Thermally Induced Flavor Compounds

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Given the number of recent reviews on flavor chemistry (Acker et al., 1990; Berger, 1995; Mathlouthi et al., 1993; Schab and Crowder, 1995; Shallenberger, 1993; Spielman and Brand, 1995), especially relative to thermally generated volatiles such as those produced via the Maillard reaction (For, 1983; Ikan, 1996; Mottram, 1994; Parliment et al., 1994; Whitfield, 1992), we have confined our review to a critique of chemical components and reactions modulating flavor, touching upon how thermally derived flavors overlap into the sphere of horticulture. Why would horticulturists be even remotely interested from a professional standpoint in the flavor of cooked products? Isn't this really the realm of food scientists or food chemists, i.e., changes in food products during or after cellular death?

Thermally generated flavors are in fact a relevant horticultural topic. First, flavors of most horticultural food products are largely generated during cooking. Vegetable crops, for example, are usually cooked before they are eaten [e.g., 370 of 390 commercially cultivated vegetable crops from around the world are routinely to intermittently cooked (Kays and Silva Dias, 1996)], and cooking significantly alters their flavor. In addition, although fruits tend to be thought of as eaten raw, a major portion of the total production is processed (Table 1). In many cases, processing involves a thermal treatment, which alters the flavor of the final product. Therefore, a major portion of horticultural food crops are cooked and much of their final flavor is the result of cooking.

Second, the eventual cooked flavor of such products varies with the chemistry of the product and how it is handled prior to cooking. There are many examples of differences in flavor among cultivars of a particular fruit or vegetable. The basic chemistry of the fruit or

Table 1. Total U.S. production of several fruits in 1995 and their use.[z]

Crop	Total production (kt)	Used fresh (%)	Processed[y] (%)
Apple (*Malus* ×*domestica* Borkh.)	5665.5	56.2	43.8
Cherry (sour) (*Prunus cerasus* L.)	150	0.9	99.1
Peach [*Prunus persica* (L.) Batsch.]	1119	50.9	49.1
Pear (*Pyrus communis* L.)	943.5	58.6	41.4

[z] 1994 data (U.S. Dept. of Agriculture, 1997).

[y] Canned, dried, frozen, juiced—processes generally involving thermal treatments.

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vegetable as it arrives from the field largely dictates the subsequent flavor potential of the product. Thus, alteration of the basic flavor of a product is a plant breeding problem in that food scientists can only optimize the existing flavor potential.

Flavor perception. The sensory characteristics of foods can be loosely grouped into three categories: flavor, texture, and appearance. Flavor, in particular, plays a major role in both our selection and enjoyment of foods, and is generally considered to be the combination of taste and odor. Flavor perception can also be significantly influenced by heat, pain, and tactile sensations.

The flavor of an individual food product is derived from the collective mosaic of numerous compounds that impact odor and taste. It is important to note that a taste or odor is not an inherent property of a specific compound but is the physiological and psychological assessment of the individual sensing it. Therefore, the same compound can be perceived differently by different individuals or by the same individual at different times. Interactions among stimuli may occur at the taste bud/olfactory level or at signal processing in the brain (Thomson, 1986).

The flavor quality of food, therefore, is more than just odor and taste; it is a complex pattern that has different critical characteristics depending upon the food (Thomson, 1986). In contrast to visual or auditory sensations, flavor has a complex sensory basis involving receptors in both the oral and nasal cavities. These receptors include cells sensitive not only to taste and odor but also to pressure, touch, stretch, temperature, and pain (Moulton, 1982). Although odor and taste are well integrated in their contribution to the overall flavor, odor is often considered to play a dominant role in flavor delineation. This is, in part, due to the number of odor receptors and their ability to discriminate among odors. For example, the ability to identify the flavors of molasses, whiskey, salt, and sugar are superior with odor cues than without (Mozell et al., 1969). Thus, the uniqueness of many flavor substances appears to rely upon their ability to stimulate the olfactory organ. Because of the distinct differences between taste and odor, this review is separated into sections on taste and odor, followed by an overview of how flavor chemistry can be modified through plant breeding.

Taste. Taste is a sensation assessed through the contact of water-soluble compounds with the mouth and tongue. Four primary taste sensations are widely accepted: sweet, sour, salt, and bitter, though alkaline and metallic are considered by some as important in taste responses (Moncrieff, 1967). The sensation of taste is achieved through taste buds, which are distributed over the tongue and in certain areas of the buccal cavity. The number of taste buds in humans is estimated to be ≈4500 (Miller et al., 1990), with individual buds consisting of ≈15 to 18 receptor cells. The taste buds are located within specialized structures called papillae, found mainly on the tip, sides, and rear of the upper surface of the tongue (Thomson, 1986).

Of the primary taste sensations, the taste threshold concentration on a molar basis varies considerably (Table 2). When ranked, giving sucrose a value of 1.0, perception sensitivity proceeds from bitter > sour > sweet > salty (Pfaffmann et al., 1971). For example, quinine sulfate (bitter) can be perceived at 8×10^{-6} M while potassium chloride (salty) requires 1.7×10^{-2} M. Within categories, the threshold concentration varies among compounds (Table 2). In addition, a single compound can elicit more than one taste sensation. Sodium chloride is sweet at low (e.g., 0.020 M), but salty at higher (0.050 M) concentrations. Such interactions can greatly complicate the quantification of taste.

