by a need for improved functionality in the paper industry. In the food industry, too, an increased understanding of starch functionality and how it is affected by other ingredients and processing methods should lead to improvements in the quality of both new and traditional food products.

## Acknowledgements

The authors would like to express their appreciation to Siw Kidman for skilful microscopy work.

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## Review

# Production, properties and applications of food-grade oligosaccharides

## R.G. Crittenden and M.J. Playne

Oligosaccharides are relatively new functional food ingredients that have great potential to improve the quality of many foods. In addition to providing useful modifications to food flavour and physicochemical characteristics, many of these sugars possess properties that are beneficial to the health of consumers. These include non-cariogenicity, a low calorific value and the ability to stimulate the growth of beneficial bacteria in the colon. Both the production and the applications of food-grade oligosaccharides are increasing rapidly. Major uses are in beverages, infant milk powders, confectionery, bakery products, yoghurts and dairy desserts. Research continues into the development of new oligosaccharides with a range of physiological properties and applications in the food industry.

Oligosaccharides of various types are found as natural components in many common foods including fruit, vegetables, milk and honey. During the past decade, their popularity as food ingredients has grown rapidly, particularly in Japan and Europe. This has largely been due to the possible health benefits associated with the consumption of these compounds. In 1991, the Japanese Government legislated for 'foods for specified health use' (FOSHU); fructo-, galacto-, soybean and palatinose oligosaccharides were listed. In the same year, more than 450 products were manufactured using oligosaccharides as a food ingredient[1]. The 1996 list of FOSHU comprises a total of 58 approved foods, of which 34

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PII: S0924-2244(96)10038-8

incorporate oligosaccharides as the functional ingredient. Lactulose, lactosucrose, xylo- and isomalto-oligosaccharides now have FOSHU status in addition to those listed in 1991. The main claim made for these products is that they are 'foods designed to help maintain a good gastrointestinal environment, and act to increase intestinal bifidobacteria'. Along with dietary fibre, the Japanese food industry has indicated that oligosaccharides are the most popular components to use in emerging functional foods[2]. Although the majority of companies manufacturing and applying oligosaccharides are Japanese, their usage by food manufacturers outside Japan is becoming widespread. The types of food-grade oligosaccharides currently available commercially, their properties and applications as well as recent developments and trends in the manufacture of new products are discussed in this article.

**Glossary**

**Prebiotic:** A non-digestible food ingredient that beneficially affects the host by selectively stimulating the growth and/or activity of one or a limited number of bacterial species already resident in the colon[6].

**Probiotic:** A live microbial feed supplement that beneficially affects the host animal by improving its intestinal balance[5].

**Synbiotic:** A food product that contains both probiotic and prebiotic ingredients[6].

## Properties of oligosaccharides

Oligosaccharides are usually defined as glycosides that contain between three and ten sugar moieties. However, many disaccharides possess similar properties to the larger sugars, and are often major components of food-grade oligosaccharide products. Hence, disaccharides such as lactulose are included as oligosaccharides in this discussion. In general, food-grade oligosaccharides are not pure products, but are mixtures containing oligosaccharides of different degrees of polymerization, the parent polysaccharide or disaccharide, and monomer sugars. Most manufacturers produce several classes of products; higher grades contain purer oligosaccharide mixtures with lower levels of contaminating monosaccharides and reactant di- or polysaccharides.

Oligosaccharides provide several manufacturing and health benefits, which make their use as food ingredients particularly attractive. The specific physicochemical and physiological properties of food-grade oligosaccharide products vary depending on the type of mixture purchased. Accordingly, the most appropriate oligosaccharide for a particular food application will also vary. However, some properties are common to almost all oligosaccharide products.

Oligosaccharides are water soluble and mildly sweet, typically 0.3–0.6 times as sweet as sucrose. The sweetness of the oligosaccharide product is dependent on the chemical structure and molecular mass of the oligosaccharides present, and the levels of mono- and disaccharides in the mixture. Their relatively low sweetness is useful in food production when a bulking agent with reduced sweetness is desirable to enhance other food flavours. Compared with mono- and disaccharides, the higher molecular weight of oligosaccharides provides increased viscosity, leading to improved body and mouthfeel. They can also be used to alter the freezing temperature of frozen foods, and to control the amount of browning due to Maillard reactions in heat-processed foods. Oligosaccharides provide a high moisture-retaining capacity, preventing excessive drying, and a low water activity, which is convenient in controlling microbial contamination[3]. Many have also been shown to be strong inhibitors of starch retrogradation[3].

Although oligosaccharides possess these useful physicochemical characteristics, most of the interest in their use as food ingredients stems from their many beneficial physiological properties. Unlike starch and simple sugars, the currently available food-grade oligosaccharides are not utilized by mouth microflora to form acid or polyglucans. Hence, they are presently used as low-cariogenic sugar substitutes in confectionery, chewing gums, yoghurts and drinks. Many oligosaccharides are not digested by humans[1]. This property makes them suitable for use in sweet, low-calorie diet foods, and for consumption by individuals with diabetes. In the case of very sweet foods, they may be used as bulking agents in conjunction with intense artificial sweeteners such as aspartame, phenylalanine or sucralose. Oligosaccharides can be used to mask the aftertastes produced by some of these intense sweeteners. The indigestible quality of oligosaccharides means that they have effects similar to dietary fibre, and thus prevent constipation. However, the corollary to this is that excessive consumption may cause flatulence or diarrhoea. For fructo-oligosaccharides, the minimum dose causing diarrhoea is ~40–50 g/d (Ref. 4).

