

ROYAL SOCIETY OF CHEMISTRY
PAPERBACKS

FOOD

The chemistry of its components

T P COULTATE



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Food – the chemistry of its components

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1. Introduction

For the chemists of the 18th and 19th centuries an understanding of the chemical nature of our food was a major objective. They realised that this knowledge was essential if dietary standards, and with them health and prosperity, were to improve. Inevitably it was the food components present in large amounts, the carbohydrates, fats and proteins that were first to be described. As physiologists and physicians began to relate their findings to the chemical knowledge of foodstuffs the greatest need became one for analytical techniques, a demand no less pressing today. The food components that occur in much smaller amounts, the pigments, vitamins and flavour compounds for example, required 20th century laboratory techniques for their isolation and characterisation. Thus in spite of the more or less similar importance of the different classes of food components the extent of knowledge has not advanced evenly.

By the time of World War II it appeared that most of the questions being asked of food chemists by nutritionists, agriculturalists and others had been answered. This was certainly true as far as questions of the 'what is this substance and how much is there?' variety were concerned. However, as reflected in this book, over the past 20 years or so new questions have been asked, and so far only a few answers have been obtained. Food chemists nowadays are required to explain the *behaviour* of food components - on storage, processing, cooking, even in the mouth and during digestion. Much of the stimulus to this type of enquiry has come from the food manufacturing industry - and the legislative bodies which attempt to control the industry's activities. For example the observation that the starch in a dessert product provides a certain amount of energy has been overtaken in importance by the need to know which type of starch will give just the right degree of thickening, and what is the molecular basis for the differences between one starch and another.

The later chapters of this book show that with regard to the quantitatively less prominent components the examination of their properties

in food systems is only just beginning. With the obvious exception of the vitamins this delay has been caused, at least in part, by the failure of nutritionists, physiologists and other scientists to recognise what housewives* and the food manufacturing industry have always known. That is that there is more to the business of feeding people than compiling a list of nutrients in the correct proportions. Furthermore, this is as true if one is engaged in famine relief as it is in a five star restaurant. To satisfy a nutritional need a foodstuff must be acceptable, and to be acceptable it must first look and then taste 'right'.

The search for the answers to questions of food texture, colour and flavour as well as simple composition have turned the chemical study of food into a mongrel discipline. Its present vigour, which stimulated the writing of this book, comes from the necessary integration of normally separate scientific disciplines. For example in Chapter 4 the chemistry of meat is shown to require a knowledge of cell biology allied to free radical chemistry. Similarly in Chapter 8 it would have been foolish to consider the chemistry of preservatives without some insights from food microbiology.

With such a far ranging subject no book of this size can claim to be comprehensive. It is ironic that the most abundant food component of all, water, has not been give the chapter to itself that it deserves. Other omissions, particularly of many aspects of nutrition, have been provoked by the abundance of excellent textbooks, at all academic levels, rather than any indifference on the part of the author. A number of excellent texts covering related areas of food science have been listed in Appendix 1.

No attempt has been made to make this a manual of laboratory experiments, although frequent references to laboratory methods have been made. In the area of practical food chemistry there is no substitute for 'Pearson' (see Appendix 1). In view of the increasing use of sophisticated instrumental methods which may well be beyond the scope of school or college laboratories there is much to be said for one of the earlier editions of Pearson's book (*eg* the 5th or 6th), written in the days when the burette still reigned unchallenged in the analytical laboratory.

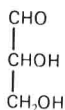
*Throughout this book the term 'housewife' is to be taken to mean anyone, of either sex, married or single, responsible for the retail purchase of food and its preparation in the home.

2. Carbohydrates

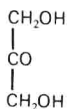
Sugars and their derivatives

Sugars, such as sucrose and glucose, together with polysaccharides such as starch and cellulose, are the principal components of the class of substances we call *carbohydrates*. Although chemists never seem to have difficulty in deciding whether or not a particular substance should be classified as a carbohydrate they have been unable to provide a concise, formal definition. The empirical formulae of most of the carbohydrates we encounter in foodstuffs approximate to $(\text{CH}_2\text{O})_n$, hence the name. More usefully it is simpler to regard them as aliphatic polyhydroxy compounds which usually carry a carbonyl group (and, of course, derivatives of such compounds).

