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Dietary carbohydrates: classification by chemistry and physiology

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Food carbohydrates consist of mono-, di-, oligo- and polysaccharides, the latter composed of starch and non-starch polysaccharides (NSP). The glycaemic response to both sugars and starches is dependent on the types of sugars present and the form of the starches, and 'complex carbohydrates' do not necessarily produce slower or lower glycaemic responses than the sugars. Carbohydrates not absorbed in the small intestine are fermented more or less extensively by the large intestinal microflora. There is a fundamental difference nutritionally between digestible and undigestible ('unavailable') carbohydrates. NSP, resistant starch (RS) and oligosaccharides are the main forms of undigestible carbohydrates. Dietary fibre is generally conceived as more or less synonymous with 'unavailable' carbohydrates. The nutritional effects of dietary fibre are related to its undigestibility in the small intestine, and to the physical and chemical properties of its constituent polysaccharides. Food structures built of dietary fibre as plant cell-walls, and also of other food components, are increasingly recognized as nutritionally important. Food databases should include as much specific and detailed information as possible on food carbohydrates. For food labelling, carbohydrates have to be divided into a number of nutritionally meaningful classes. A first classification should then aim at differentiating the digestible and undigestible carbohydrates, i.e. dietary fibre. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Whereas recommendations to increase the intake of carbohydrates in Western diets (Anonymous, 1990*a*) were originally a consequence of the recommendations to decrease the fat intake and keep the protein intake unchanged, the specific nutritional importance of different food carbohydrates has recently received increasing attention. The dietary fibre concept has revived and developed the interest in 'unavailable' carbohydrates, a concept first introduced the 1920s (McCance & Lawrence, 1929).

There is now evidence that dietary fibre has a number of beneficial effects related to its undigestibility in the small intestine. Main effects are exerted in the large intestine. Owing to physical properties, dietary fibre polysaccharides also influence digestion and absorption processes in the small intestine (for review, see e.g. Schweizer & Edwards, 1992; Cherbut *et al.*, 1995). Recommendations regarding dietary fibre intake (for review see Anonymous, 1990*a*) are based primarily on effects on the large intestinal function and faecal bulk. Originally, the dietary fibre concept focused on the plant cell-wall as the main source of undigestible material, but recently resistant starch and oligosaccharides have emerged as other important sources of fermentation substrates for the large intestinal microflora.

Starch—the only quantitatively important digestible polysaccharide—has long been regarded as nutritionally superior to low-molecular weight carbohydrates or 'sugars'. This was based on the assumption that starch is more slowly digested and absorbed than sugars. The importance of the blood glucose response after a meal, often expressed as the glycaemic index (GI), has been increasingly documented. In maturity onset diabetes, low GI foods improve the metabolic control (for review see Brand Miller, 1994) and a number of potential advantages of low GI foods in general are currently being explored (for review see Truswell, 1992). Such conceivable advantages include longer satiety, lower blood pressure and lower plasma low density lipoprotein (LDL)-cholesterol levels related to the less pronounced insulin response to low GI foods. Simultaneously, starch has been shown to elicit highly variable glycaemic responses owing to the origin and treatment of the starch, and to food properties such as gross and cellular structure, soluble gel-forming types of dietary fibre, and organic acids (for review see Björck *et al.*, 1994). Sugars also give variable glycaemic response, mainly related to the very low GI of fructose (Wolever & Brand Miller, 1995). These developments have profoundly challenged the usefulness of the 'complex carbohydrates' concept in relation to glycaemic response.

Table 1. Main food carbohydrates and their digestibility in the small intestine

	Monomers	Digestibility
Monosaccharides		
Glucose		+
Fructose		+[1]
Galactose		+
Disaccharides		
Sucose	glucose, fructose	+[2]
Lactose	glucose, galactose	+[2]
Oligosaccharides		
α-Galactosides, e.g. raffinose, etc.	galactose, glucose, fructose	—
Fructooligosaccharides	fructose, glucose	—
Maltooligosaccharides	glucose	+
Polysaccharides		
Starch		
amylose, amylopectin, modified starches	glucose	+, (−)[3]
Non-starch polysaccharides		
cellulose	glucose	
hemicelluloses, pectins, β-glucans, gums, mucilages, algal polysaccharides	galactose, glucose, mannose, arabinose, xylose, rhamnose, uronic acids	—
fructans	fructose	
'New' carbohydrate food ingredients		
Inulin	fructose	—
Polydextrose	glucose	—
Polyols	various sugar	(+)
	alcohols	(−)
Pyrodextrins	glucose	—

[1]Limited in some individuals when ingested without glucose.
[2]Except in disaccharidase deficiency.
[3]Resistant starch is undigestible.