Table 2. Molar recognition thresholds of individual compounds and relative activity ranking of taste sensations.[z]

Taste	Compound	Median taste threshold (mM)	Relative activity[y]
Sweet	Sucrose	17	1.0
	Sodium chloride	20	
Salty	Sodium chloride	30	0.6
	Potassium chloride	17	
Sour	Hydrochloric acid	0.09	18.8
	Acetic acid	1.8	
Bitter	Quinine sulfate	0.008	
	Caffeine	0.7	24.3

[z] After Pfaffmann et al. (1971).

[y] Activity relative to sucrose.

Taste is dominated by sugars, acids, several amino acids, and nucleotides, salts, and a number of bitter compounds (Maga, 1990). Often these are present prior to cooking. There are, however, cases where distinct taste compounds are formed during cooking. For example, some of the Maillard reaction products impact taste. Perhaps a classic example of the synthesis of taste components upon cooking is the sweetpotato [*Ipomoea batatas* (L.) Lam.], in which a major portion of the final sugar concentration develops during exposure to high temperatures (Sun et al., 1994).

a. Sweetness. Sugars are the most widespread form of sweet compounds found in plant products, and in recent history man has selected certain species that have the ability to synthesize and store large quantities; e.g., sugar cane (*Saccharum officinarum* L.) and sugar beet (*Beta vulgaris* L. Vulgaris Group). A relatively wide range of sugars is present in plants, and the individual sugars vary substantially in both concentration and relative sweetness. The common sugars (L-form) are ranked in the following order of sweetness: fructose (1.2) > sucrose (1.0) > glucose (0.64) > galactose (0.5) > maltose (0.43) > lactose (0.33) (Shallenberger, 1993). A number of the amino acids [i.e., L forms of alanine, isoleucine, leucine, valine, serine, threonine, asparagine, glutamine, arginine, lysine, cysteine, methionine, phenylalanine, glycine (D-, L-form), tryptophan, and histidine] are also sweet (Haefeli and Glaser, 1990), the latter two in particular. Most of the D-amino acids are not sweet and, in the case of tryptophan and histidine, the taste shifts from very sweet (L-form) to bitter (D-form). Generally, the concentration of free amino acids in plants is too low to significantly impact sweetness.

In addition to sugars and amino acids, a wide range of other natural and synthetic compounds are sweet (Sardesai and Waldshan, 1991). These are typically found in either small quantities or in obscure plant species and, as a consequence, do not significantly impact the sweetness of horticultural products. The range of types of compounds that exhibit sweetness is impressive: peptides, proteins, flavanones, flavonols, dihydrochalcones, isovanillyl, sesquiterpenes, urea compounds, sulfones, and others.

The methyl ester of L-aspartyl-L-phenylalanine (aspartame) is very sweet (Mazur et al., 1969). Other synthetic peptides such as alitame [L-α-aspartyl-*N*-(2,2,4,4-tetramethyl-3-thietanyl)-D-alaninamid] is exceptionally sweet (i.e., 2000 times sweeter than aspartame) (Glowaky et al., 1991). The discovery of aspartame led to a greatly expanded research effort on artificial sweeteners and has resulted in several commercial products (e.g., Nutrasweet®, Sucralose®) that allow a reduction in calories while maintaining sweetness in processed foods.

Sweet compounds or compounds modulating sweetness have been isolated in a number of obscure plant species. For example, miraculin, a protein found in the berries of *Synsepalum dulcificum* (Schumach. & Thonn.) Daniell, has the unique property of being able to convert the sour taste of acids into the sensation of sweetness (Inglett, 1971; Kurihara 1971). The protein reacts with the taste buds, and at very low concentrations (i.e., 7×10^{-7} M), can render 0.02 M citric acid as sweet as 0.4 M (14%) sucrose. The duration of the effect is concentration-dependent, lasting from ≈20 min at low concentrations of the protein to as long as 3 h at high concentrations. Another sweet protein, monellin, found in the berries of *Dioscoreophyllum cumminsii* (Stapf.) Diels, is ≈1000 to 2250 times as sweet as sucrose on a weight basis (Inglett and May, 1968, 1969) or ≈100,000 to 130,000 times as sweet on a molar basis (Ariyoshi et al., 1991; Kim et al., 1991). Thaumatin, a protein from the fruit of *Thaumatococcus danielli* Benth. (van der Wel and Loeve, 1972) is ≈100,000 times as sweet as sucrose on a molar basis. Phyllodulcin, an isocoumarin from the leaves of *Hydrangea macrophylla* (Thunb.) Ser., is ≈400 times as sweet as 3% sucrose (Yamato and Hashigaki, 1979). Several flavanones and flavonols are also sweet. For example, (+)-dihydroquercetin-3-acetate from *Tessaria dodoneifolia* (Hook. & Arn.) Cabrera. (Kinghorn and Soejarto, 1991) is ≈80 times as sweet as sucrose, and (+)-dihydroquercetin-3-α-L-rhamnosyl from *Englelhardtia chrysolepis* Hance is likewise sweet (Dick, 1981). However, in virtually all instances, sweet compounds