The simplest carbohydrates are the monosaccharides. These have between three and eight carbon atoms but only those with five or six are common. The suffix ‘-ose’ is included in the names of monosaccharides that have a carbonyl group and in the absence of any other identification the number of carbon atoms is indicated by terms such as triose, tetrose and pentose. The prefixes aldo- and keto- are used to show whether the carbonyl group is at the first or a subsequent carbon atom so that we may refer to, for example, aldohexoses or ketopentoses. To complicate matters further the two triose monosaccharides are almost never named in this way but are referred to as glyceraldehyde (2,3-dihydroxypropanal) [2.1] and dihydroxyacetone (dihydroxypropanone) [2.2].

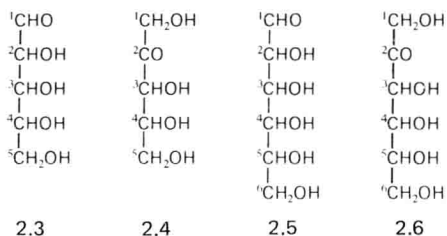


2.1

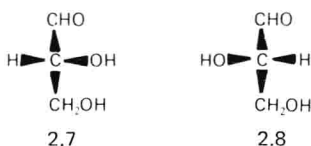


2.2

Of greatest concern to us will be the aldo- [2.3] and [2.5] and keto- [2.4] and [2.6] pentoses [2.3] and [2.4] and hexoses [2.5] and [2.6], shown here with the conventional numbering of the carbon atoms:



The carbon atom of each CHOH is of course asymmetrically substituted and all carbohydrates show optical isomerism. Almost all naturally occurring monosaccharides belong to the so-called D-series. That is to say their highest numbered asymmetric carbon, the one furthest from the carbonyl group, has the same configuration as D-glyceraldehyde [2.7] rather than its isomer L-glyceraldehyde [2.8].



The structural relationships of the higher aldose monosaccharides are shown in *Fig. 2.1*. For simplicity in this diagram and most subsequent structural formulae the carbon atoms within the chain are indicated by the intersections of the vertical and horizontal bonds. The optical configuration corresponds to the conventional representation of the asymmetric carbon atom of glyceraldehyde shown above. The names of the numerous optical isomers of the aldoses will best be remembered by use of the awful mnemonics 'Get Raxl!' and 'All altruists gladly make gum in gallon tanks' (I would be delighted to hear of any improved versions). A corresponding table of ketose sugars may be drawn up but with the exception of D-fructose [2.9] none of the ketoses are of much significance to food chemists.

It is important to remember that the monosaccharides of the L-series are related to L-glyceraldehyde [2.8] and have the mirror image configurations to the corresponding D-series sugars. Thus L-glucose is [2.10] rather than [2.11] which is in fact L-idose. It is not surprising, in view of their asymmetry, that the monosaccharides are optically active, *ie* their solutions and crystals rotate the plane of polarized light. The symbols (+) and (–) can be used to denote rotation to the right and left respectively. The old fashioned names of dextrose and laevulose

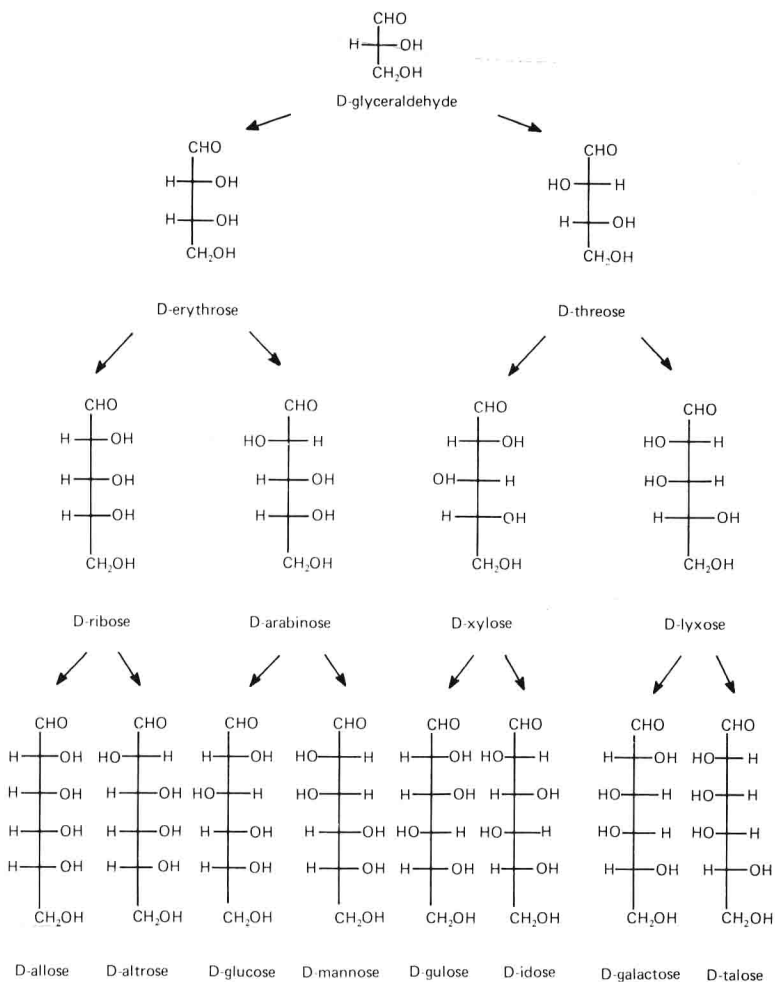
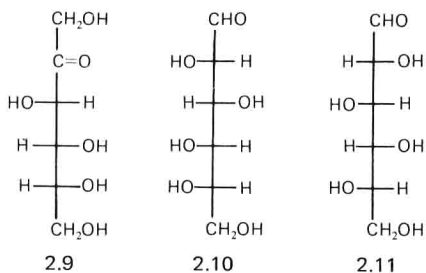


