SWEETENERS—A REVIEW

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SWEETNESS is a quality of some substances that the human race has always associated with pleasure. A high value has been placed on materials exhibiting sweetness. Honey and fruits have been sought throughout history for their sweet properties; by the 14 century A.D., sugar was being refined. It was regarded, however, as a rare delicacy. Today, one accepts the presence of sugar as being commonplace. Human cravings for sweetness are generally satisfied by beverages, breads, pastries, and confectioneries.

NATURAL SWEETENERS

- Sucrose. In the late 20th century the vastly increased demand for sucrose was met commercially from cane (60%) and beet (40%) sources. Cane and sugar beets are the most agriculturally efficient crops for the production of sucrose. Therefore, as a source of calories, these crops produce more calories per acre than potatoes, corn, or wheat.

Acceptability and palatability of sucrose are unique qualities, along with its ready availability, general low cost, simplicity of production, purity, and long history of usages.

The sweetness of fruits is attributed to the combination of sucrose and its component sugars, glucose and fructose. The high proportions of these sugars in fruits such as grapes and sweet cherries are good reasons for selecting these fruits for yeast fermentations to give wine beverages (Bucke, 1979).

- Corn Sweeteners. During the past two decades the corn sweetener industry has been in an exciting and rapidly developing stage. First, the enzyme technology of glucoamylase was applied to the starch conversion process, giving added economic benefits to dextrose and dextrose syrups. These economics resulted because of the higher starch concentrations that could be used in the process, which required less steam in subsequent evaporation steps. Furthermore, higher yields of dextrose were produced along with a product having greater purity (Inglett, 1963).

The second enzyme technology applied to the corn sweetener industry was the application of glucose isomerase in immobilized forms. Glucose isomerase catalyzes the conversion of dextrose to fructose. For the first time, this conversion allowed the dextrose industry to produce fructose. Fructose was previously an expensive sugar derived from sucrose. The dextrose industry had long suffered from low-level sweetness in their dextrose syrups; it is now possible to make sweeter dextrose syrups because of the presence of fructose introduced by glucose isomerization. Isomerized dextrose syrups are called high-fructose corn syrups.

- High-Fructose Corn Syrups. High-fructose corn syrups (HFCS) first commercially produced in the early 1970s were composed of 42% fructose, 52% dextrose, and 6% higher saccharides in a syrup containing 71% solids.

The 42% fructose syrup is manufactured from starch. In the United States, corn starch is used as the starting material. The corn starch in water is continuously liquefied with alpha-amylase at elevated temperatures. This liquefied hydrolysate has a dextrose equivalent (D.E.) in the range of 90 to 95%. The saccharified liquor is refined by filtering to remove insolubles, with subsequent carbon and ion exchange treatment. The refined dextrose solution is isomerized by passing it through reactors containing immobilized glucose isomerase. The solution from the reactors, with a fructose content of approximately 42%, is refined with carbon and ion exchange before being concentrated to about 71% solids.

Some applications for 42% HFCS are in soft drinks, yeast-raised baked goods, frozen desserts, canned fruits, jams, jellies, salad dressings, and confections.

Second generation high-fructose corn syrups contain fructose from 55% to 90% of the total solids. A 55% HFCS contains 55% fructose, 40% dextrose, and 5% higher saccharides in a syrup of 77% total solids. The 90% HFCS syrup contains 90% fructose, 7% dextrose, and 3% higher saccharides in a syrup containing 80% total solids. These products have been available since 1976 and are prepared by fractionation of the 42% fructose syrups.

The major uses of 55% HFCS are in soft drinks, salad dressings, frozen desserts, canned fruits, jams, jellies, and breakfast cereals.

The 90% HFCS is finding applications in “light” foods and beverages. Fructose has a variable sweetness value, generally between 110 and 170% greater than sucrose, depending on the type of materials, concentrations, flavor, temperature, and pH of the food and beverage. Under some situations, smaller quantities of fructose can give sweetness values equivalent to larger quantities of corn and sucrose sweetness. In other words, a reduced quantity of 90% HFCS may be used to achieve the same level of sweetness in the final food, which results in a lower calorie product.

The 90% HFCS is used in soft drinks (full calorie and reduced calorie), salad dressings, jams, jellies, table syrups, wines, low-calorie frozen yogurts, and desserts.

SWEET POLYHYDRIC ALCOHOLS

Sweet polyhydric alcohols include such sweeteners as sorbitol, mannitol, maltitol, and xylitol. These materials impart low levels of sweetness when compared to many of the intense sweeteners, but the individual polyhydric alcohols can be considered desirable for specific applications in foods. In the case of xylitol, it can be considered an aid to dental health. —Continued on next page
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INTENSE SWEETENERS OF NATURAL ORIGIN

Many people around the world use intensely sweet plant materials of natural origin to sweeten foods; also, these plant parts are used for medicinal purposes in the daily lives of some societies. Intense sweetness of natural origin is tasted in these societies today as it has been done throughout the ages (Inglett, 1976).

