FLAVOR FORMATION IN FRUIT AND VEGETABLES

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SUMMARY

Flavor is an important sensory aspect of the overall acceptability of food. The sensation of flavor is comprised of aroma, taste, which are most affecting the sensation of flavor, texture and psychological perception. Determination of flavor is most emphasized on the constituents flavor rather than the mechanism and metabolic pathway. However, this paper will have a discussion on the flavor formation in fruit and vegetables.

Key words: Flavor, flavor chemistry, flavor formation, aroma, taste.

INTRODUCTION

Flavor is a complex sensation (Moncrieff, 1951). It is described as the total sensory attributes of a food material (Berger, 1995). It is also represents the characteristics or properties of a food material which produce the flavor sensation (deMan, 1990). Basically, the overall sensation of flavor is comprised of aroma, taste, texture and psychological perception (Craske, personal communication). While the main factors affecting sensation are taste and aroma (deMan, 1990). Each of these components plays an important role in contributing to the overall sensory quality of a food material, as well as the acceptability of food. According to a recent market survey found by Berger (1995), the sensory quality of a food has been ranked higher than nutritional value, price or safety.

When a person ingests food, flavor involves not only the sensory quality, but also the receptor mechanism in both the oral and nasal cavities (Moulton, 1982). The study of flavor includes the composition of food compounds having taste and smell, as well as the interaction of these compounds with the receptors in the taste and smell sensory organs. Following an interaction, the organs produce signals that are carried to the central nervous system, thus creating what we understand as flavor (deMan, 1990).

Flavor is an important sensory aspect of the overall acceptability of food (Sahidi, 1994). The analysis of flavor volatiles has been a challenge to many researchers for over 40 years. The flavor industry is worldwide and has incorporated a considerable amount of development research (Steffen and Pawliszyn, 1996).

Emphasis has mostly been placed on determining what constitutes flavor rather than on the mechanism of flavor formation and metabolic pathway. Hence it is worthwhile to have a closer look at different mechanism, as well as metabolic pathways that give rise to the flavor formation in fruit and vegetables (Heath, 1994).

Flavor Formation in Fruit

The development of fruit flavor occurs during the ripening period, but not during early fruit formation. During this period, metabolism of the fruit changes to catabolism and stimulates the formation of flavor (Heath, 1994). There are three major mechanism of flavor formation.

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a. Fatty Acid Metabolism

Volatile compounds are formed from lipids through several different metabolic pathways which include hydroxyacid cleavage, beta oxidation and lipoxygenase catalysed oxidation. The primary products obtained from these pathways are aldehydes and ketones. Meanwhile, additional oxidations, reductions and esterifications also yield substantial quantities of acids, alcohols, lactones and esters (Heath, 1990).

b. Amino Acid Metabolism

The metabolic pathways for the formation of volatile compounds start with deamination of amino acid followed by decarboxylation. After various reductions and esterifications, this will then generate various volatile compounds, such as aliphatic and branched chain alcohols, acids, carbonyls and esters which, are significant to the fruit flavor (Heath, 1990).

c. Carbohydrate Metabolism

Generally, the formation of flavor compounds from carbohydrate metabolism is very rare. Howevr, terpenes- the characteristic flavor of citrus products may arise from this metabolism. Terpenes are formed via condensation of two molecules of isotoprene to form the backbone of the monoterpenes followed by a cyclisation to close the ring and then rearrangement to create the compound (Heath, 1990).

Flavor Formation in Vegetables

Vegetables do not have a ripening period as fruits do, thus the flvor formation is also different. Vegetables develop flavor primarily during cellular disruption. Cellular disruption may due to cutting a vegetable prior to use, or cooking or chewing process. Cellular disruption permits the mixing of enzymes and substrates, which had been separated within the cell, thereby resulting in the generation of volatile flavor substances. Meanwhile, fatty acid, carbohydrate and amino acid metabolism also serve to provide precursors of vegetable flavor like the formation of flavor in fruit (Heath, 1990).

Flavor Chemistry of Fruit

In the flavor chemistry of fruit or vegetables, a complex mixture of compounds makes up the flavor and aroma which, in turn, gives its characteristic odor. The most important volatile materials of citrus fruit include terpene hydrocarbons, carbonyl components, alcohols, esters and volatile organic acids. These compounds are found in the flavedo and oil sacs that are embedded in the juice vesicles (Kirchener, 1961). The major classes of flavor chemicals that contribute to the flavor and aroma of fruit are described in the subsequent chapters.