FIG. 2.1. The configurations of the D-aldoses



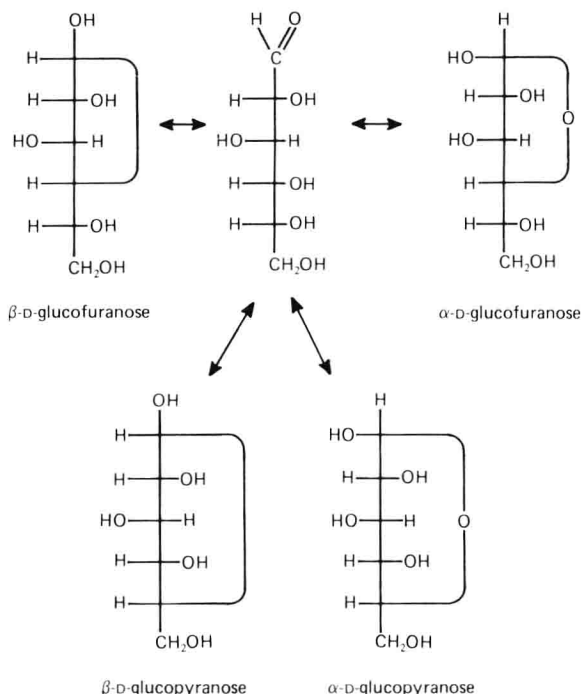


FIG. 2.2. Hemiacetal ring structures and mutarotation in D-glucose. Only the pyranose forms of D-glucose actually occur in significant amounts. The actual mechanism of mutarotation is not fully established. It occurs most rapidly at extremes of pH and apparently involves concerted acidic and basic catalysis.

stem from the respectively dextrorotatory and laevorotatory properties of D(+)-glucose and D(–)-fructose.

The straight chain structural formulae that have been used so far in this account do not satisfactorily account for many monosaccharide properties. In particular their reactions, while showing them to possess a carbonyl group, are not entirely typical of carbonyl compounds generally. The differences are explained by the formation of a ring structure by a condensation of the carbonyl group with a hydroxyl group at the far end of the chain to form a *hemiacetal*. As Fig. 2.2 shows, there are four possible ring structures for D-glucose, differing in the configuration of the new asymmetric centre and the size of the ring. When the ring is six membered, as in Fig. 2.2, it is referred to as *pyranose* and when five membered *furanose*, from the structures of pyran [2.12] and furan [2.13] respectively. The two isomeric forms of the particular monosaccharide are known as *anomers* and are designated α and β .



2.12



2.13

The α anomer is the one that has the hydroxyl group derived from the reducing group (the anomeric hydroxyl) on the opposite face of the ring to carbon six (see *Fig. 2.2*). The α and β anomers of a particular monosaccharide will differ in optical rotation. For example, α -D-glucopyranose, which is the form in which D-glucose crystallises from aqueous solution, has a specific rotation* of $+112^\circ$ whereas that of β -D-glucose, which is the form which crystallises from pyridine solution, is $+19^\circ$.