- **Phyllodulcin.** A sweet tea, Amacha, is served at Hanamatsuri, the flower festival celebrating the birth of Buddha. Amacha is the dried leaves of *Hydrangea macrophylla* Seringe var. *Thunbergii* Makino. The sweet principle, phyllodulcin, was isolated, and its absolute configuration was shown to be the 3R configuration at the asymmetric center at C(3) by identification of a malic acid from ozonized phyllodulcin. Recently, an analog of phyllodulcin, 2-(3-hydroxy-4-methoxyphenyl)-1,3-benzodioxan, was found to be intensely sweet (Dick and Hodge, 1978).

- **Stevioside.** The sweet herb of Paraguay (Yerba dulce) has long been the source of an intense sweetener. Natives use the leaves of this small shrub, *Stevia rebaudiana* (Bert.) Hemsl, to sweeten their bitter drinks. The sweet, crystalline glycoside extracted from the leaves of *S. rebaudiana* is named stevioside.

Also from the leaves of *Stevia rebaudiana*, two sweet glucosides, rebasiosides A and B, were isolated besides the known glucosides, stevioside and steviolbioside. On the basis of IR, MS, IH and 13C NMR, as well as chemical evidences, the structure of rebasioside B was assigned as 13-O-[1-3]-,8-glucosyl-1β-D-glucosyl-(1-3)-,8-D-glucosyl-steviol, and rebasioside A was formulated as its β-glucosyl ester (Kohda et al., 1976).

- **Glycyrrhizin.** Licorice, well known for centuries and widely used, is obtained from the roots of *Glycyrrhiza glabra*, a small shrub grown and harvested in Europe and Central Asia. The roots contain from 6 to 14% glycyrrhizin.

Glycyrrhizinic acid exists in licorice root as the calcium-potassium salt in association with other constituents (Nieman, 1957). Glycyrrhizinic acid is a glycoside of the triterpene, glycyrhetinic acid, which is condensed with o-β-D-glucuronosyl-(1→2)-β-D-glucuronic acid. The absolute configuration of the aglycone, glycyrhetinic acid, is determined as the result of investigations too numerous to cite completely. Important contributions were made by Ruzicka et al. (1943); Voss and Butter (1937); Voss et al. (1937A, 1973B); and Beaton and Spring (1955). Although two isomers (18α and 18β) have been isolated, Beaton and Spring indicated that 18β-glycyrrhetinic acid is the only natural isomer that occurs in glycyrrhizin.

The extracts are universally employed in the flavoring and sweetening of pipe, cigarette and chewing tobaccos, and they are regularly used in confectionery manufacture. Some segments of the flavor industry long have utilized these extracts in root beer, chocolate, vanilla, liqueur, and other flavors. Ammonium glycyrrhizin (AG), the fully ammoniated salt of glycyrrhizic acid, is commercially available. Further treatment and repeated crystallizations yield the more costly, colorless salt, monoammonium glycyrrhizinate (MAG). Both derivatives have the same degree of sweetness, but they differ markedly from each other in solubility properties and sensitivity to pH. AG is the sweetest substance on the FDA list of natural GRAS flavors and is 50 times sweeter than sucrose.

- **Lo Han Fruit (Momordica grosvenorii) Swingle.** Lo Han Kuo (Lo Han fruit), from *Momordica grosvenorii* Swingle, is a dried fruit from Southern China. The brownish-gray pulp dries to a light fibrous mass. Swingle (1941) also reported that 1,000 tons of the green fruits were delivered every year to the drying sheds at Kwailin (Kwangsi Province). The dried fruit is a valued folk medicine used for colds, sore throats, and minor stomach and intestinal troubles. Lee (1975) found that the sweet principle could be extracted by water either from the fibrous pulps or from the thin rinds of Lo Han Kuo; 50% ethanol was also found to be a good extractant. Rinds afforded a more easily purified extract. Sweetening by Lo Han fruit was accompanied by a lingering taste described as licorice-like, somewhat similar to that of stevioside, glycyrrhizin and the dihydrochalcones. Structural studies indicated the sweetener to be a triterpenoid glycoside with 5 or 6 glucose units (Lee, 1977). The purified sweetener has a more pleasant sweet taste than the impure material. The purest sample is about 400 times sweeter than sucrose.