In recent years, the ability of many oligosaccharides to promote the proliferation of bifidobacteria in the colon has been recognized. These bacteria are believed to be beneficial to health, and together with other health-promoting microorganisms are termed probiotics[5] (see Glossary). Subsequently, oligosaccharides have recently been described as one of several 'prebiotics', which can stimulate the growth of beneficial microflora[6] (Box 1). Much of the present marketing and research on oligosaccharides is focusing on this functional property. Effective bifidogenic doses appear to vary among the different oligosaccharide types. However, most oligosaccharides have been demonstrated to increase bifidobacteria numbers in the colon at doses of <15 g/d (Refs 1 and 11–14).

## Production of oligosaccharides

To obtain data on the oligosaccharides currently available commercially, all major manufacturers were surveyed, and extensive business and patent searches were conducted. Worldwide, there are 12 classes of food-grade oligosaccharides currently in commercial production (Table 1). Both the volume and diversity of oligosaccharide products are increasing rapidly as their functional properties become further understood. Excluding

**Box 1. Oligosaccharides and the gut microbial ecosystem**

The colon of the human gastrointestinal tract contains a large population of resident bacteria. In fact, ~55% of the solids in faeces is microbial biomass. In adults, these bacteria are balanced in a complex ecosystem consisting of more than 40 major species and more than 400 species in total[7]. In a healthy individual, most of these species are advantageous or benign to the host, but some are potentially pathogenic if their numbers are allowed to increase to high levels. Disturbances to the ecological balance in the intestinal microflora caused by, for example, changes in diet, stress or antibiotic treatment can lead to the overgrowth of deleterious bacteria, and subsequently to gastrointestinal disorders[8]. These disorders may be as minor as intestinal discomfort or increased flatulence, or relatively serious health problems such as severe diarrhoea, irritable bowel syndrome and colitis. Undesirable bacteria in the colon have even been implicated in the development of colon cancer[1].

The idea of ingesting beneficial bacteria to maintain a healthy microbial balance in the gut was proposed by Elie Metchnikoff[9] in 1907, although fermented milk products have been consumed by humans for perhaps thousands of years. The term probiotics has relatively recently been coined to describe deliberately ingested, health-promoting microorganisms. Worldwide, the bacteria currently being examined as potential probiotics are predominantly from the genera *Lactobacillus* and *Bifidobacterium*[10], which are used to produce probiotic yoghurts and yoghurt drinks. Capsules containing dried probiotic cultures are also sold.

Oligosaccharides in the diet can enhance the growth of these probiotic bacteria in the gut. In particular, they promote the proliferation of bifidobacteria, and are therefore referred to as bifidogenic or bifidus factors. They achieve this by acting as a selective carbon and energy source that these microorganisms can utilize, but that potentially harmful residents of the colon such as Enterobacteriaceae and clostridia generally cannot[1]. Subsequently, oligosaccharides have been termed prebiotics. Several products are now appearing in Japan and Europe that include both probiotics and prebiotics. Foods containing this combination are often now referred to as synbiotics.

lactulose, oligosaccharide production in 1990 was estimated at 35 000 t [A.W.M.H. van den Broek (1992) *Development of the Functional Food Market in Japan* (MSc thesis), Agricultural University of Wageningen, The Netherlands]. We have estimated that this figure exceeded 65 000 t in 1995, based on the responses received from the companies surveyed, with lactulose accounting for a further 20 000 t. Patent activity into new oligosaccharide products continues to be strong, and approximately half the companies surveyed for this review indicated that they were actively developing new products. Recent patent activity in the production and applications of new oligosaccharides has been reviewed previously[15], but is briefly summarized here.

With the exception of soybean oligosaccharides (which are produced by direct extraction) and lactulose (which is produced using an alkali-catalysed reaction), food-grade oligosaccharides are manufactured using enzymatic processes. They are either 'built up' from simple sugars, such as sucrose or lactose, by transglycosylation reactions[16,17], or formed by controlled hydrolysis of polysaccharides, such as starch[3], inulin[17] or xylan[18]. These processes usually produce a range of oligosaccharides differing in their degree of polymerization and sometimes in the position of the glycosidic linkages. Unreacted substrate and monosaccharides are also present after oligosaccharide formation. Such contaminating sugars are often removed by membrane or chromatographic procedures to form higher-grade products that contain purer oligosaccharides. Detailed production methods for various oligosaccharides have been reviewed by Nakakuki[3] in 1993 and by Playne[19] in 1994.