When crystals of either α - or β -D-glucose are dissolved in water the specific rotation is observed to change until, regardless of the form one started with, the solution finally gives a value of $+52^\circ$. This phenomenon is known as *mutarotation*. The transition of one anomer to another proceeds through the open chain or *aldehyde*-form and it is clear that it is this isomer which is involved in the sugar reactions that are typical of carbonyl compounds, even though in aqueous solutions only 0.02 per cent of D-glucose molecules are in this form.

The structural relationships between L and D isomers, α and β anomers, pyranose and furanose rings in both aldose and ketose sugars are by no means easily mastered. If available the use of a set of molecular models will help to clarify the issues but the structural formulae set out in *Fig. 2.3* illustrate the essential features of terminology in this area.

Over the years chemists have synthesised innumerable derivatives of monosaccharides but only a few occur naturally or have particular significance to food. Oxidation of the carbonyl group of aldose sugars leads to the formation of the 'onic' series of sugar acids. Thus the enzyme glucose oxidase catalyses the formation of D-gluconolactone [2.14] which hydrolyses spontaneously to D-gluconic acid [2.15]. This enzyme is highly specific for the β anomer of D-glucose and forms the basis of a popular analytical technique for glucose determination in food materials as well as a process for removing traces of glucose from the bulk liquid egg used in commercial bakeries and elsewhere (to prevent the Maillard reaction – see page 23).

*The specific rotation at a temperature of 20°C using light of the D line of the sodium spectrum is given by the expression

$$[\alpha]_D^{20} = \frac{100\alpha}{l \times c}$$

where α is the rotation observed in a polarimeter tube of length l decimeters and a sugar concentration of c grams per 100 ml.

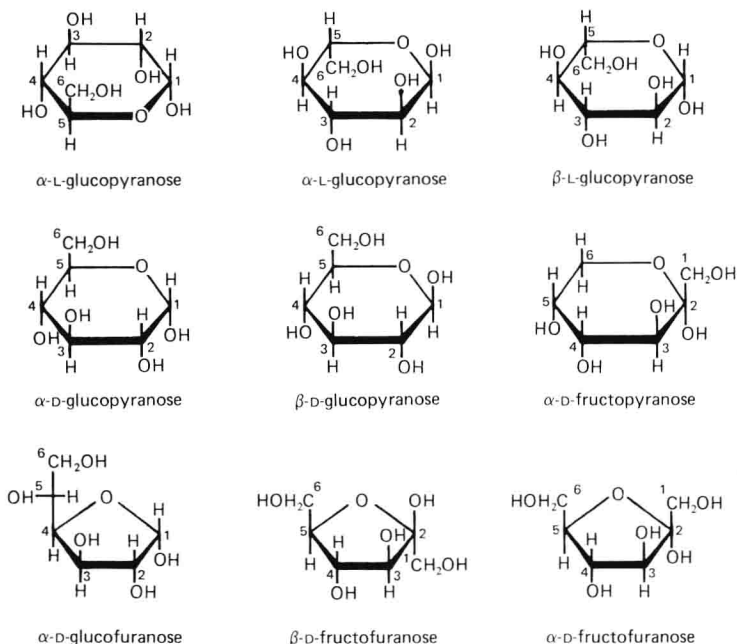
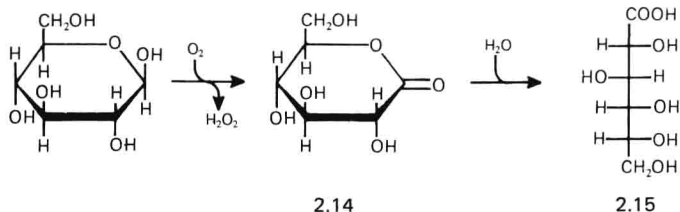
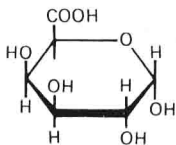


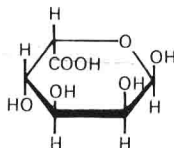
FIG. 2.3. Isomers of glucose and fructose. The obvious shortcomings of the formulae used so far in this chapter as representing molecular structure can be partially resolved, as here, by the adoption of the Haworth convention for ring structures. The ring is treated as planar and drawn to appear perpendicular to the plane of the page. These structures should be compared with those in *Fig. 2.2*. The numbering of carbon atoms may be correlated with that in the open chain structures [2.5] and [2.6] shown on page 4. It should be remembered that only a few of the isomers shown here actually occur naturally in significant amounts and also that not all the possible isomers have been included.



