A review

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Abstract
Resistant starch (RS) refers to the portion of starch and starch products that resist digestion as they pass through the gastrointestinal tract. RS is an extremely broad and diverse range of materials and a number of different types exist. Dietary starches are important sources of energy for many human societies and it is clear that they can also make quite specific contributions to health. Resistant starch has received much attention for both its potential health benefits (similar to soluble fibre) and functional properties. Resistant starch positively influences the functioning of the digestive tract, microbial flora, the blood cholesterol level, the glycemic index and assists in the control of diabetes. Apart from the potential health benefits of resistant starch, another positive advantage is its lower impact on the sensory properties of food compared with traditional sources of fibre, as whole grains, fruits or bran. Among its desirable physicochemical properties are its swelling capacity, viscosity, gel formation and water-binding capacity, which make it useful in a variety of foods. In this review, we discuss different types of resistant starch, food sources, and potential health benefits and food applications of resistant starch.

Keywords: strach, dietary, glycemic index, health benefits

Introduction

The increase in consumer demand for high quality food products has led to a growth in the use of new technologies and ingredients. Several factors influence changes in consumer demand, including: health concerns (cholesterol, cancer, obesity, etc.), changes in demographic characteristics (ethnics, population ageing, etc.). The need for convenience, changes in distribution systems and price. As a result of these changes, interest in new products, particularly convenience oriented products prepared using new technologies. The greater awareness on the part of consumers of the relationship between a nutritious diet and health and well-being has been one of the reasons for the increase in popularity of novel food with good nutritional properties [1]. Actually, considerable importance is given to functional foods, which, in principle, apart from their basic nutritional functions, provide physiological benefits and/or reduce the risk of chronic diseases. Functional foods either contain (or add) a component with a positive health effect or eliminate a component with a negative one. One of the added components could be resistant starch (RS) [2] which is widely used as a functional ingredient, especially in foods containing high dietary fibre levels.Resistant starch definition Starch is the major source of carbohydrate in the human diet [3]. It occurs in many plant tissues as granules, usually between 1 and 100 lm in diameter, depending upon the plant source. Chemically, starches are polysaccharides composed of a-D-glucopyranosyl units linked together with a-D- (1–4) and/or a-D-(1–6) linkages, and are comprised of two molecular types: amylose, the straight chain polyglucan comprised of approximately 1000, a-D-(1–4) linked glucoses; and amylopectin, the branched glucan, comprised of approximately 4000 glucose units with branches occurring as a-D-(1–6) linkages) [4]. Two crystalline structures of starch have been identified (an ‘A’ and ‘B’ type), which contain differing proportions of amylopectin. A-type starches are found in cereals, while B-type starches are found in tubers and amylose-rich starches. A third type called ‘C-type’ appears to be a mixture of both A and B forms and is foundin legumes. In general, digestible starches are broken down (hydrolyzed) by the enzymes a-amylases, glucoamylase and sucrase–isomaltase in the small intestine to yield free glucose that is then absorbed [5]. However, not all starch in the diet is digested and absorbed in the small intestine [6]. Resistant starch refers to the portion of starch and starch products that resist digestion as they pass through the gastrointestinal tract. RS is an extremely broad and diverse range of materials and a number of different types exist (RS1–4). At present, these are mostly defined according to physical and chemical characteristics [5]. Resistant starch is the fraction of starch which is not hydrolyzed to D-glucose in the small intestine within 120 min of being consumed, but which is fermented in the colon. Many studies have shown that RS is a linear molecule of a-1,4-D-glucan, essentially derived from the retrograded Amylose fraction, and has a relatively low molecular weight (1.2 105 Da)) [6]. Resistant starch may not be digested for four reasons: (i) This compact molecular structure limits the accessibility of digestive enzymes, various amylases, and explains the resistant nature of raw starch granules [7]. The starch may not be physically bioaccessible to the digestive enzymes such as in grains, seeds or tubers. (ii) The starch granules themselves are structured in a way which prevents the digestive enzymes from breaking them down (e.g. raw potatoes, unripe bananas and high-amylose maize starch) [5]. (iii) Starch granules are disrupted by heating in an excess of water in a process commonly known as gelatinization, which renders the molecules fully accessible to digestive enzymes. Some sort of hydrated cooking operation is typical in the preparation of starchy foods for consumption, rendering the starch rapidly digestible [7]. However, if these starch gels are then cooled, they form starch crystals that are resistant to enzymes digestion. This form of 'retrograded' starch is found in small quantities (approximately 5%) in foods such as ''corn-flakes" or cooked and cooled potatoes, as used in a potato salad. (iv) Selected starches that have been chemically modified by etherisation, esterisation or cross-bonding, cannot be broken down by digestive enzymes [8]. The physical properties of resistant starch, particularly its low water-holding capacity, make it a functional ingredient that provides good handling and improves texture in the final product [9]. By careful control of the processing conditions employed, for example, the moisture content, pH, temperature, duration of heating, repeated heating–cooling cycles, etc., the content of RS may reach as much as 30%. RS is shown to improve eating qualities because of its increased expansion, enhanced crispiness, and reduced oil ''pick up" in deep-fat-fried foods, contrary to the traditional dietary fibre, which imparts a gritty texture and strong flavor [6]. In comparison with traditional fibres, such as whole grains, bran or fruit fibres [1]. RS possesses the advantage of affecting the sensory properties of the final products less, which is very positive for consumer acceptability. Resistant starch provides many technological properties, such as better appearance, texture, and mouthfeel than conventional fibres [10]. A wide range of foods has been enriched with RS including bread, cakes, muffins, pasta and battered foods [11].