1. Alcohols

Many alcoholic components can be found in the flavor materials of citrus, bur their contribution to overall flavor is less than that of the carbonyl components. In orange, the predominant alcohol components are linalool and other compounds that are present in significant amount include octanol, terpinen-4-ol and ά-terpineol. Trace amounts of methanol, ethanol, n-propanol, isobutanol, n-butanol, isopentanol, n-pentanol, n-hexanol, 3-hexanol, n-heptanol, methyl heptanol, 2-nonanol, n-nonal, n-decanal, citronellol, nerol, geraniol, carveol, undecanol and dodecanol are also present in orange fruit (Kirchner, 1961).

2. Esters

Esters make up only a small fraction of the overall weight as compound to other compounds. Some identified esters include ethyl formate, ethyl acetate, ethyl butyrate, ethyl isovalerate, ethyl caproate, ethyl caprylate, linalyl acetate, octyl acetate, nonyl acetate, decyl acetate, terpinyl acetate, geranyl acetate, ethyl 3-hydroxyhexanote, citronellyl butyrate, geranyl butyrate, methyl anthranilate and methyl N-methylanthranilate. Despite, so many ester compounds identified, the only ester found in substantial amount is ethyl butyrate (Kirchner, 1961).

3. Carbonyls

Ketones, together with aldehydes give significant contribution to the flavor and aroma of cireus fruits. Some important ketones and aldehydes include 2-hexenal, n-octanal, n-decanal, and geranial. Others found in trace amounts include acetaldehyde, acetone, n-butanal, n-hexanal, methyl ethyl ketone, n-hepatanal, n-nonanal, furfural, methyl heptenone, citronellal, n-undencanal, n-dodecanal, neral carvone, perilaldehyde, piperitenone and β-sinensal (Kirchner, 1961; Shaw, 1977).

4. Phenols

Phenols are present in the form of "tannin" and these compounds are associated with the sensation of astringency. They are largely undefined in term of structure and are usually detected and measured by various color reaction (Thurston, 1923).

5. Terpenes

Qualitatively hydrocarbons are the most important classes of orange oil components since they comprise over 95% by weight of the oil (Shaw, 1977). The majority of the constituent are terpene hydrocarbons, and terpene alcohols which are found to change significantly in amount at different time of the year. Limonene, a terpene hydrocarbone has been reported to vary between 52 to 95% in Hamlin oranges. Linalool, which is a terpene alcohol, varies between 0.6 to 27%. Other oxygenated terpenes were also reported to vary in concentration. In orange oil, geranial decreased from 3.5% to 0.2%, geraniol from 0.5% to 0%, citronellal from 0.55% to 0%, terpinen-4-ol from 5.5% to 0.6% and α-terpinol from 4.3% to0.2%. The only compound that shows an increase is myrene which increases from 0.69% to 1.76% (Kirchner, 1961).

Aroma/Odor

Aroma or odor plays an important role in the determination of food acceptance of food sensory quality. Before a food material is consumed, the aroma of that food will greatly affect one's appetite or acceptance. The nose, which is the olfactory organ, is primarily responsible for odor sensation (Moulton, 1982). There are hundreds or thousands of odors which can be distinguished or discriminated easily by the human nose (Farmer, 1992). Furthermore, olfaction (the sense of smell) is more sensitive to low concentrations of chemical substances than the taste (Moulton, 1982). It is found that the sensitivity of the smell organ is about 10,000 times greater that that of the taste organ (deMan, 1990). Although taste carries fewer distinctive characteristics than odor, it provides an essential base on which aroma builds to generate the widely varying flavor of our foods and beverages (Breslin, 2001).

Only volatile chemical compounds can facilitate the production of aroma. Generally, aroma compounds in food origin are from microbial, plant metabolism, as well as animal metabolism. Aroma of food is detected in the nose and the sensation of odor is perceived by receptor cells of the olfactory epithelium inside the nasal cavity (Berger, 1995). Sniffing may increase the amount of aroma reaching the olfactory tissue (deMan, 1990). Meanwhile, when eating foods, the passage of breath during exhalation reaches the nasal cavity through the channels at the back of the nose (deMan, 1990; Farmer, 1992).

