IT SEEMS UNUSUAL that a compound first isolated from the bark of the larch tree over a century ago could have such a powerful impact on the food flavoring industry and lead to the synthesis of an even more powerful homolog. But such was the case with maltol.

The compound known as maltol was found to enhance or modify the flavor and aroma of foods and beverages for heightened consumer appeal. Its demand eventually surpassed the capacity to isolate it from natural sources, and so now maltol is produced synthetically. A related compound, ethyl maltol, was introduced to the food industry several years after the shift to chemically produce maltol. When compared to maltol, it has qualitatively similar yet much improved flavor- and aroma-enhancing capabilities.

This article will review the history, production, and application of these two successful food additives.

History

In 1861, maltol was first isolated from the bark of the larch tree (Pinus larix, Linn.) by the British chemist J. Stenhouse (1861, 1862) during his investigations on the chemistry of tanning. The larch was considered at that time to be a pine and its scientific name provided Stenhouse the basis for naming this substance larixinic acid. Stenhouse obtained larixinic acid from larch bark by water extraction, evaporation, and crystallization, followed by sublimation which purified the substance. Care had to be taken to prevent exposure of larixinic acid to iron or iron salts and avoid the formation of a deep-purple-colored liquid, from which it could not be recovered. Physical properties such as melting point, sublimation temperature, and crystalline geometry provided Stenhouse with evidence to distinguish larixinic acid from substances that had been previously isolated from plants. Stenhouse concluded that larixinic acid existed in the bark and was not a product of the isolation procedure. An interesting feature in Stenhouse's original publication was an error in the empirical formula of larixinic acid due to confusion concerning the composition of water (which was thought to be HO) and relative atomic masses. When Stenhouse's combustion data is used with the correct water formula and relative atomic mass values, the empirical formula of larixinic acid (maltol) results. Stenhouse was the first to comment on its pleasant odor (at room temperature) and its slightly bitter and astringent taste in pure form. A description based on taste during Stenhouse's period was considered part of the procedure for characterizing new substances.

In the late 1800s, the brewing industry introduced a caramel-colored malt, which contained a higher sugar content than ordinary malts. The beer prepared from this malt gave a violet color with ferric chloride. The causitive agent, originally thought to be salicylic acid, was determined by Brand (1894) to be a substance other than salicylic acid. This crystalline substance that reacted with ferric chloride to produce the violet color was recovered from malt by sublimation. In spite of a negative reaction with Millon's reagent (a test for phenols such as salicylic acid), its possession of a positive ferric chloride test for phenols and its isolation from malt provided Brand with the basis for naming this substance maltol. Brand showed that maltol was produced during the roasting process in malt production. The correct molecular formula of C₆H₆O₃ for maltol was determined by Brand who suspected that this formula resulted from the loss of three molecules of water from glucose (or any other hexose). Brand suggested that maltol was 3,6-dihydroxy-7-oxabicyclo[2.2.1]hepta-2,5-diene.

Shortly after Brand's discovery of maltol, Kiliani and Bazlen (1894) oxidized maltol with potassium permanganate and observed water, carbon dioxide, and acetic acid as products. They observed that only one acidic hydrogen and just the monoacyl derivative of maltol could be formed. These observations required the existence of only one hydroxyl group and a methyl group in the structure of maltol, thereby excluding the structure proposed by Brand. By comparisons made with the chemistry of pyrroleconic acid, Kiliani and Bazlen deduced that maltol must be a methylpyrroleconic acid.

Several years later, Feuerstein (1901) isolated a...
Maltol and Ethyl Maltol (continued)

substance from the needles of the silver fir (*Abies alba*, Mill.) and found it to be identical with maltol. This latter observation soon led to the conclusion by Peratoner and Tamburello (1903) that maltol was larixinic acid. Peratoner and Tamburello (1905) later went on to hydrolyze the methyl derivative of maltol with barium hydroxide and analyze the products recovered. In addition, derivatives of maltol were compared with those of pyromeconic acid and it was concluded that the 2-methyl derivative of pyromeconic acid was maltol (3-hydroxy-2-methyl-4-pyrene).