Resistant starch as a component of dietary fibre

The above description of dietary fibre refers especially to nonstarch polysaccharides, resistant oligosaccharides and analogous carbohydrates. It also includes resistant starch [12]. Traditionally, in the UK, the definition of dietary fibre includes only non-starch polysaccharides and lignin, and does not include RS [12]. However, currently, naturally occurring resistant starch (such as found in whole grains, legumes, cooked and chilled pasta, potatoes and rice, unripe bananas) is considered dietary fibre, while resistant starches added to foods for health benefits are classified as functional fibre under the AACC (American Association of Cereal Chemists, 2000) [13] and NAS (National Academy of Sciences, 2002) [14] definition [13]. The increased awareness of consumers concerning the relationship between food, lifestyle and health has been one of the reasons for the popularity of food rich in fibre, so resistant starch (RS) has gained importance as a new source of dietary fibre [16]. The general behavior of RS is physiologically similar to that of soluble, fermentable fibre, like guar gum. The most common results include increased fecal bulk and lower colonic pH [17]. Additional observations suggest that resistant starch, such as soluble fibre, has a positive impact on colonic health by increasing the crypt cell production rate, or decreasing colonic epithelial atrophy in comparison with non-fibre diets. There are indications that resistant starch, like guar, a soluble fibre, influences tumorigenesis, and reduces serum cholesterol and triglycerides. Overall, since resistant starch behaves physiologically as a fibre, it should be retained in the total dietary fibre assay [7]. The recent increased interest in RS is related to its effects in the gastrointestinal tract, which in many ways are similar to these of dietary fibre. Like soluble fibre, RS is a substrate for the colonic microbiota, forming metabolites including short-chain fatty acids (SCFA), i.e. mainly acetic, propionic and butyric acid. Butyric acid is largely metabolised by the colonocyte, and is the most import energy source for the cell [18]. RS consumption has also been related to reduce postprandial glycemic and insulinemic responses, which may have beneficial implications in the management of diabetes [19]. Therefore, there is wide justification for assuming that RS behaves physiologically like fibre [15]. RS is not a cell wall component but is nutritionally more similar to NSP than to digestible starch. Of late, RS has been considered a new ingredient for creating fibre-rich foods, although one of the problems of including RS is that it does not have all the properties of soluble and insoluble fibre together [12]. Several studies have attempted to quantify the dietary intake of resistant starch in different populations. Worldwide, the dietary intake of resistant starch varies considerably. It is estimated that resistant starch intake in developing countries with highstarch consumption rates ranges from approximately 30–40 g/ day [20]. Intakes in the EU are thought to be from 3 to 6 g/day [21], and 5–7 g/day in Australia [22]. It should be noted that intakes of resistant starch in Australia are likely to be higher than in Europe, because of the commercial availability of top-selling breads, baked goods and cereals that contain ingredients high in resistant starch. Australia's Commonwealth Scientific and Industrial Research Organization (CSIRO) has recommended that the total intake of resistant starch should be around 20 g a day based on a study by [20] for good health. However, compared with current resistant starch intake rates in the UK population and elsewhere, to achieveintakes at this level would require substantial dietary changes and, indeed, may only be reached by the consumption of foods containing resistant starches as a food ingredient, rather than in the natural form. However, resistant starch could make a valuable contribution to dietary fibre intakes, as it is fermented slowly in the large bowel and is therefore tolerated better than other soluble fibres [22].