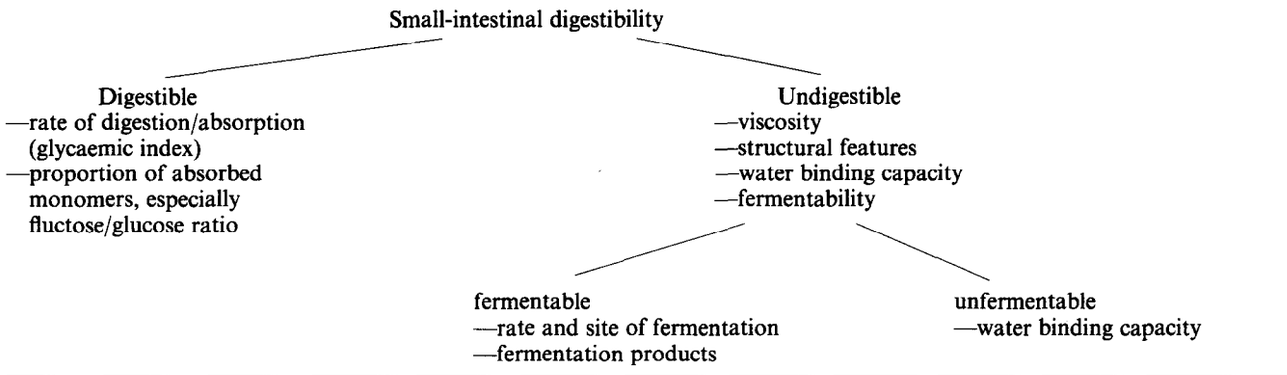
CLASSIFICATION BY CHEMISTRY

The quantitatively most important food carbohydrates are listed in Table 1. By convention, polysaccharides are defined as having 10 or more monomeric residues (International Union of Pure and Applied Chemistry, IUPAC). The low-molecular weight carbohydrates, often referred to as 'sugars', consist of mono-, di- and oligosaccharides, the latter having between three and nine monomeric residues. Nutritionally, sugars usually mean mono- and disaccharides. Glucose and fructose are the principal dietary monosaccharides derived mainly from fruits, berries and sweeted drinks, whereas free galactose is rare, except in fermented milk products. Sucrose and lactose are the main disaccharides, maltose occurring mainly in glucose syrups. The main forms of oligosaccharides are the raffinose series of α-galactosides, fructo-oligosaccharides from vegetables and malto-oligosaccharides especially from starch hydrolysates (for review, see e.g. Southgate, 1995).

The polysaccharides can be divided into starches, which are linear (amylose) or branched (amylopectin) homopolymers of glucose with α-glucosidic bonds (α-glucans), and non-starch polysaccharides (NSP). NSP consist of cellulose, which is a linear β-glucan, and a range of heteropolysaccharides without α-glucosidic linkages. Plant cell-walls are the main source of dietary NSP. The non-cellulosic NSP can be classified according to many different criteria, for example neutral (containing mainly neutral sugar residues), acidic (containing mainly uronic acid residues, also referred to as pectic substances) and hemicellulose A, B and C depending on solubility at various pH. Gums and mucilages naturally occurring in some plant foods, and used as polysaccharide food additives, contribute to the dietary intake of NSP. The relative proportions of main monomeric residues, i.e. rhamnose, xylose, arabinose, galactose, glucose, mannose and uronic acids, is another common way to characterize and name food polysaccharides, for example arabinoxylans, galactans, galactomannans, rhamnogalacturonans, etc.