- **Osladin.** The sweet taste of rhizomes of the widely distributed fern, *Polypodium vulgare* L., has attracted the interest of many chemists and pharmacists. Osladin comprises only 0.03% of the dry weight of the rhizomes; its chemical structure has been revealed as a bis-glycoside of a new type of steroidal sapogenin (Jizba et al., 1971A). The glycoside that results from replacement of the monosaccharide radical with hydrogen was isolated separately and named polypodosaponin. Its absolute configuration was determined by Jizba et al. (1971B). The disaccharide of osladin was shown to be neohesperidose, 2-O-α-L-rhamnopyranosyl-β-D-glucopyranose.

PROTEIN SWEETENERS

Substances having sweet taste are known that vary immensely in their organic chemical structures. Sugars, sugar alcohols, and some amino acids are well recognized for their sweet taste, but only in the last decade has a new class of sweeteners from nature, the proteins, been found to be sweet. The intensity of their sweetness is surprising; all are more than 1,000 times sweeter than sucrose.

- **Miracle Fruit (Synsepalum dulcificum).** An important approach to sweet taste perceptions is the study of the strange properties of the miracle fruit (*Synsepalum dulcificum*). Although the miracle fruit’s capacity to cause sour foods to taste sweet has been known in the literature since 1852, scientific investigations of the fruit were not initiated until Inglett and his associates found some experimental evidence that the active principle was macromolecular (Inglett et al., 1965). This berry possesses a taste-modifying substance that causes sour foods such as lemons, limes, grapefruit, rhubarb, and strawberries to taste delightfully sweet. The berries are chewed by West Africans for their sweetening effect on some sour foods. The taste-modifying principle was independently isolated by two different research groups (Kurilhara and Beidler, 1968, Brouwer et al., 1968). Kurilhara and Beidler (1968) separated the active principle from the fruit’s pulp with a carbonate buffer (pH 10.5). The destruction of the active principle by trypsin and pronase suggested its proteinaceous character. The taste-modifying protein was also separated from the fruit’s pulp with highly basic compounds, salmine, and spermine (Brouwer et al., 1968).

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The basic glycoprotein has a molecular weight between 42,000 and 44,000. The purified glycoprotein has no inherent taste. Sweetening of acid taste, observed at $5 \times 10^{-3}$ M concentration of the glycoprotein solution, reached a maximum at $4 \times 10^{-3}$ M and slowly declined over a period up to 2 hr.

- Serendipity Berries (Dioscoreophyllum cummin-si Diels). While studying various natural sweeteners previously mentioned, the author discovered the intense sweetness of some red berries indigenous to tropical West Africa. The fruit was called the serendi-pity berry, and its botanical name, Dioscoreophyl­lum cumminsi, was established many months later (Inglett and Findlay, 1967, Inglett and May, 1968, 1969, Inglett, 1974).

Researchers at the Monell Senses Center (Philadelphia, Pa.) and the Unilever Research Laboratory (The Netherlands), working independently, confirmed the protein nature of the serendipity sweetener (Morris and Cagan, 1972, van der Wel, 1972). Amino acid composition of monellin was determined by van der Wel and Loewe (1973) and Morris et al. (1973). The most outstanding observation is the complete absence of histidine. Monellin is composed of two dissimilar polypeptide chains with known amino acid sequences that are noncovalently associated (Bohak and Li, 1976). The sweetness of monellin is approximately 2,500 times sweeter than sucrose on a weight basis. The molecular weight of the sweetener is 11,000.

- Katemfe (Thaumatococcus danielli). Besides studies on miracle fruit and the serendipity berry, a large variety of plant materials were examined systematically by Inglett and May (1968) for intensity and quality of sweetness. Another African fruit containing an intense sweetener was katemfe, or the miraculous fruit of the Sudan. Botanically the plant is Thauma-tococcus danielli of the family Marantaceae. The mucilaginous material around the aril at the base of the seeds is intensely sweet and causes other foods to taste sweet. Katemfe yields two sweet-tasting proteins, which are called thaumatin I and II (van der Wel and Loewe, 1972, van der Wel, 1974).

The purified sweetener is 1,600 times sweeter than sucrose at 7% concentration. Thaumatin I contains 193 amino acids (van der Wel and Loewe, 1972, van der Wel, 1974). Polyacrylamide gel electrophoresis in the presence of sodium dodecyl sulfate indicated that the protein is a single polypeptide chain with alanine as the N-terminal amino acid. Thaumatin I was crystallized, and physical characteristics and diffraction data of the crystals were obtained (van der Wel et al., 1975). A process for extraction of the thaumatins from the fruit was reported (Higginbotham, 1977) and commercial interest in this sweetener is developing (Higginbotham, 1979). Tate and Lyle Limited, in England, is marketing the sweetener under the name Talin. In addition to its sweetener value, it also has flavor potentiator utility. Large purchases of Talin have been made by at least two Japanese companies.