Types of resistant starch

Resistant starch has been classified into four general subtypes called RS1–RS4. The natural types of RS are frequently destroyed when processed. The manufacture of resistant starch usually involves partial acid hydrolysis and hydrothermal treatments, heating, retrogradation, extrusion cooking, chemical modification and repolymerisation [10]. The four distinct classes of RS in foods are: (1) RS1 – physically inaccessible starch, which is entrapped within whole or partly milled grains or seeds; (2) RS2 – some types of raw starch granules (such as banana and potato) and high-amylose (high-amylose corn) starches; (3) RS3 – retrograded starch (either processed from unmodified starch or resulting from food processing applications); (4) RS4 – starches that are chemically modified to obtain resistance to enzymatic digestion (such as some starch ethers, starch esters, and cross-linked starches) [3]. RS1 and RS2 represent residues of starch forms, which are digested very slowly and incompletely in the small intestine. RS1 is the term given to RS where the starch is physically inaccessible to digestion, e.g. due to the presence of intact cell walls in grains, seeds or tubers [23]. RS1 is heat stable in most normal cooking operations, which enables its use as an ingredient in a wide variety of conventional foods [15]. RS2 are native, uncooked granules of starch, such as raw potato or banana starches, whose crystallinity makes them poorly susceptible to hydrolysis [23]. RS2 describes native starch granules that are protected from digestion by the conformation or structure of the starch granule. This compact structure limits the accessibility of digestive enzymes, various amylases, and accounts for the resistant nature of RS2 such as, ungelatinized starch. In the diet, raw starch is consumed in foods like banana [15]. A particular type of RS2 is unique as it retains its structure and resistance even during the processing and preparation of many foods; this RS2 is calledhigh-amylose maize starch [24]. RS3 refers to non-granular starch-derived materials that resist digestion. RS3 forms are generally formed during the retrogradation of starch granules RS3 are retrograded starches, which may be formed in cooked foods that are kept at low or room temperature [23]. Most moistheated foods therefore contain some RS3 [12]. RS3 is of particular interest, because of its thermal stability. This allows it to be stable in most normal cooking operations, and enables its use as an ingredient in a wide variety of conventional foods. Food processing, which involve heat and moisture, in most cases destroys RS1 and RS2 but may form RS3 [25]. RS3 has shown a higher water-holding capacity than granular starch [26]. Some examples of RS3 are cooked and cooled potatoes and ‘‘corn-flakes” [24]. About 80–90% of the glucose produced by the enzymic hydrolysis of standard starch is metabolized in the human body. Most studies have indicated that 30–70% of RS is degraded to shortchain fatty acids in the colon by bacterial amylases, while the balance of the RS escapes even colonic fermentation and gets excreted in the feces. The overall digestibility of RS depends on the category and source of RS consumed. Of the total amount of RS3 present in corn and wheat, about 84% and 65%, respectively, are degraded by bacterial fermentation in the colon. Similarly, 89% RS2 from raw potato and 96% RS2 from green banana is degraded by bacterial fermentation in the colon. The degradation of RS is also affected by various food processing conditions under which RS is generated. The digestibility of RS was also found to vary per individual. This variability may be attributed to individual differences regarding enzymic responses [12]. Retrograded amylose is responsible for the generation of resistant starch RS3. According to this, the prolonged intake of an amylose-rich diet improves fasting triglyceride and cholesterol levels more than a corresponding amylopectin-rich diet [27]. In addition to the three main types of RS, chemically-modified starch has been defined as RS type 4, similar to resistant oligosaccharides and polydextrose [24]. RS4 describes a group of starches that have been chemically modified and include starches which have been etherised, esterified or cross-bonded with chemicals in such a manner as to decrease their digestibility. RS4 may be further subdivided into four subcategories according to their solubility in water and the experimental methods by which they can be analyzed [5]. RS4 can be produced by chemical modifications, such as conversion, substitution, or cross-linking, which can prevent its digestionby blocking enzyme access and forming atypical linkages such as a(1-4) and a(1-6) linkages [28]. Different sources of RS2 and RS3 of different origins and with different percentages of RS are available as commercial ingredients in the European market to be included in food. As RS4 is made up of chemically-modified starches, with a far higher number of modifications than the usual chemically-modified starches authorized in Europe, it is a novel food not yet approved by the European Union. However, RS4 is authorized in Japan [22]. In addition to the structural factors mentioned above whereby the chemical structure of starch can influence the amount of RS present, other factors intrinsic to starchy foods can affect a-amylase activity and therefore starch breakdown. These include the formation of amylose–lipid complexes, the presence of native a-amylase inhibitors and also non-starch polysaccharides, all of which can directly affect a-amylase activity. Extrinsic additives, e.g. phosphorus, may also bind to starch, making it more or less susceptible to degradation. In addition, physiological factors can affect the amount of RS in a food. Increased chewing decreases particle size (smaller particles being more easily digested in the gut), while intra-individual variations in transit time and biological factors (e.g. menstrual cycle) also affect the digestibility of starch. At present, it is not known how RS4 is affected by digestion in vivo [5].