## Galacto-oligosaccharides

The establishment of a bifidus microflora in the intestines of breast-fed infants has been attributed to the presence of galactose-containing oligosaccharides in human milk[20,21]. Hence, the inclusion of galacto-oligosaccharides as prebiotic food ingredients has attracted considerable commercial interest, and several companies are currently involved in their production. They are produced commercially from lactose (Fig. 1) using the galactosyltransferase activity of β-galactosidase (EC 3.2.1.23), which dominates lactose hydrolysis at high lactose concentrations[21]. Major companies involved in galacto-oligosaccharide production are Yakult Honsha (Tokyo, Japan), Nissin Sugar Manufacturing Company (Tokyo, Japan) and Snow Brand Milk Products (Tokyo, Japan). Snow Brand Milk Products produces galacto-oligosaccharides to incorporate into its infant milk formulas, but does not sell them outside its organization. Additionally, Borculo Whey Products (Borculo, The Netherlands) has received approval to produce and market a galacto-oligosaccharide product in The Netherlands, whereas Unitika (Osaka, Japan) has developed a production process but is not yet operating commercially.

## Lactulose

Of all oligosaccharides, lactulose is produced in the largest quantity. Like galacto-oligosaccharides, it is manufactured from lactose (Fig. 1). An alkali isomerization process is used to convert the glucose moiety in lactose to a fructose residue[22]. The resulting disaccharide, lactulose, is not digested by humans and promotes the preferential growth of bifidobacteria in the colon[12,23]. It therefore has applications as a prebiotic food ingredient and low-calorie sweetener. However, lactulose is currently used predominantly as a pharmaceutical for the control of constipation and portosystemic encephalopathy. Solvay (Hannover, Germany) is the world's largest producer of lactulose, manufacturing ~10 000 t/year. More than 90% of its product is marketed in the pharmaceutical field in products such as 'Duphalac', 'Bifiteral', 'Chronulac' and 'Cephulac'. Morinaga Milk Industry Co. (Kanagawa, Japan) is another major producer, and has long been an advocate of the use of lactulose as a food ingredient[12]. Morinaga has been exporting some 3000 t annually to Europe, and has set up a marketing arm of the company in Belgium. Milei GmbH (Germany) uses Morinaga technology for the production of lactulose. Other European producers are Laevosun, in Austria, and the Italian company Inalco SPA. In North America, lactulose is produced by the

**Table 1. Currently produced food-grade oligosaccharides**

| Class of oligosaccharide | Estimated[a] production in 1995 (t) | Major manufacturers | Trade names |
|---|---|---|---|
| Galacto-oligosaccharides | 15 000 | Yakult Honsha (Japan) | Oligomate |
| | | Nissin Sugar Manufacturing Company (Japan) | Cup-Oligo |
| | | Snow Brand Milk Products (Japan) | P7L and others |
| | | Borculo Whey Products (The Netherlands) | TOS-Syrup |
| Lactulose | 20 000 | Morinaga Milk Industry Co. (Japan) | MLS/P/C |
| | | Solvay (Germany) | |
| | | Milei GmbH (Germany) | |
| | | Canlac Corporation (Canada) | |
| | | Laevosun (Austria) | |
| | | Inalco SPA (Italy) | |
| Lactosucrose | 1600 | Ensuiko Sugar Refining Co. (Japan) | Nyuka-Origo |
| | | Hayashibara Shoji Inc. (Japan) | Newka-Oligo |
| Fructo-oligosaccharides | 12 000 | Meiji Seika Kaisha (Japan) | Meioligo |
| | | Beghin–Meiji Industries (France) | Actilight |
| | | Golden Technologies (USA) | NutraFlora |
| | | Cheil Foods and Chemicals (Korea) | Oligo-Sugar |
| | | ORAFTI (Belgium) | Raftilose and Raftiline |
| | | Cosucra (Belgium) | Fibruline |
| Palatinose (isomaltulose) oligosaccharides | 5000 | Mitsui Sugar Co. (Japan) | ICP/O |
| | | | IOS |
| Glucosyl sucrose | 4000 | Hayashibara Shoji Inc. (Japan) | Coupling Sugar |
| Malto-oligosaccharides | 10 000 | Nihon Shokuhin Kako (Japan) | Fuji-Oligo |
| | | Hayashibara Shoji Inc. (Japan) | Tetrup |
| Isomalto-oligosaccharides | 11 000 | Showa Sangyo (Japan) | Isomalto-900 |
| | | Hayashibara Shoji Inc. (Japan) | Panorup |
| | | Nihon Shokuhin Kako (Japan) | Biotose and Panorich |
| Cyclodextrins | 4000 | Nihon Shokuhin Kako (Japan) | Celdex |
| | | Ensuiko Sugar Refining Co. (Japan) | Dexy Pearl |
| | | Asahi Kasei Kagyo Co. (Japan) | |
| Gentio-oligosaccharides | 400 | Nihon Shokuhin Kako (Japan) | Gentose |
| Soybean oligosaccharides | 2000 | The Calpis Food Industry Co. (Japan) | Soya-oligo |
| Xylo-oligosaccharides | 300 | Suntory Ltd (Japan) | Xylo-oligo |

[a] Data were obtained by surveying major manufacturers of food-grade oligosaccharides

Canlac Corporation (Quebec, Canada), a joint venture of ACIC Inc., Ault Foods (Canada) and Signa SA (Mexico). Canlac markets to Canada, the USA and Cyprus.

