Kirk-Othmer Encyclopedia of Chemical Technology.

SUGAR, SPECIAL SUGARS

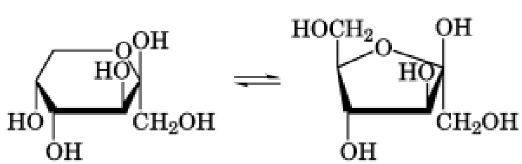
Although sucrose is commercially the most important sugar, there are also special sugars with special applications, among which fructose is the most important.

1. Fructose

D-Fructose [57-48-7] (levulose, fruit sugar) is a monosaccharide constituting one-half of the sucrose molecule. It was first isolated from hydrolyzed cane sugar (invert sugar) in the late nineteenth century (1, 2). Fructose constitutes 4–8 wt % (dry sugar basis (dsb)) of many fruits, where it primarily occurs with glucose (dextrose) and sucrose (see Carbohydrates; Sweeteners). It also makes up 50 wt % (dsb) of honey (3, 4).

Despite this ubiquity, fructose remained a noncommercial product until the 1980s because of the expense involved in its isolation and the care required for its handling. The development of technologies for preparing fructose from glucose in the isomerized mixture led to a greater availability of pure, crystalline fructose in the 1970s (5–7). However, the price for pure fructose was high enough in 1981 that the product was not competitive with sucrose and corn syrups as a commercial sweetener (see Syrups). With the entry of corn wet-milling companies into the crystalline fructose market in the late 1980s, raw material economies and enlarged manufacturing scale led to a nearly 10-fold production increase within a five-year period, making fructose prices competitive with other sweeteners for specific applications.

Pure D-fructose is a white, hygroscopic, crystalline substance and should not be confused with the high fructose corn syrups (HFCS) which may contain 42–90 wt % fructose and 23–29% water (8, 9). The nonfructose part of these syrups is glucose (dextrose) plus small amounts of glucose oligomers and polymers. Fructose is highly soluble in water; at 20°C it is 79% soluble, compared with only 47% for glucose and 67% for sucrose.



(1) **(2)**

The sweetness of fructose is 1.3–1.8 times that of sucrose (10). This property makes fructose attractive as an alternative for sucrose and other commercially available sweeteners. Fructose is probably sweetest in comparison with sucrose when cold and freshly made up in low concentrations at a slightly acidic pH (5). This relative sweetness difference is commonly attributed to changes in fructose structure when cold (β-D-fructopyranose **(1)**, sweet) as compared to the structure when the sweetener is warm (β-D-fructofuranose **(2)**, less sweet). Based on nmr spectroscopy and sensory panel evaluation of sweetness, however, it has been observed that the absolute sweetness of fructose is the same at 5°C as at 50°C, and is not dependent on anomeric distribution (11). Rather, it may be the sweetness of sucrose, which changes with temperature, that gives fructose sweetness the appearance of becoming sweeter at low temperatures.

Also notable is the unique sweetness response profile of fructose compared to other sweeteners (3, 4). In comparison with dextrose and sucrose, the sweetness of fructose is more quickly perceived on the tongue, reaches its intensity peak earlier, and dissipates more rapidly. Thus, the sweetness of fructose enhances many food flavor systems, eg, fruits, chocolate, and spices such as cinnamon, cloves, and salt. By virtue of its early perception and rapid diminution, fructose does not have the flavor-masking property of other common sugars.

The sweetness of fructose is enhanced by synergistic combinations with sucrose (12) and high intensity sweeteners (13), eg, aspartame, saccharin, acesulfame K, and sucralose. Information on food application is available (14, 15). Fructose also reduces the starch gelatinization temperature relative to sucrose in baking applications (16–18).

Fructose possesses colligative properties that distinguish it from sucrose, glucose, and other nutritive sweeteners. It is one of the more effective monosaccharide humectants, binding moisture and lowering water activity, A_w, in food applications, thereby rendering the food products less susceptible to microbial growth and more stable to moisture loss (3, 4). Ratios of fructose and higher molecular weight saccharides, oligosaccharides, and polysaccharides can be balanced to give increased control over freezing temperatures and storage stability in frozen products.

Fructose is a highly reactive molecule. When stored in solution at high temperatures, fructose not only browns rapidly but also polymerizes to dianhydrides [38837-99-9], [50692-21-2], [50692-22-3], [50692-23-4], [50692-24-5]. Fructose also reacts rapidly with amines and proteins in the nonenzymatic or Maillard browning reaction (5). This is a valued attribute in baked food products where crust color is important. An appreciation of these properties allows the judicious choice of conditions under which fructose can be used successfully in food applications.