Sources of resistant starch.

Starch, which is the major dietary source of carbohydrates, is the most abundant storage polysaccharide in plants, and occurs as granules in the chloroplast of green leaves and the amyloplast of seeds, pulses, and tubers [15]. Resistant starch is naturally found in cereal grains, seeds and in heated starch or starch-containing foods [29]. Factors that determine whether starch is resistant to digestion include the physical form of grains or seeds in which starch is located, particularly if these are whole or partially disrupted, size and type of starch granules, associations between starch and other dietary components, and cooking and food processing, especially cooking and cooling [30]. The digestibility of starch in rice and wheat is increased by milling to flour [15]. As a food ingredient, RS has a lower calorific (8 kJ/g) value compared with fully digestible starch (15 kJ/g); however, it can be incorporated into a wide range of mainstream food products such as baked products without affecting the processing properties or the overall appearance and taste of the product [31]. Unripe banana is considered the RS-richest non-processed food. Several studies have suggested that consumption of unripe bananas confers beneficial effects for human health, a fact often associated with its high resistant starch (RS) content, which ranges between 47% and 57%. Recently, the preparation of unripe banana flour was described, with 73.4% total starch content, 17.5% RS content and a dietary fibre level of 14.5%. Although banana represents an alternative source of indigestible carbohydrates, mainly RS and dietary fibre, it is important to keep in mind that, when the unripe fruit is cooked, its native RS is rendered digestible [32]. As a percentage of total starch, potato starch has the highest RS concentration and corn starch has the lowest. Raw potato starch contain 75% RS as a percentage of Total Starch (TS). Starches from tubers such as potatoes tend to exhibit B-type crystallinity patterns that are highly resistant to digestion. Amylomaize contains mostly amylose, which has been shown to lower not only digestibility but also blood insulin and glucose values in humans [33]. Whole grains are rich sources of fermentable carbohydrates including dietary fibre, resistant starch and oligosaccharides [30]. Fibre provided by the whole grain includes a substantial resistant starch component, as well as varying amounts of soluble and fermentable fibres, depending on the whole grain source [22]. RS concentrations are low for the flour group as a whole. Cereal flours display an A-type crystalline pattern, which is more readily hydrolyzed than raw cereals that are not as highly processed as flours. Therefore, cereal flours contain more RDS and SDS than RS. The nutrient profile of cereal grains and their corresponding flours vary considerably. Grain flours are made up primarily of two components: protein and starch. Cereal grains, in contrast, contain the pericarp, aleurone layers and germ portions of the grain that provide lipid and fibre, Cereal grains are processed and milled to flours, thereby altering the chemical composition of the flour compared with the cereal grain. The RS concentrations are five times higher in the cereal grains than in the flours. Prepared grain products contain moderate levels of RS (mean 9.6% as a percentage of TS). Starch in foods like spaghetti is more slowly digested because of the densely packed starch in the food [33]. Legumes are known for their high content of both soluble and insoluble dietary fibre. Pulse grains are high in RS and retain their functionality even after cooking [31]. Legume starches have higher amylose levels than cereal and pseudocereal starches [2]. Legumes has high TDF and RS concentrations (mean 36.5% and 24.7%, respectively). RS concentrations generally constituted the highest proportion of the starch fractions of legumes. Leguminous starches display a C-type pattern of crystallinity. This type of starch is more resistant to hydrolysis than that with an A-type crystallinity pattern and helps explain why legumes have high amounts of RS. Another possible reason for the higher RS concentrations in legumes could be the relationship between starch and protein. When red kidney beans are preincubated with pepsin, there is an increase in their susceptibility to amylolytic attack [33]. Cooked legumes are prone to retrograde more quickly, thereby lowering the process of digestion. Processed legumes contain significant amount of RS3. The digestibility of legume starch is much lower than that of cereal starch. The higher content of amylose in legumes, which probably leads to a higher RS content, may account for their low digestibility. High-amylose cereal starch has been shown to be digested at a significantly lower rate [34]. There is a very high diversity of the content of resistant starch in seeds of leguminous plants (from 80% to only a few percent). Nevertheless, is very important influence processing on part resistant starch. Hydrothermal processing can cause an increase or reduction in the fraction of resistant starch (depending on the parameters of processing and varieties of legumes) [35].