Sensitivity of the nose to perceive a particular aroma or odor compound (also known as odor threshold) varies greatly between individuals (Farmer, 1992). It has been known that several factors can significantly affect the ability to smell and the degree of pleasantness or unpleasantness can also become variable (deMan, 1990; Moulton, 1982). These are due to factors such as colds, menstrual cycle, and drugs (deMan, 1990). However, the concentration of aroma compound itself also affects olfactory sensitivity (Farmer, 1992). Aromas are obtained from a mixture of several or many different aroma compounds. The combined effect creates an impression that may be very different from that of the individual components (deMan, 1990).

1. Odor and Molecular Structure

The relationship between molecular structure and odor is very complicated, that none of the theories of olfaction can explain. These are due to several facts. For example, there can be similarities between the chemical structure of compounds and their odors, but there are also some compounds that have similar structure and very different odors. Meanwhile, there are also compounds with different structures that all give similar odors. The odor character of stereoisomers also provides different odor sensations. For instance, only the menthol isomer has the ability to provide peppermint aroma, but on the other hand, the iso-, neo-, and neoiso-menthols provide the unpleasant musty flavor. Furthermore, increase in the length of the carbon chain may significantly affect odor properties. A very good example can be shown by saturated acids as the lower fatty acids give very intense and unpleasant aromas while fatty acids with 16 or 18 carbon atoms provide only a faint aroma. Therefore, at present, the classification of odor and the correlation of chemical structure and odor still remains a mystery (deMan, 1990). However, odor sensations can be categorized into seven primary classes. These primary odors are camphoraceous, pungent, ethereal, floral, peppermint, musky, and putrid. It was also suggested that there may be more than seven primary sensations.

2. Taste

Generally, taste has been misunderstood as flavor and people always think or assume that taste basically refers to flavor and they are actually the same. However, taste should be taken as that part of the flavor perception that describes what the tongue perceived.

Chemical substances that are responsible for the taste sensation are water soluble, relatively non-volatile and generally present at higher concentrations in foods compared to aroma compounds (Lindsay, 1996). During eating of a complex food, these taste substances are released in a continually evolving pattern as the food is broken down and mixed with saliva (Moulton, 1982). Taste is then detected through the contact of taste substances with the taste buds located on the surface of tongue. The most common four basic types of taste sensations are sweet, sour, bitter, and salt (Heath, 1994). Each receptor which is responsible for different kind of taste sensations is distributed at different region of the tongue.

Meanwhile, there is also less defined taste sensations such as pungency, astringency and cooling that contribute to the trigeminal effects. These chemical substances directly interact with bare nerve endings in the olfactory membrane and on the tongue to provide certain kinds of taste sensations (Heath, 1994).

Due to the genetic differences in humans, it is not surprising to see that taste perception varies between individuals (Lindsay, 1996). Meanwhile, there are no significant age- or sex-related differences in taste sensitivity. But, heavy smokers may undergo deterioration in taste sensitivity along with age (deMan, 1990). In addition, taste dysfunction can also occur due to drug, toxin, and disease effects (Breslin, 2001).

As we know, taste makes a significant contribution to flavor and plays an important role in the acceptance of food flavor. Hence, we shall have a closer look at the chemical compounds that are responsible for each of the flavor taste sensation.

3. Sweet

Sweetness is the property of sugar (deMan, 1990). It is a desirable taste sensation which is able to increase acceptance of food flavor. The taste of sweetness can be produced by different kinds of compounds and these compounds can be classified into three different categories: sugar, polyhydric alcohol, and α-amino acids. Each of these compounds differs widely in term of molecular constitution, relative sweetness, solubility, functional group, color, odor, or appearance (Heath, 1990). If any minor changes occur in chemical structure as well as positional isomers, it will greatly affect and modify the taste of a compound, such as from sweet to bitter or tasteless (deMan, 1990). Simple sugars are the most widely occurring natural sweeteners in the form of crystalline polyhydroxy carbohydrates, which can be categorized in terms of number of carbon atom into three classes: monosaccharides (5 or 6 carbon atoms), disaccharides (12 carbon atoms), and polysaccharides (> 12 carbon atoms) (Heath, 1994). As the molecular weight of saccharaides increases, their sweetness decreases. This is best explained by the decrease in solubility and increase in size of the molecule (deMan, 1990).