Because of its relatively high degree of sweetness, fructose has been the object of commercial production for decades. Early attempts to isolate fructose from either hydrolyzed sucrose or hydrolyzed fructose polymers, eg, inulin (Jerusalem artichoke), did not prove economically competitive against the very low cost for sucrose processed from sugarcane or sugar beets.

Commercial quantities of crystalline fructose initially became available when the Finnish Sugar Company developed ion-exchange methods first for hydrolyzing sucrose and then for separating the hydrolysate into the constituents, ie, glucose and fructose. The latter step involves the calcium form of a sulfonated-polystyrene ion-exchange resin. Further economies in production were realized when the same company developed a method for crystallizing fructose from an aqueous rather than a water–alcohol solution (5).

More recent technologies also involve ion-exchange separation of fructose from glucose in a mixture obtained through the isomerization of glucose by means of immobilized glucose isomerase or microbial cells containing the enzyme (7), a technique pioneered by Hoffmann-La Roche. Another procedure for making crystalline fructose has been detailed (19), in which glucose (dextrose) is oxidized by glucose-2-oxidase to glucosone, which is then selectively hydrogenated to fructose. This procedure has the advantage of not requiring isomer separation in order to isolate the crystalline product.

Prior to 1970, commercially available crystalline fructose in Europe cost ca $17.6/kg and was produced at an annual rate of ca 7500 metric tons. By 1981, the amount of crystalline fructose available had risen to ca 20,000 metric tons, largely the result of the increased capacity of Hoffman-La Roche's plant in Thomson, Illinois (20). Prices in Europe and in the United States as of this writing (1996) were ca $8.80/kg and $2.20/kg, respectively. At these high prices relative to sugar, crystalline fructose use is relegated to high margin health foods and specialty dietary products, which account for a minute percentage of nutritively sweetened foods and beverages.

With the acquisition of the Thomson plant and technology, and the construction of their own plant in Lafayette, Indiana, in the late 1980s, the A. E. Stanley Manufacturing Company dramatically increased crystalline fructose production. On the strength of a growing appreciation for crystalline fructose's unique physical and functional properties, its competitive pricing, and its successful penetration of specific mainstream food applications, worldwide crystalline fructose production grew to more than 50,000 metric tons by 1992. In the same time period, crystalline fructose prices fell dramatically to ca \$0.88/kg, a price equivalent to \$0.75/kg sucrose on a sweetness basis (4).

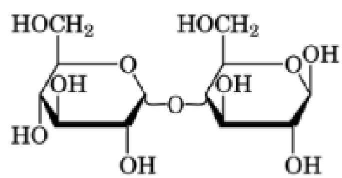
Early applications of crystalline fructose focused on foods for special dietary applications, primarily calorie reduction and diabetes control. The latter application sought to capitalize on a significantly lower serum glucose level and insulin response in subjects with noninsulin-dependent diabetes mellitus (21, 22) and insulin-dependent diabetes (23). However, because fructose is a nutritive sweetener and because dietary fructose conversion to glucose in the liver requires insulin in the same way as dietary glucose or sucrose, recommendations for its use are the same as for other nutritive sugars (24). Review of the health effects of dietary fructose is available (25).

Fructose has in the 1990s been successfully incorporated into formulas for the preparation of light and reduced calorie beverages and sports beverages; table syrup and table top sweeteners; baked goods; dairy products, including yogurt and chocolate milk; jams, jellies, and preserves; dry mix beverages, puddings, gelatins, and cake mixes; confectionery caramel fillings and starch-based jelly candies; and frozen dairy products and novelties (see Food processing).

Because of its hygroscopicity, fructose must be properly dried, packaged, and stored to prevent lumping and preserve free-flowing handling. Recommended storage and bulk handling conditions call for conditioned air at a relative humidity of less than 50% and a maximum temperature of 24°C (9).

2. Maltose

Maltose [69-79-4] (malt sugar) is a disaccharide, 4-*O*-α-D-glucopyranosyl-D-glucose **(3)**, comprising two molecules of glucose (dextrose). Although occurring in some plants and fruits (26, 27), it is more frequently recognized as a structural component of starch. Pure maltose is isolated with difficulty from a directed starch hydrolysate, ie, high maltose corn syrup, by precipitation with ethanol. Purification can be achieved by way of the β-maltose octaacetate. Removal of the acetate groups allows crystallization of the monohydrate of β-maltose. Commercial maltose typically contains 5–6 wt % of the trisaccharide maltotriose with traces of glucose (28). High maltose syrups from starch typically contain ca 8–9 wt % glucose, 40–80 wt % maltose, with higher saccharides as the remainder (29, 30).