Beneficial physiological effects of resistant starch

RS has received much attention for both its potential health benefits and functional properties [15]. Resistant starch is one of the most abundant dietary sources of non-digestible carbohydrates [5]. and could be as important as NSP (non-starch polysaccharides) in promoting large bowel health and preventing bowel inflammatory diseases (IBD) and colorectal cancer (CRC) but has a smaller impact on lipid and glucose metabolism [5]. A number of physiological effects have been ascribed to RS, which have been proved to be beneficial for health [15]. The physiological properties of resistant starch (and hence the potential health benefit) can vary widely depending on the study design and differences in the source, type and dose of resistant starch consumed [36]. It is possible that modern processing and food consumption practices have led to lower RS consumption, which could contribute to the rise in serious large bowel disease in affluent countries. This offers opportunities for the development of new cereal cultivars and starch-based ingredients for food products that can improve public health. These products can also be applied clinically [37]. RS acts largely through its large bowel bacterial fermentation products which are, in adults, short-chain fatty acids (SCFA) but interest is increasing in its prebiotic potential. There is also increasing interest in using RS to lower the energy value and available carbohydrate content of foods. RS can also be used to enhance the fibre content of foods and is under investigation regarding its potential to accelerate the onset of satiation and to lower the glycemic response The potential of RS to enhance colonic health, and to act as a vehicle to increase the total dietary fibre content of foodstuffs, particularly those which are low in energy and/or in total carbohydrate content [5].

Conclusion

With the aim of increasing fibre intake in the diet, many fibre-enriched foods have been developed. Resistant starch (RS) is a recently recognized source of fibre and is classified as a fibre component with partial or complete fermentation in the colon, producing various beneficial effects on health. RS also offers an exciting new potential as a food ingredient. As a functional fibre, its fine particles and bland taste make the formulation of a number of food products possible with better consumer acceptability and greater palatability than those made with traditional fibres. Technically, it is possible to increase the RS content in foods by modifying the processing conditions such as pH, heating temperature and time, the number of heating and cooling cycles, freezing, and drying. RS shows improved crispness and expansion in certain products, which have better mouthfeel, color and flavor than products produced with traditional insoluble fibres.

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