A number of more recently introduced carbohydrate food ingredients, such as maltose and dextrins from glucose syrups, inulin, polydextrose, various oligosaccharides, polyols and starches that are modified

Table 2. Physiologically important properties of food carbohydrates



chemically or physically, have also to be considered in classification and analysis of food carbohydrates.

CLASSIFICATION BY PHYSIOLOGY

The following properties of food carbohydrates are of major importance for their nutritional effects (Table 2).

1. The extent of absorption in the small intestine, determining the proportion of the carbohydrate that will provide carbohydrate substrate to body cells and fermentation substrate to the large intestinal microflora, respectively.
2. The rate of absorption in the small intestine, determining the blood glucose (glycaemic index) and thereby the metabolic response related not the least to the insulin response.
3. The relative proportions of absorbed monomers, especially the fructose/glucose ratio, as fructose is metabolized differently and independently of insulin. Furthermore, some individuals have a limited capacity to absorb fructose, which may also have specific effects on plasma triglyceride levels.
4. The extent and rate of colonic fermentation, and the nature and proportions of fermentation products. The main fermentation products are the short-chain fatty acids acetate, propionate and butyrate. All contribute to the lowering of the pH in the large intestinal content, decreasing the formation and solubility of co-carcinogenic bile salt derivatives. Butyrate has specific effects as a main source of energy of colonic epithelial cells, with tumour preventive properties. Propionate and acetate are absorbed from the colon, excerting effects on lipid and probably also on carbohydrate metabolism.
5. The extent and rate of fermentation by dental plaque bacteria. Both sugars and starch can be fermented in dental plaques resulting in a drop in pH and thereby in the potential carcinogenicity.

As shown in Tables 1 and 2, the chemical and physiological classifications of carbohydrates do not coincide. Both oligosaccharides and polysaccharides may be undigestible in the small intestine. Starch is a polysaccharide and the quantitatively most important digestible carbohydrate in most diets, but a fraction of the starch (RS) contributes, together with the non-starch polysaccharides and oligosaccharides, to the undigestible carbohydrate fraction. Whereas polysaccharides ('complex carbohydrates') were previously regarded as being more slowly absorbed than sugars, starchy foods are found in the whole range from low to high glycaemic index foods. Fructose, a monosaccharide, gives a very low glycaemic response, and sucrose a lower response than the most easily available forms of starch.

The physiological properties of dietary fibre in terms of hypoglycaemic and hypolipidaemic properties, as well as fermentability and proportions of fermentation products, is poorly predictable from the monomeric composition of the dietary fibre constituents. Such properties are more related to physical characteristics such as solubility and viscosity.

ANALYTICAL CONSIDERATIONS

Mono-, di- and oligosaccharides, including polyols, can be analysed specifically by enzymatic or HPLC methods that are used in most food analysing laboratories. Depending on the food matrix to be analysed, extraction of the low molecular-weight carbohydrates in aqueous ethanol, usually 80% (v/v), may be advisable before analysis (Greenfield & Southgate, 1992).

Precipitation at about 80% alcohol concentration is also used to recover soluble non-starch polysaccharides in dietary fibre analysis. Polysaccharides are usually defined as having 10 or more monomeric units, but it should be noted that the solubility of polysaccharides is much dependent upon the molecular structure. For instance, arabans in sugar beet fibre are soluble in 80% ethanol in spite of a considerably higher degree of polymerization (Asp, 1990).

Starch in foods is usually analysed as glucose liberated after enzymatic hydrolysis. Combinations of α-amylase and amyloglucosidase ensure complete hydrolysis. A heat-stable α-amylase in a combined gelatinization and

hydrolysis step, followed by an amyloglucosidase step, is used, for example, in the method of Holm *et al.* (1986).

Resistant starch (RS) is defined as starch and products of starch degradation not absorbed in the small intestine (Englyst & Cummings, 1990; Asp, 1992). Originally this starch fraction was discovered as a component of dietary fibre that could be removed by solubilization with potassium hydroxide or dimethylsulphoxide prior to the starch hydrolysis steps (Englyst *et al.*, 1982) or determined in the residue prepared for gravimetric dietary fibre analysis (Johansson *et al.*, 1984). With the now generally accepted definition mentioned above, RS determination methods have to simulate the normal digestion of starch in the gastrointestinal tract. The quite different forms of RS that have now been identified should be included, that is, in the first instance physically enclosed starch, resistant starch granules in raw or incompletely gelatinized foods and retrograded amylose (RS 1, 2 and 3; Englyst & Cummings, 1990). Chemically and thermally modified food starches may also add to the total RS content of foods (Asp & Björck, 1992).