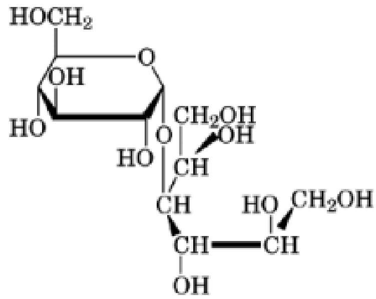


(3)

Such syrups are used in the preparation of confections, preserves, and other foodstuffs. The maltose in malt syrups is important in brewing (see Beer). Intravenous feeding (primarily in Europe and Japan) and sports beverage formulations take advantage of the fact that energy release from maltose becomes accessible to the body at a slower rate than energy supplied by monosaccharides (31).

Important physical and functional properties of maltose and maltose syrups include sweetness, viscosity, color stability, humectancy, freezing point depression, and promotion of beneficial human intestinal microflora growth. Maltose possesses ca 30–40% of the sweetness of sucrose in the pure state (32).

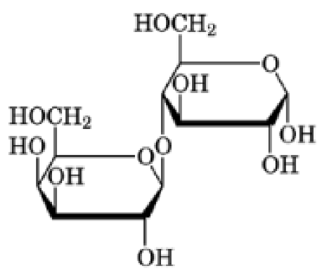
Hydrogenation of high maltose syrups gives a mixture of sugar alcohols, from which maltitol [585-88-6] **(4)** can be isolated in crystalline form. Maltitol is almost as sweet as sucrose (0.9 times) and has been promoted as a sweetener in various food applications (33).



(4)

3. Lactose

Lactose [63-42-3] (milk sugar) is the only commercially available sugar that is derived from animal rather than plant sources. It is a disaccharide consisting of one galactose and one glucose moiety, 4-*O*- β-D-galactopyranosyl-D-glucose **(5)**. The concentration of lactose in milk products ranges from 4.8 wt % in whole milk to 73.5 wt % in sweet dried whey (34). There have been reports of the presence of lactose in plant materials, eg, sapote and acacia, but this has not been confirmed (35, 36).



(5)

Lactose is isolated commercially as the crystalline α-monohydrate from the whey by-products of cheese or caseinate production. It is available in varying degrees of purity. Fermentation grade is 98 wt % pure, whereas USP lactose is refined to 99.8 wt % purity (37). Although the α-monohydrate is the commercially available form of lactose, the sugar can be crystallized at high temperature to give the β-anhydride [56907-28-9]. The sugar is not very soluble in water (ca 22 g/100 g water at 25°C), nor is it very sweet (ca one-fifth the sweetening power of sucrose) (38). Lactose is a reducing sugar that reacts with amines and amino compounds with resultant browning.

Uses of lactose production by application include baby and infant formulations (30%), human food (30%), pharmaceuticals (25%), and fermentation and animal feed (15%) (39). It is used as a diluent in tablets and capsules to correct the balance between carbohydrate and proteins in cow-milk-based breast milk replacers, and to increase osmotic property or viscosity without adding excessive sweetness. It has also been used as a carrier for flavorings, volatile aromas, and synthetic sweeteners. Physiologically, lactose promotes the absorption of calcium, phosphorus, and essential trace minerals; has low cariogenicity; and is more slowly and gradually absorbed than sucrose, therefore of potential benefit to diabetes mellitus patients (38).

Lactose, and the lactose in substances such as milk and whey, has been hydrolyzed commercially by enzymes to yield products that can be tolerated physiologically much more easily by people who have a lactose intolerance (40–42).

BIBLIOGRAPHY

"Commercial Sugars" in *ECT* 1st ed., Vol. 13, pp. 244–251, by J. L. Hickson, Sugar Research Foundation; "Special Sugars" in *ECT* 2nd ed., Vol. 19, pp. 237–242, by J. L. Hickson, International Sugar Research Foundation, Inc.; in *ECT* 3rd ed., Vol. 21, pp. 944–948, by G. N. Bollenback, The Sugar Association, Inc.