### Lactosucrose

Lactosucrose is the third bifidogenic oligosaccharide that is produced using lactose as a raw material (Fig. 1). This trisaccharide consists of a lactose molecule to which a fructose moiety is joined at the glucose residue by a β(2→1) glycosidic bond. It is manufactured from a mixture of lactose and sucrose using the transfructosylation activity of the enzyme β-fructofuranosidase (EC 3.2.1.26)[24]. Lactosucrose was developed in Japan by a cooperative venture involving Ensuiko Sugar Refining

Co. (Yokahama), Hayashibara Shoji Inc. (Okayama) and Biofermin Pharmaceutical Co. Ltd. The demand for lactosucrose is increasing rapidly. In 1992, Ensuiko produced 500 t of this product. In two years, production more than tripled, with 1600 t being manufactured in 1994. The lactosucrose products manufactured by Ensuiko are distributed mainly through Maruha Corporation (Japan).

## Fructo-oligosaccharides

Fructo-oligosaccharides represent one of the major classes of bifidogenic oligosaccharides in terms of their production volume. Their safety and health benefits as food ingredients have been reviewed by Spiegel *et al.* (1994)[4]. They are manufactured by two different processes, which result in slightly different end products (Fig. 2). In the first method, fructo-oligosaccharides are produced from the disaccharide sucrose using the transfructosylation activity of the enzyme β-fructofuranosidase. As for the production of galacto-oligosaccharides, a high concentration of the starting material is required for efficient transglycosylation[25-27]. The fructo-oligosaccharides formed in this process contain between two and four β(1→2)-linked fructosyl units linked to a terminal α-D-glucose residue. These are named 1-kestose (Glu-$Fru_2$), 1-nystose (Glu-$Fru_3$) and $1^F$-fructosylnystose (Glu-$Fru_4$). Glucose and small amounts of fructose formed as by-products in the reaction, as well as unreacted sucrose, are removed from the oligosaccharide mixture using chromatographic procedures to produce fructo-oligosaccharide products of higher purity. Meiji Seika Kaisha (Tokyo, Japan) is the major producer of transfructosylation fructo-oligosaccharides. These are marketed in Japan as 'Meioligo'. Meiji has also established joint ventures with Beghin Say in France (Beghin–Meiji Industries, Paris),