A method introduced by Berry (1986) and later modified (Champ, 1992; Faisant *et al.*, 1995) employs milling and extensive α-amylolysis, but does not include gelatinization. RS 2 and 3 are then analysed. Two approaches have been published for assay of all types of RS: the method of Englyst *et al.* (1992) using a standardized ball milling technique to simulate the disintegration of foods at chewing, and that of Muir & O'Dea (1992) using chewing as the disintegration step before pepsin and pancreatin treatments.

Dietary fibre

There are two principally different approaches for dietary fibre analysis: (1) gravimetric methods in which a dietary fibre residue is prepared, weighed and corrected for non-fibre components; and (2) component analysis methods in which the monomeric constituents are analysed more or less specifically and summed to a total fibre estimate. In both approaches, soluble and insoluble components can be separated. The solubility of the dietary fibre components is, however, much dependent on temperature and pH conditions for the extraction of the soluble components. For a review see, for example, Asp *et al.* (1992).

The enzymatic gravimetric methods approved by the AOAC for total and insoluble fibre (Prosky *et al.*, 1985, 1988; Lee *et al.*, 1992) have been tested in several collaborative studies and recently adopted as first action also for the determination of soluble fibre (Prosky *et al.*, 1994).

The component analysis methods of Englyst *et al.* (1995) and Theander *et al.* (1995) (the 1995 Uppsala Method) are similar in employing acid hydrolysis, derivatization to alditol acetates and determination of neutral monomers with GLC (or HPLC as an alternative). Uronic acid components are determined colorimetrically. Colorimetric measurement of the total reducing power after acid hydrolysis is an alternative and more simple variation of the Englyst method. The different steps in these methods are similar in many respects, but there are two conceptually and, in some foods, quantitatively important differences: (1) the Englyst method employs solubilization with DMSO, removing RS, whereas RS not hydrolysed after milling and gelatinization–heat-stable amylase digestion in the Uppsala method is classified as dietary fibre; and (2) a gravimetric Klason lignin (sulphuric acid lignin) determination is performed in the Uppsala method and included in the dietary fibre estimate. Thus, the Uppsala method is conceptually similar to the enzymatic, gravimetric methods approved by the AOAC. The Englyst methods aim at measuring only non-starch polysaccharides (NSP) as dietary fibre. This is often claimed to be an estimate of plant cell-wall polysaccharides, but it should be noted that the Englyst methods are unable to differentiate between the plant cell-wall located and the added polysaccharides.

Soluble and insoluble fibre components can be determined separately with both methods. The extraction conditions for soluble components, however, determine the solubility (for review, see Asp *et al.*, 1992). Nevertheless, a soluble fibre estimate gives a useful indication of the proportion of fibre that can be expected to exert effects on plasma glucose and cholesterol levels.

CARBOHYDRATE ANALYSES FOR FOOD DATABASES

In view of the nutritional importance of various food carbohydrates, it is essential to replace carbohydrate by difference figures in food tables with specifically analysed carbohydrates or carbohydrate fractions. A primary step is to estimate dietary fibre as a measure of undigestible components. A measure of total dietary fibre should include as many undigestible carbohydrates as possible, to be nutritionally most meaningful, and to correspond to the other main carbohydrate fraction, the digestible carbohydrates. The sum of digestible carbohydrates and dietary fibre should equal total carbohydrate. A total fibre estimate can be obtained most easily by the enzymatic, gravimetric AOAC methods. RS of the retrograded amylose type (RS 3) is then included, as well as lignin. Whenever possible, however, component analysis methods should be used to provide compositional data of the fibre for the database.