**Formation**

Maltol occurs naturally in certain conifers, but it also forms when certain disaccharides are heated (pyrolysis). Maltol has been identified in a wide variety of heated materials such as bread crusts, coffee and cocoa beans, cereals, dried whey, soy sauce, and chicory (Ensminger et al., 1983). Maltol (1905) later went on to hydrolyze the methyl group. A compound isomeric with maltol, thus called ethyl maltol (on the model of ethyl vanillin) was produced (Rennhard, 1971). To date, ethyl maltol has not been observed as a naturally occurring substance (Freydberg and Gortner, 1982). Pfizer produces and markets maltol and ethyl maltol under the trade names of Veltol and Veltol-Plus, respectively. The most significant foreign producers include Firmenich Inc. of Geneva, Switzerland, who several years ago marketed the maltols under the name Corps Praline, and Otsuka Chemical Co., Osaka, Japan, who currently markets these compounds under the trade name Piromaltol and Ethyl Pyromaltol (Stettler, 1988).

The increase in flavor enhancement properties (see below) in the maltol to ethyl maltol transition is analogous to the increase in vanilla-like flavor of ethyl vanillin over vanillin (Hodge, 1967). Vanillin, the naturally occurring substance responsible for the flavor/odor of vanilla, contains a methoxy group; ethyl vanillin, a component of most synthetic vanilla preparations, contains the ethoxy group.

A compound isomeric with maltol, thus called isomaltol, has also been found to contribute to the odor/flavor of baked goods (Hodge and Moser, 1961). Many aspects of the history of this compound are similar to that of maltol, including a publication reporting an incorrect structure (Backe, 1910). The correct structure, 3-hydroxy-2-furyl methyl ketone, has appeared in the literature (Fischer and Hodge, 1964).

**Properties**

Maltol and ethyl maltol are both slightly acidic substances that form salts with bases. Both compounds are white, crystallize readily, have low melting points, and sublime at room temperature. They possess a cotton candy, caramel-like aroma. The sublimation of these compounds is significant because they are responsible, in part, for their aroma and odor-altering properties. Better retention of maltols is provided if packaging and storage is in tight, inert containers. Ethyl maltol sublimes more readily and has a greater solubility in water than maltol, a factor which might account for its greater flavor-enhancing activity. Because both substances are chelators and readily form complexes (many are colored) with metals, care should be taken to ensure that the maltols or products composed of them are not packaged in certain containers made of metals or some grades of stainless steel; glass or plastic containers are more suitable (Pfizer, 1977). Judging from nuclear magnetic resonance data,
Maltol and Ethyl Maltol (continued)

Maltol exhibits some aromatic character (Lassack and Pinhey, 1968).

Consumption and Toxicity

Maltol and ethyl maltol are added to foods in minute amounts. In 1970, the average daily intake per person in the U.S. of maltol and ethyl maltol was estimated at 0.4 and 0.3 mg, respectively. Combined, this corresponds to about 0.01 mg/kilogram of body weight for a person who weighs 60 kg (Freydberg and Gortner, 1982).

Studies indicated that ethyl maltol was slightly more toxic than maltol when administered as a single dose to laboratory animals. In repeated doses, however, the opposite was true. When maltol was fed to rats (dogs) at the rate of 1,000 (500) mg/kg/day, there was significant body weight depression, kidney damage, and death among the different individual test animals. Ethyl maltol at the same dosage caused no significant effects to either animal type except for a mild weight loss. Ethyl maltol was fed daily to rats and dogs up to and including 200 mg/kg/day for as long as two years without any adverse toxic effects. The animals mated and no effects on the fertility or offspring development were noted. Neither compound produced any allergic reaction or sensitization (Gralla et al., 1969). The metabolic fate of maltol and ethyl maltol has been investigated in the dog. Orally dosed animals readily absorbed the materials from the gastrointestinal tract; neither substance was detected in the feces after oral dosing. Within 24 hours of an orally or intravenously administered dose, both substances were rapidly metabolized and excreted in the urine as glucuronide and sulfate derivatives. These metabolic fates are both common to exogenous phenols and related compounds (Rennhard, 1971).

The U.N. Joint FAO/WHO Expert Committee on Food Additives concluded that up to 2 mg/kg/day (120 mg/day for a 60 kg person) was an acceptable level of consumption of ethyl maltol for humans. This value is many times greater than the current average consumption levels for both compounds (Freydberg and Gortner, 1982).