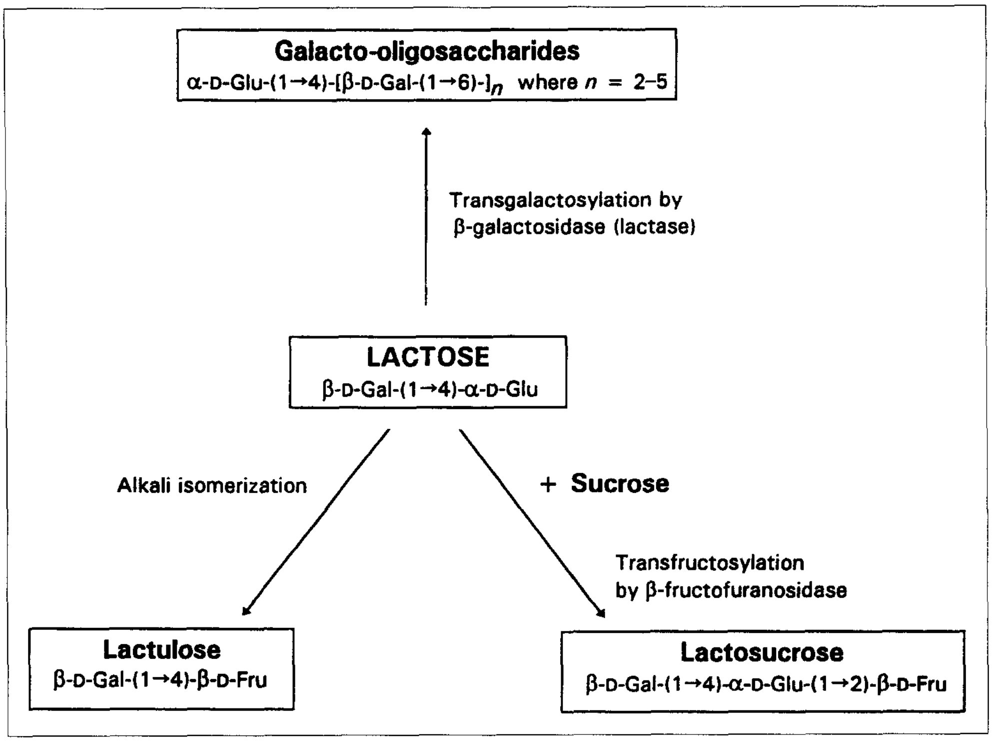


**Fig. 1**
Oligosaccharides manufactured from lactose (Gal = galactose; Glu = glucose; Fru = fructose).

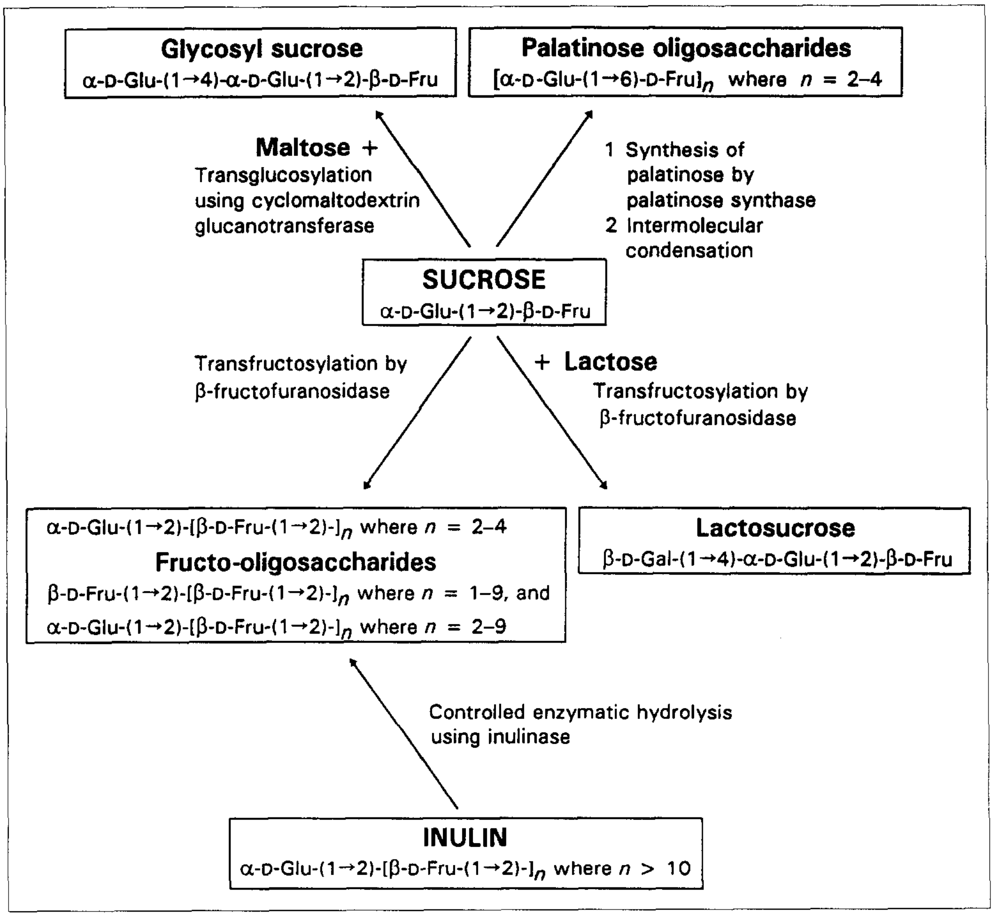


**Fig. 2**
Oligosaccharides manufactured from sucrose or inulin (Gal = galactose; Glu = glucose; Fru = fructose).

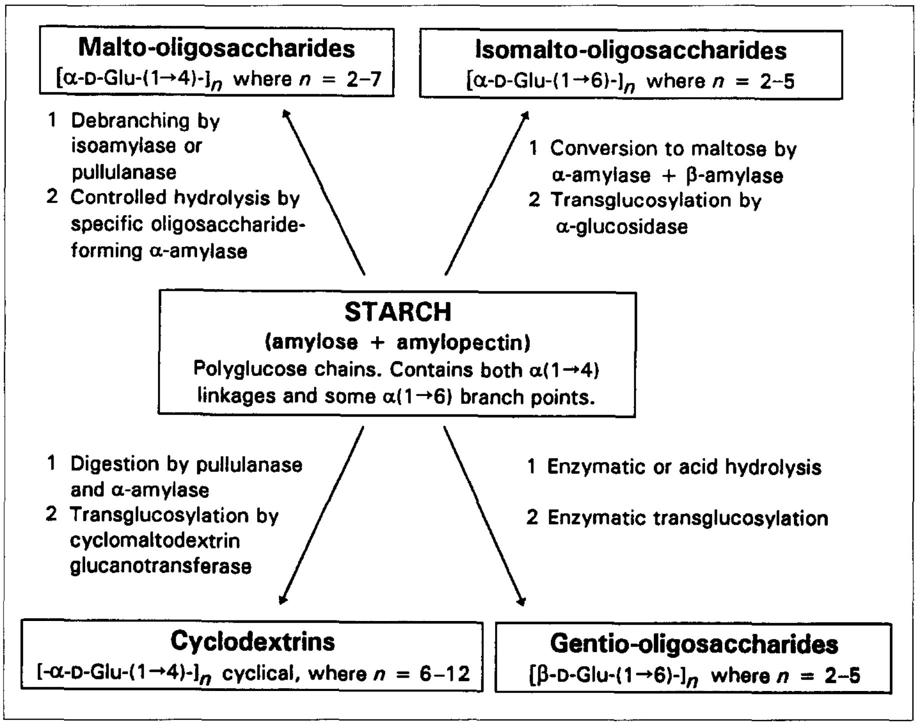


**Fig. 3**
Oligosaccharides manufactured from starch (Glu = glucose). Isomalto-oligosaccharides also contain some α(1→4) glycosidic linkages.