Starch should be analysed with a method corresponding to the dietary fibre assay, that is when KOH or DMSO solubilization is not used in the dietary fibre determinations, as in both the gravimetric and component analysis methods of the AOAC, such solubilization should also not be employed in the starch assay. Conversely, a separate assay of RS should be performed if this is not included in the dietary fibre estimate. It should be noted that only the retrograded amylose type of RS—the dominating type in processed foods—is included in the present AOAC dietary fibre methods,

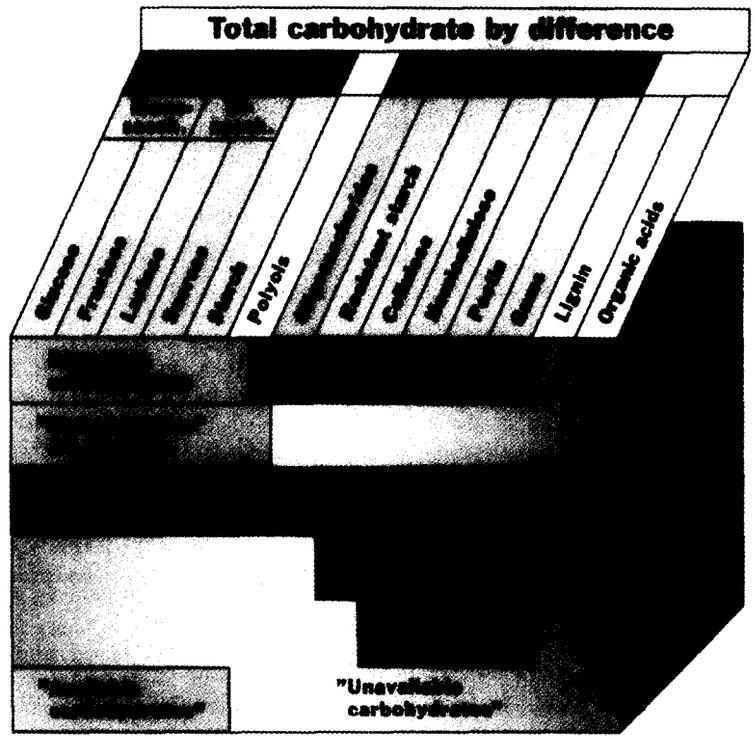


Fig. 1. Food carbohydrate fractions and their inclusion in various definitions.

due to the milling and gelatinization steps solubilizing RS 1 and RS 2, respectively. As a future development, a physiologically more correct delimitation between digestible starch and RS should be defined for both dietary fibre and starch analyses.

Individual mono-, di-, and oligosaccharides should be included as separate values in food databases, whenever available, and not grouped together in view of the different nutritional importance of different low-molecular weight carbohydrates. Oligosaccharides, inulin and other carbohydrate components should also be determined and included in the database, whenever present in significant quantity.

In conclusion, food databases should ideally include glucose, fructose, galactose, sucrose, lactose, maltose, relevant oligosaccharides, starch (available), RS (separate or as a component of dietary fibre) and dietary fibre (total, soluble/insoluble fraction, RS, monomeric composition, cellulose and β-glucan estimates when available, and other specifically determined fractions).

LABELLING CARBOHYDRATES

Carbohydrate by difference, the still most common way of estimating the total carbohydrate content for labelling, includes all types of carbohydrates, and is the basis for the carbohydrate definition of the US Nutrition Labeling and Education Act (Anonymous, 1993). In the European Union, on the other hand, carbohydrates mean 'metabolizable carbohydrates' and include polyols (Anonymous, 1990*b*). The different definitions are illustrated in the United States, as well as in most other countries, dietary fibre is defined for labelling as material determined as fibre using the enzymatic gravimetric methods of the AOAC. This fibre estimate can be used to correct the total carbohydrates before calculating the energy content from the carbohydrates. The European Union is awaiting a definition by its Standing Committee for Foods (SCF).

In view of the fundamental nutritional importance of the small-intestinal digestibility, and corresponding to the 'carbohydrate' definition as 'metabolizable', i.e. digestible, carbohydrates, a fibre definition should be as close as possible to undigestible ('unavailable') carbohydrates. Such a definition could in practice be related to a well-established routine method, such as the AOAC methods, and with the possibility of including other undigestible carbohydrates, not determined with the AOAC method, provided that they have some physiological effects in common with dietary fibre and that they can be determined in foods with reasonably simple routine methods.

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