Both compounds are included in a list proposed by the Flavor and Extract Manufacturers’ Association (FEMA) as substances generally recognized as safe (GRAS) for use in foods. Maltol and ethyl maltol have been given the following respective FEMA (or GRAS) reference numbers: 2656 and 3467. The Food and Drug Administration (FDA) includes both compounds in its list of “synthetic flavoring substances and adjuvants” that are safe for use in foods. The Bureau of Alcohol, Tobacco, and Firearms claims that both compounds can be safely added to alcoholic beverages if amounts do not exceed 100 ppm for use as a stabilizing agent or 250 ppm for use as a smoothing agent. Typically, maltol is added to foods at levels ranging from 50 to 200 ppm while ethyl maltol is added at amounts corresponding to the range of 1 to 50 ppm (Pfizer, 1977).

Applications

At the recommended concentrations, the maltols do not contribute a flavor of their own but modify or enhance the inherent flavors of the foods to which they are added. Their diversity of action in modifying flavors offers a variety of routes to the production of new food products with unusual flavor sensations (Pfizer, 1977). The actual mechanism for the flavor-modifying effects of the maltols is unknown (Lindsay, 1985) so food flavor research must proceed in the future in an empirical manner.

Pfizer states that maltol creates a “velvet mouth” sensation, especially in sweet foods (Anonymous, 1962). The commercial trade name “Vel-tol” might have originated as a contraction of velvet-maltol, which is reminiscent of Brand’s original malt-phenol combination suspected of producing maltol’s name.

Maltol, a potent enhancer, replaced flavor and aroma enhancers which were not as effective in low concentrations. Coumarin, an enhancer widely used in the past, had to be cautiously added so that its powerful natural aroma, resembling that of vanilla beans, would not overpower the desired enhancing qualities. Maltol could easily replace four times its weight of coumarin (Stephens and Allingham, 1968). Since 1954, coumarin has been classed by the FDA as a toxic substance and subsequently was banned as a food additive. Because of its effectiveness and lack of toxicity, maltol filled the void left by the demise of coumarin.

Tests conducted by Pfizer (1977) and independent groups have shown that ethyl maltol is two to six times more effective as a flavor enhancer than maltol. In addition, effects not possible to achieve with maltol are observed with ethyl maltol because of its effectiveness at such low concentrations (Pfizer, 1977). Upon realization that the relative costs per weight of maltol and ethyl maltol are comparable, it becomes apparent that ethyl maltol is a more economical and convenient flavor enhancer than maltol (Stephens and Allingham, 1968).

The maltols may be added to the food or perfume directly in a dry form or as a solution. Care must be taken to evenly distribute the additive in the final product because minute quantities have such a powerful effect (Stephens and Allingham, 1968).

The greatest application of maltol, and later ethyl maltol, it was discovered, was in synthetic berry and citrus fruit flavorings. These additives intensify and produce the characteristic fruity flavors of strawberry and raspberry in fruit-flavored drinks and enhance the flavors of orange, pineapple, and black cherry as well. They have been used along with sodium citrate and sodium gluconate to minimize the bitter aftertaste of the artificial sweetener saccharin, used in dietetic products. The maltols are added to other beverages which improve in overall flavor and aroma such as grape and apple juice, fortified wines (port, tokay, muscatel, and sherry), liqueurs (cordial and bran-
Maltol and Ethyl Maltol (continued)

A Call to Consumers

The maltols have outlasted other food additives, because, in addition to being powerfully effective at low concentrations, they have unique flavor- and aroma-enhancing properties. As long as consumers search for food products possessing an attractive flavor and aroma, there will be a demand for these two successful food additives, and as food producers are aware, any food product having a wider consumer acceptance will show an increase in sales.

References


Stenhouse, J. 1862. On Larixinic acid, a crystallizable volatile principle found in the bark of the larch tree (Pinus larix, Linn.). Phil. Trans. 53.

Stenhouse, J. 1862. On Larixinic acid, a crystallizable volatile principle found in the bark of the larch tree (Pinus larix, Linn.). Phil. Trans. 53.


The authors would like to thank Dr. H.H. Rennhard and B.O.G. Schueler for their interest and help with this literature investigation.

—Edited by Donald E. Pszczola, Assistant Editor