producing fructo-oligosaccharides that are marketed as 'Actilight', and with Golden Technologies (Westminster, CO) in the USA, which distributes Meiji Seika's fructo-oligosaccharides (60 t/year) as 'NutraFlora'. Cheil Foods and Chemicals (Seoul, Korea) also manufactures trans-fructosylation fructo-oligosaccharides.

The second method used for fructo-oligosaccharide production is the controlled enzymatic hydrolysis of the polysaccharide inulin (inulin oligofructose). The fructo-oligosaccharide mixture formed by this process closely resembles the mixture produced by the transfructosylation process. However, not all of the β(1→2)-linked fructosyl chains end with a terminal glucose. Additionally, the oligosaccharide mixture produced from inulin hydrolysis contains longer fructo-oligomer chains than that produced by the sucrose transfructosylation process. Inulin oligofructose is produced by the Belgian company ORAFTI (previously called Raffinerie Tirlemontoise SA, Brussels) from inulin extracted from chicory. It is marketed as 'Raftilose' in a variety of purities, either as a powder or in syrup form. The fructo-oligosaccharides in 'Raftilose' range from two to nine monosaccharide units in length, with an average length of four sugar moieties.

The inulin extracted from chicory roots contains some fructo-oligosaccharides in addition to polysaccharides. ORAFTI markets its inulin products under the trade name 'Raftiline'. 'Raftiline' contains fructose chains of varying degrees of polymerization, ranging from three to more than 50 sugar moieties. Cosucra (Momalle, Belgium) produces similar products, which it markets as 'Fibruline'. These longer-chain oligosaccharide products have applications as fat replacers.

## Palatinose (isomaltulose) oligosaccharides

Palatinose (also referred to as isomaltulose) is produced from sucrose using an immobilized isomaltulose synthase (EC 5.4.99.11) (Fig. 2). This disaccharide does not promote tooth decay and is used as a low-cariogenic sweetener. It is digested in the small intestine of humans and therefore cannot act as a prebiotic. However, palatinose oligosaccharides, formed by the intermolecular dehydration of palatinose, do survive passage to the colon to stimulate the growth of bifidobacteria[28]. Palatinose oligosaccharides are produced by Mitsui Sugar Co. in Kanagawa, Japan.

## Glycosyl sucrose ('Coupling Sugar')

The trisaccharide glycosyl sucrose ('Coupling Sugar') is manufactured from the disaccharides maltose and sucrose using the enzyme cyclomaltodextrin glucanotransferase (EC 2.4.1.19) (Fig. 2). It is produced in Okayama, Japan, by Hayashibara Shoji Inc. Glycosyl sucrose is approximately half as sweet as sucrose and, like most oligosaccharides, can be used as a substitute sweetener. The major health benefit provided by the use of this oligosaccharide in place of sucrose is the reduction of dental caries[29]. Glycosyl sucrose is susceptible to hydrolysis by intestinal enzymes[30], and is therefore unlikely to induce a bifidogenic response when consumed. However, it provides other benefits to food manufacturers including the suppression of crystal formation, browning reactions and retrogradation.

## Malto-oligosaccharides

Malto-oligosaccharides are not generally claimed to increase the numbers of bifidobacteria in the human colon. They are hydrolysed and absorbed in the small intestine and do not reach the colon intact. However, Nakakuki (1993)[3], in his review paper on malto-oligosaccharides, reported that the consumption of maltotetraose-rich corn syrup has been demonstrated in human trials to reduce the levels of intestinal putrefactive bacteria such as *Clostridium perfringens* and members of the family Enterobacteriaceae. Therefore, malto-oligosaccharides may be effective in improving colonic conditions.

Malto-oligosaccharides contain α-D-glucose residues linked by α(1→4) glycosidic linkages. They are produced commercially from starch by the action of debranching enzymes such as pullulanase (EC 3.2.1.41) and isoamylase (EC 3.2.1.68), combined with hydrolysis by various α-amylases (Fig. 3). These α-amylases have differing reaction specificities and can be used to produce syrups that are rich in malto-oligosaccharides of different chain lengths. Nihon Shokuhin Kako (Japan Maize Products, Tokyo) is one of the largest producers of malto-oligosaccharides in Japan.