Cited Publications

1. C. P. Barry and J. Honeyman, *Adv. Carbohydr. Chem.* **7**, 53 (1952).
2. T. E. Doty and E. Vanninen, *Food Technol. (Chicago)*, **26**, 24 (1975).
3. J. S. White and D. W. Parke, *Cereal Foods World*, **34**(5), 392 (1989).
4. L. M. Hanover, in F. W. Schenck and R. E. Hebeda, eds., *Starch Hydrolysis Products: Worldwide Technology, Production and Applications*, VCH Publishers, Inc., New York, 1992, p. 201.
5. E. Vanninen and T. Doty, in G. G. Birch and K. J. Parker, eds., *Sugar: Science and Technology*, Applied Science Publications Ltd., London, U.K., 1979, p. 311.
6. T. Doty, in P. Koivistoinen and L. Hyvonen, eds., *Carbohydrate Sweeteners in Foods and Nutrition*, Academic Press, New York, 1980, p. 259.
7. W. P. Chen, *Process Biochem.* **15**, 36 (1980).
8. J. S. White, in Ref. 4, p. 177.
9. L. M. Hanover and J. S. White, *Am. J. Clin. Nutr.* **58**(5), 724S (1993).
10. R. S. Shallenberger, *J. Food Sci.* **28**, 584 (1963).
11. D. C. White, *Proceedings of the American Chemical Society Low Calorie Sweetener and Carbohydrate Symposium*, Los Angeles, Calif., 1988.
12. T. E. Doty and E. Vanninen, *Food Technol.* **11**, 34 (1975).
13. P. Van Tornout, J. Pelgroms, and J. Van Der Meeren, *J. Food Sci.* **50**, 469 (1985).
14. U.S. Pat. 4,676,991 (1987), C. K. Batterman, M. E. Augustine, and J. R. Dial (to A. E. Staley Manufacturing Co.).
15. World Pat. 88/08674 (1988), C. K. Batterman (to A. E. Staley Manufacturing Co.).
16. R. D. Spies and R. C. Hosney, *Cereal Chem.* **59**(2), 128 (1982).
17. D. C. White and G. N. Lauer, *Cereal Foods World* **35**(8), 728 (1990).
18. S. D. Horton, G. N. Lauer, and J. S. White, in Ref. 17, p. 734.
19. Eur. Pat. Appl. (Nov. 6, 1979), S. L. Neidelman and W. F. Amon (to Cetus Corp.).
20. *Chem. Week*, 49 (Oct. 7, 1981).
21. S. Akgun and N. H. Ertel, *Diabetes Care*, **8**, 279 (1985).
22. P. A. Crapo, O. G. Kolterman, and R. R. Henry, *Diabetes Care*, **9**, 111 (1986).
23. J. P. Bantle, D. C. Laine, and J. W. Thomas, *JAMA*, **256**, 3241 (1986).
24. American Dietetic Association, *J. Am. Diet. Assoc.* **93**(7), 816 (1993).
25. A. L. Forbes and B. A. Bowman, eds., *Am. J. Clin. Nutr*. **58**(5) (1993).
26. J. H. Pazur, in J. H. Pazur, *The Carbohydrates*, 2nd ed., Vol. **IIA**, Academic Press, New York, 1970, p. 107.
27. R. S. Shallenberger, in H. L. Sipple and K. W. McNutt, eds., *Sugars in Nutrition*, Academic Press, New York, 1974, p. 74.
28. *Maltose Monohydrate*, NRC, Catalog No. M-105, Pfanstiehl Laboratories, Inc., Waukegan, Ill., 1981.
29. H. M. Pancoast and W. R. Junk, *Handbook of Sugars*, 2nd ed., Avi Publishing Co., Inc., Westport, Conn., 1980, p. 178.
30. S. M. Cantor, in Ref. 27, p. 116.
31. I. MacDonald, in Ref. 27, p. 310.

32. M. Okada and T. Nakakuki, in Ref. 4, p. 335.
33. C. A. M. Hough, in C. A. M. Hough, K. J. Parker, and A. J. Vlitos, eds., *Developments in Sweeteners*, Vol. 1, Applied Science Publishers, Ltd., London, 1979, p. 75.
34. T. A. Nickerson, *Food Technol.* (*Chicago*), **32**, 40 (1978).
35. J. H. Pazur, in Ref. 26, p. 104.
36. R. S. Shallenberger, in Ref. 27, p. 71.
37. *Lactose*, Foremost Foods Co., Foremost-McKesson, Inc., San Francisco, Calif., 1970.
38. J. J. Dijksterhuis, in E. H. Reimerdes, ed., *Lactose as a Food Ingredient*, Expoconsult Publishers, the Netherlands, 1990, p. 5.
39. W. A. Roelfsema and co-workers, in B. Elvers, S. Hawkins, and G. Schulz, eds., *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed., VCH Publishers, Inc., Germany, 1990, p. 107.
40. N. S. Shah and T. A. Nickerson, *J. Food Sci.* **439**, 1575 (1978).
41. V. H. Holsinger, *Food Technol. (Chicago)*, **32**, 35 (1978).
42. S. M. Cantor, in Ref. 27, p. 368.

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Related Articles

Carbohydrates; Sweeteners; Syrups; Food processing