SYNTHETIC SWEETENERS

A variety of synthetic compounds have been prepared that have intense sweetness. Saccharin was discovered in 1879, which means that the history of synthetic sweeteners is slightly over 100 years old. It still survives as the only synthetic sweetener allowed in food in the United States for specific uses and levels. Progress in the development of synthetic sweetener uses was especially active between 1950 to 1969 when saccharin and cyclamate were both approved for use. The sweetness of saccharin-cyclamate blends was well perceived in soft drinks, which made these sweeteners particularly attractive and widely used. Cyclamate production reached a peak rate of 21 million pounds per year in the U.S.A. prior to being banned by the FDA in 1969. Some of the synthetic sweetener candidates being explored for filling intense sweetener needs in the U.S. market are discussed as follows.

- Peptide-Based Sweeteners. Similar to the accidental discovery of the sweetness of saccharin and cyclamate, the sweetness of L-asparyl-L-phenylala-nine methyl ester, also called aspartame (Mazur, 1974), was discovered by accident in the laboratories of G. D. Searle (Skokie, Ill.) in 1965. Many L-amino acids were substituted for aspartic acid and phenylalanine, and aspartic acid was shown to be required for sweetness. The taste of aspartame could not have been predicted from its constituent amino acids. L-phenylalanine is bitter and L-aspartic acid is flat.

<table>
<thead>
<tr>
<th>Sweetener</th>
<th>Sweetness* (sucrose = 1)</th>
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<tbody>
<tr>
<td>D-Saccharin</td>
<td>100</td>
</tr>
<tr>
<td>Cyclamate</td>
<td>80-150</td>
</tr>
<tr>
<td>Neohesperidin dihydrochalcone</td>
<td>150</td>
</tr>
<tr>
<td>L-Phenylalanine</td>
<td>300</td>
</tr>
<tr>
<td>L-Aspartic acid</td>
<td>100</td>
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</tbody>
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When these amino acids are properly combined and the phenylalanine carboxyl is converted to a methyl ester, a sucrose-type sweet product results. Its sucrose-like sweetness allows it to blend well with other food flavors. The sweetness of aspartame is inversely related to the concentration of sucrose. At 3% sucrose, aspartame is 215 times the sweetness of sucrose, but it is only 133 sweetness potency at 10% sucrose concentration.

**Dihydrochalcone Sweeteners.** Citrus peels contain flavonoids that can be converted by simple chemical modification to dihydrochalcones. Horowitz and Gentili discovered that neohesperidin from the peel of the “Seville” orange gave an intensely sweet glycoside of dihydrochalcone upon alkaline hydrolysis. Naringin from grapefruit peel also was found to give a sweet tasting dihydrochalcone (Horowitz and Gentili, 1963). Following these discoveries, a large number of analogs were prepared for structure-taste study. Some of the most interesting analogs, prepared by Krcherchek et al. (1968), involved substituting the methoxyl of the isovanillin group with ethoxyl and propoxyl groups.

Recent analogs prepared at Dynapal (Palo Alto, Calif.) have shown that the structural elements of the dihydrochalcone responsible for inducing the taste response reside entirely on the aromatic nucleus. Non-glycoside dihydrochalcone derivatives were prepared having 4-carboxyalkyl and 4-sulphoalkyl substituents (DuBois et al., 1977). They contained an intense sweetness that compared favorably with neohesperidin dihydrochalcone.

**Acesulfame-K.** Acesulfame-K is the potassium salt of 3,4-dihydro-6-methyl-1,2,3-oxathiazin-2,2-dioxide, which is a derivative of acetoacetic acid. This substance has some structural similarity to saccharin and represents one of the newest classes of intensely sweet substances. The sensory properties of acesulfame-K are similar to saccharin. The sensory potency is roughly 130 times sucrose at a 4% sucrose concentration (Crosby and Wingard, 1979). Hothect AG (Frankfurt, West Germany) is working on the applications of this sweetener. Hothect AG reports that toxicological evaluations of acesulfame-K have been completed successfully (Gruettemann, 1981).

**Other Synthetic Sweeteners.** Perillartine is a naturally occurring aldoxime present in the oil of *Perilla namkemonis* Deone. Aldoxine analogs have been synthesized, and some are claimed to be superior to perillartine (Crosby and Wingard, 1979). The relative sweetness of a wide variety of organic chemicals are summarized and updated in Table 1 (Crosby and Wingard, 1979; Beck, 1974).

**References**


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The mention of firms and trade names does not imply that they are endorsed or recommended by the USDA over other firms or similar products not mentioned.