### Isomalto-oligosaccharides

Like malto-oligosaccharides, isomalto-oligosaccharides are produced using starch as the raw material (Fig. 3). However, unlike malto-oligosaccharides, there is evidence to suggest that these oligosaccharides induce a bifidogenic response[11,31]. Isomalto oligosaccharides consist of α-D-glucose residues linked by α(1→6) glycosidic bonds. The isomalto-oligosaccharide mixtures also contain oligosaccharides with both α(1→6)- and α(1→4)-linked glucose such as the trisaccharide panose. They are produced using a combination of immobilized enzymes in a two-stage reactor. In the first stage, starch is liquefied using α-amylase (EC 3.2.1.1). The liquefied starch is then processed in a second stage that involves reactions catalysed by both β-amylase (EC 3.2.1.2) and α-glucosidase (EC 3.2.1.20). The β-amylase first hydrolyses the liquefied starch to maltose. The transglucosidase activity of α-glucosidase then produces isomalto-oligosaccharides. Several companies currently manufacture isomalto-oligosaccharides; of these, Showa Sangyo (Tokyo, Japan) is the major producer.

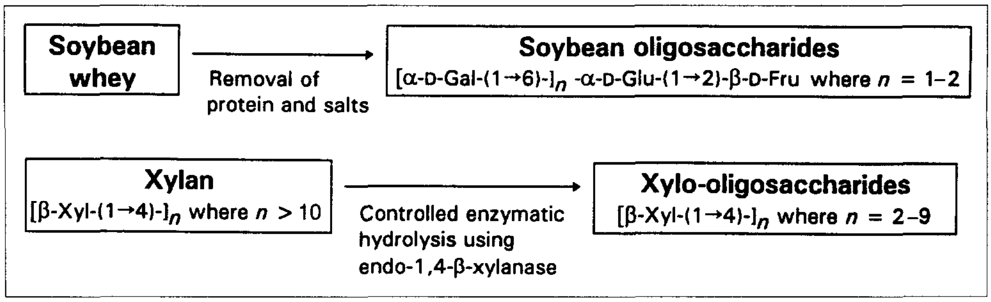


**Fig. 4**
Production of soybean and xylo-oligosaccharides (Gal = galactose; Glu = glucose; Fru = fructose; Xyl = xylose).

### Cyclodextrins

Cyclodextrins are cyclic α(1→4)-linked malto-oligosaccharides consisting of 6–12 glucose units. They are formed from starch digests by the action of cyclomaltodextrin glucanotransferase (Fig. 3). These oligosaccharides are capable of forming inclusion complexes with various organic compounds by incorporating them into the cavity of their cyclical structure. This can lead to desirable changes in the physical and chemical properties of the incorporated compound. Uses of cyclodextrins include stabilization of deliquescent or volatile compounds in foods and chemicals; emulsification of oils and fats; protection of substances that are susceptible to oxidation and photodegradation; and masking bitterness in foods and drugs. They are not generally regarded as bifidogenic. In Japan, they are produced predominantly by Nihon Shokuhin Kako, which controls ~60–70% of the market. Other producers include Ensuiko Sugar Refining Co., which markets its product as 'Dexy Pearl', and Asahi Kasei Kagyo Co.

### Gentio-oligosaccharides

Gentio-oligosaccharides consist of several glucose residues linked by β(1→6) glycosidic bonds. They are produced from glucose syrup by enzymatic transglucosylation. Nihon Shokuhin Kako is the sole producer of gentio-oligosaccharides, which it markets under the trade name 'Gentose'. These oligosaccharides are not hydrolysed in the stomach or small intestine, and are claimed by the manufacturer to promote the growth of bifidobacteria[32] and lactobacilli. They presently account for only a small proportion of the total oligosaccharide production volume, with just 300–400 t being manufactured annually.

### Soybean oligosaccharides

Unlike other oligosaccharides, soybean oligosaccharides are extracted directly from the raw material and do not require enzymatic manufacturing processes (Fig. 4). Soybean whey, a by-product from the production of soy protein isolates and concentrates, contains the oligosaccharides raffinose and stachyose, as well as sucrose, glucose and fructose. These sugars are extracted from the soybean whey and concentrated to produce soybean-oligosaccharide syrup. Raffinose and stachyose are both indigestible and therefore reach the colon intact, where they act as prebiotics, stimulating the growth of bifidobacteria[33]. Soybean oligosaccharides are produced in Japan by The Calpis Food Industry Co. (Tokyo).

### Xylo-oligosaccharides

At present, xylo-oligosaccharides represent only a small proportion of the total oligosaccharide market. However, demand for these oligosaccharides is increasing rapidly. In 1994, Suntory Ltd (Tokyo, Japan) produced ~70 t of xylo-oligosaccharides, and expects to produce more than 300 t in 1996. These oligosaccharides promote the growth of bifidobacteria in the colon[34], and are used predominantly in prebiotic drinks.

The raw material for xylo-oligosaccharide synthesis is the polysaccharide xylan, which is extracted mainly from corncobs. The xylan is hydrolysed to xylo-oligosaccharides by the controlled activity of the enzyme endo-1,4-β-xylanase (EC 3.2.1.8) (Fig. 4). To produce higher-purity oligosaccharide products, the monosaccharide xylose and high molecular mass carbohydrates are removed from the oligosaccharides using ultrafiltration and reverse osmosis processes.