The ‘-uronic’ series of sugar acids are aldohexoses with a carboxyl group at carbon 6, such as D-galacturonic acid [2.16] and L-guluronic acid [2.17]. These are important as constituents of polysaccharides such as pectins and alginates but are of little interest in their own right.

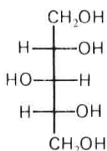


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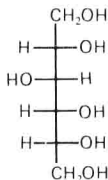


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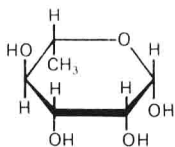
Reduction of the carbonyl group to a hydroxyl gives sugar alcohols such as xylitol [2.18] and sorbitol [2.19]. Though sweet, these are not absorbed from the intestine. They are synthesised industrially by reduction with hydrogen of the corresponding aldose sugar and are used to replace sugars in diabetic and other 'calorie-reduced' food products. Reduction at other positions gives deoxy sugars such as L-rhamnose (6-deoxy-L-mannose) [2.20], an important minor constituent of pectins, and 2-deoxy-D-ribose [2.21], the sugar component of DNA.



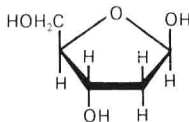
2.18



2.19

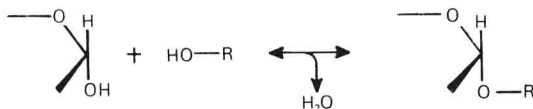


2.20



2.21

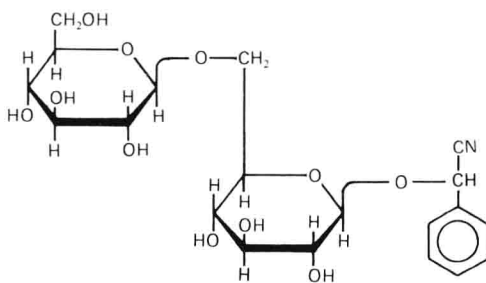
The most important derivatives of monosaccharides are those in which the 'hemiacetal' or 'reducing' group forms an 'acetal' or 'glycosidic' link with a hydroxyl group of another organic compound:



Glycosidic links are stable under ordinary conditions but are readily hydrolysed in acid conditions or in the presence of appropriate hydrolytic enzymes. The formation of the glycosidic link has the effect of

fixing the hemiacetal structure in either the α or β configuration and of course abolishing mutarotation. As we will see later in the description of oligosaccharides and other compounds having glycosidic links it will be necessary to specify whether the link in a particular compound is α or β .

Although any compound containing a glycosidic link is, strictly speaking, a glycoside, the term is usually reserved for a class of compounds which occur naturally in plants. These particular glycosides have a sugar component linked to a non-sugar component, termed the aglycone, which is most frequently a flavanoid, or a more simple aromatic substance, or a steroid. The anthocyanin pigments of plants, considered in Chapter 5, are some of the best known glycosides that occur in food but amygdalin [2.22], which occurs particularly in bitter almonds, does give rise to traces of hydrogen cyanide (too little to be hazardous) in some foods.



2.22

By far the most numerous and important glycosidic links are those between the reducing groups of one monosaccharide and one of the hydroxyl groups of another. The result is a disaccharide and if the linkage is repeated trisaccharides, tetrasaccharides and, ultimately, polysaccharides will result. The polysaccharides, where hundreds or thousands of monosaccharide units may be combined in a single molecule, are considered in the next section, here we are concerned with the oligosaccharides. (Remember that in Greek 'oligo-' means 'few' whereas 'poly-' means 'many'.) Even when a disaccharide is composed of two identical monosaccharides there are numerous possible structures. This is illustrated in Fig. 2.4 which shows four of the more important glucose/glucose disaccharides, maltose, cellobiose, gentiobiose and trehalose; many others of course are known. Although the configuration of the hemiacetal involved in the link is no longer free to reverse, it should not be overlooked that the uninvolved hemiacetal (*ie* that of the right hand ring as maltose, cellobiose and gentiobiose are portrayed in Fig. 2.4) is still subject to mutarotation in

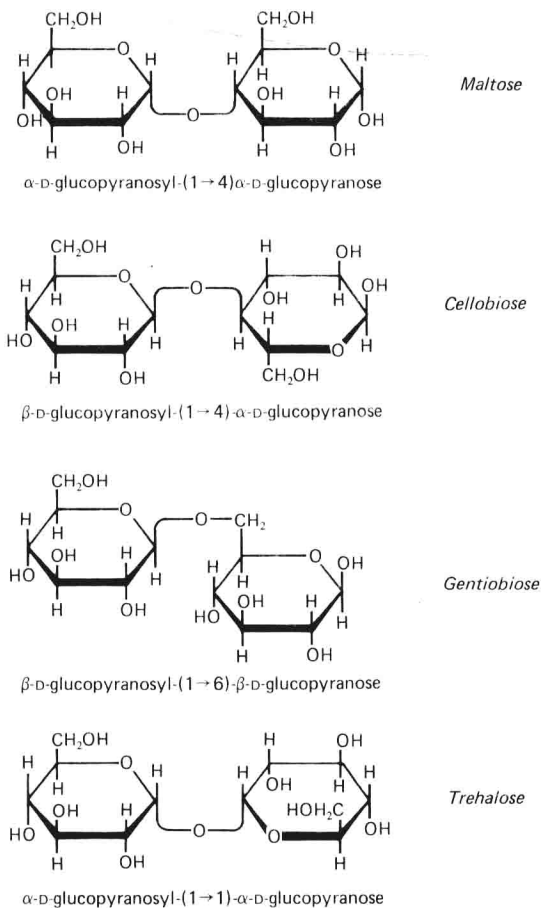
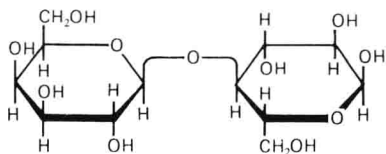


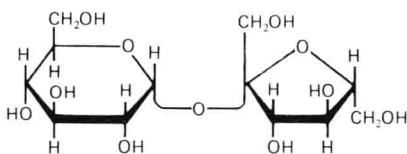
FIG. 2.4. Disaccharides of glucose. The trivial and systematic names are given. Maltose and cellobiose are breakdown products of starch and cellulose respectively. Gentiobiose is a component of many glycosides including amygdalin. Trehalose occurs in yeast.

aqueous solution. Thus these three sugars occur as pairs of α and β anomers. Furthermore, these three sugars continue to show similar reducing properties, associated with the carbonyl group, that monosaccharides have. The failure of trehalose and sucrose to reduce Cu^{2+} ions in alkaline solutions such as 'Fehling's' provides a useful laboratory test to distinguish these sugars from mono- and oligosaccharides which do possess a free reducing group.

The two most important food sugars, lactose and sucrose, are both disaccharides. Lactose, β -D-galactopyranosyl-(1 \rightarrow 4)- α -D-glucopyranose [2.23], is the sugar of milk (approximately 5 per cent w/v in cow's milk) and is of course a reducing sugar. Sucrose, α -D-glucopyranosyl-(1 \rightarrow 2)- β -D-fructofuranose [2.24] is the 'sugar' of the kitchen and commerce. The sucrose we buy has been extracted from sugar cane or



2.23



2.24

sugar beet but sucrose is also abundant in most plant materials, particularly fruit. As the glucose and fructose units are joined through both of their hemiacetal groups sucrose is not a reducing sugar. Under mildly acid conditions or the action of the enzyme invertase sucrose is readily hydrolysed to its component monosaccharides. This phenomenon is termed *inversion* and the resulting mixture, *invert sugar*, due to the effect of the hydrolysis on the optical rotation properties of the solution. The specific rotation values for sucrose, glucose and fructose are $+66.5^\circ$, $+52.7^\circ$ and -92.4° respectively so that we can see that dextrorotatory solution of sucrose will give a laevorotatory solution of invert sugar.

Of the higher oligosaccharides one group deserves particular attention from food chemists. These are the galactose derivatives of sucrose: raffinose (α -D-galactopyranosyl-(1 \rightarrow 6)- α -D-glucopyranosyl-(1 \rightarrow 2)- β -D-fructofuranose) and stachyose (α -D-galactopyranosyl-(1 \rightarrow 6)- α -D-glucopyranosyl-(1 \rightarrow 2)- β -D-fructofuranose), being the best known. They occur in legume seeds such as peas and beans and present particular problems in the utilization of soya beans. They are neither hydrolysed nor absorbed by the human digestive system so that a meal containing large quantities of beans, for example, becomes a feast for bacteria such as *Escherichia coli* in the large intestine. They produce large quantities of hydrogen and some carbon dioxide as by-products of their metabolism of sugars and the discomforts of flatulence are the inevitable result.