## Applications of oligosaccharides

The major use of oligosaccharides is in beverages. 'OligoCC', produced by The Calpis Food Industry Co., was launched in 1989 and was one of the first commercially successful functional food products. This soybean-oligosaccharide drink had estimated sales of 80 million bottles, worth Y8 billion, in 1989 (Ref. 15). Another example is 'Bikkle', the xylo-oligosaccharide-containing beverage produced by Suntory Ltd. Increasingly, oligosaccharides are being included in probiotic yoghurts and yoghurt drinks to produce synbiotic products. 'Bifiel' (Yakult, Tokyo, Japan) contains galacto-oligosaccharides, whereas 'Symbalance' (Toni Milch, Zürich, Switzerland), 'Fyos' (Nutricia, Bornem, Belgium) and 'Fysiq' (Mona, Weerden, The Netherlands) all contain fructo-oligosaccharides. Oligosaccharides are also widely used in confectionery. Other current applications include desserts such as jellies and ice creams; bakery products including biscuits, breads and pastries; spreads such as jams and marmalades; and infant milk formulas. The use of oligosaccharides in the livestock industry is also increasing. An example is the fructo-oligosaccharide sold by Golden Technologies (Meiji–Coors Biotech joint venture) in the USA. Some non-food applications have also been proposed for oligosaccharides including drug delivery, cosmetics and mouth washes.

## Future trends

The market for oligosaccharides is already substantial, and continues to expand rapidly. At present, Japanese companies still dominate worldwide oligosaccharide production, as well as research and development activity. However, European interest in oligosaccharides is increasing with several companies currently producing, or planning to produce, oligosaccharide products. In contrast, oligosaccharide production in the USA at present remains negligible. Research and development into novel oligosaccharide products with different functional properties is continuing. Chito-oligosaccharides (derived from chitin by partial hydrolysis) are emerging as an important class of oligosaccharides with a diversity of potential food and non-food applications, including antimicrobials, plant growth inhibitors, food preservatives and use in cosmetics[15]. Additionally, $\alpha$-gluco-oligosaccharides[35], lacto-neotrehalose[36] and other hetero-oligosaccharides[37] have recently been reported to have potential as prebiotics. Novel production techniques that use improved enzymes, purification systems and/or new substrates feature heavily in recent oligosaccharide patent literature[15]. New physiological effects of oligosaccharide consumption continue to be elucidated, including possible protection against the development of colon cancer[38,39]. As these beneficial functional properties become more widely understood, both the volume of use and diversity of applications of oligosaccharides in foods are expected to increase. The current high interest in the application of bifidobacteria to improve colonic health has made the bifidogenic property of oligosaccharides one of their strongest marketing points. Synbiotic health-food products containing both probiotic bifidobacteria and prebiotic oligosaccharides are emerging to take advantage of this. The advantages provided to food manufacturers by the physicochemical properties of oligosaccharides, combined with the health benefits they impart to consumers, should ensure that oligosaccharide production and use will continue to expand.

## Acknowledgements

We thank all of the companies that have contributed information on their products for their cooperation. We especially thank Mr Eric Timmermans, of Borculo Whey Products, for his helpful advice. We acknowledge the financial support of the Cooperative Research Centre for Food Industry Innovation and the Dairy Research and Development Corporation of Australia.

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**Review**

# The applications of Raman spectroscopy in food science

**E.C.Y. Li-Chan**

Raman spectroscopy is a branch of vibrational spectroscopy in which a sample is exposed to an intense light beam such as a laser, and the spectrum of Raman-active vibrational modes induced in the sample molecules is obtained through analysis of the inelastically scattered photons. The diversity of applications and high content of molecular structure information provided, combined with recent advances in instrumentation, have rekindled interest in this technique in many diverse disciplines, including food science. Suitable analytes cover the entire range of food constituents, including the macro-components (proteins, lipids, carbohydrates and water) as well as minor components such as carotenoid pigments or synthetic dyes, and even microorganisms or packaging materials in contact with foods. Raman spectroscopy may be used as a tool for quality control, for compositional identification or for the detection of adulteration, as well as for basic research in the elucidation of structural or conformational changes that occur during processing of foods.

The interactions of electromagnetic radiation with electrons and nuclei of molecules give rise to a host of spectroscopic techniques that are based on absorption, emission and scattering processes. Raman spectroscopy is a branch of vibrational spectroscopy that is based on the shifts in the wavelength or frequency of an exciting incident beam of radiation that result from inelastic scattering on interaction between the photons and the sample molecules. Because both the intensity and frequency of induced molecular vibrations are sensitive to the chemistry and environment around the individual atoms, the Raman spectrum can be used as a monitor of molecular chemistry.

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## Basic principles of Raman spectroscopy

### Relationship between infrared spectroscopy and Raman spectroscopy

Raman and infrared (IR) spectroscopy are complementary techniques based on the discrete vibrational transitions that occur in the ground electronic state of molecules, which correspond to various stretching and bending deformation modes of individual chemical bonds. IR absorption and inelastic or Raman scattering are depicted in Box 1.

A Raman spectrum is obtained by plotting the intensity of scattered light as a function of the Raman shift,




PII: S0924-2244(96)10037-6