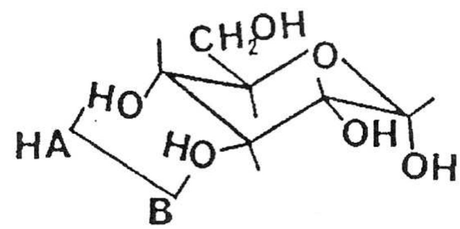

Figure 1 Structure of glucose (monosaccharide) (Lindsay, 1996)

Sugar alcohols are not considered as sugar even though they are to sweeten food. They are generally less sweet when compared to sucrose. Generally, the sugar alcohols can be found to be present naturally in small quantities in many fruits or vegetables. The most common compounds responsible for the sweet taste sensation that are available in the commercial market include sorbitol, mannitol and xyllol (Heath, 1994).

There are some naturally occurring compounds which are known as high intensity and sweeteners have the unusual property of tasting intensely sweet. Generally, these compounds can be extracted from fruits, such as berries or herbs. They are the amino acids, glycyrrhizin, miraculin, monellin, osladin, phyllodulcin, stevioside, thaumatin I and thaumatin II. However, these compounds only appear to be intensely sweet at specific situations. For example, miraculin only provides intense sweetness in the presence of acid (Heath, 1994).

At present, the development of synthetic sweeteners is increasing rapidly due to public concern regarding the health issue of obesity or overweight. These compounds include saccharin, cyclamates, aspartame, acesulfame K, sucralose and alitame. Most of these synthetic sweeteners are considered as one of the high-intensity sweeteners. For example, saccharin (shown in Figure 2) is 300 to 500 times sweeter than sucrose (Heath, 1994).

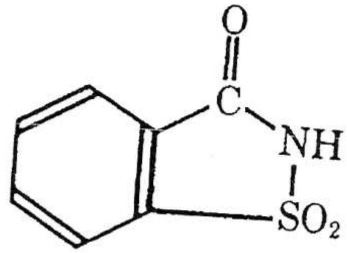

Figure 2 Structure of saccharin (Heath, 1994)

4. Salt

Thousand of years ago, humans had already discovered the existence of salt and had fully utilized it in the food area. At present, it is still widely used because of its numerous functionalities in food. The principle of salt used in food area in not only limited to seasoning or flavoring, but also serves other purposes, e.g. as dietary effect, food preservation and stability enhancement (Heath, 1994).

Salt, which commonly known as sodium chloride (NaCl), comprises a complex of tastes, consisting a psychological mixture of sweet, bitter, sour and salty perceptual components (Lindsay, 1996). According to Heath (1994), research has been carried out investigating the interrelationships of the four primary taste sensations: sweet, sour, and salt and the result shows that salt is able to reduce the sourness of acids and increase the sweetness of sugar. Meanwhile, it was found that sodium content in orange juice and parsley are 0.3-2.0 mg/ 100mg and 28.0-33.0 mg/ 100g respectively (Heath, 1994).

How can we determine the relative saltiness of a compound that contributes to the salt sensation? Compound that are responsible for the salt sensation are 2 parts: cation and anion where the cation contributes to the salty taste and the anion modifies the salty tastes. It appears that in the classic salt (NaCl), the sodium cation produces only salty tastes, while the chloride anion possesses the least inhibitory effect to the salty taste (Lindsay, 1996). On the other hand, as the molecular weight of either cation or anion or both increases, salts will develop a bitter taste (deMan, 1990).

5. Sour

All acid constituents are responsible for the sour taste sensation in food material. The degree of sourness contributed by acid substances relies strongly on the nature of the acid group, the pH, titratable acidity, buffering effects, and the presence of other compounds. Even different organic and inorganic acids at the same pH value can result in a different taste sensation. Among all of these factors, buffering effect is considered as an important and useful one in the determination of the intensity of sourness. When a food material is ingested, saliva will interact directly with it and, at the same time, act as a buffering agent to give an effect over the degree of sourness. Any chemical compounds contained in food which has a buffer capacity is also able to affect the intensity of sourness (deMan, 1990).

6. Bitter

Conventionally, bitter sensation significantly affects the acceptance of food and it is generally considered as undesirable or unpleasant in food material (Lindsay, 1996). This is basically because the sensitivity of flavor taste perception in humans against bitterness is more extreme when compared to other taste sensations. The order of sensitivity is bitter, sour, salty and sweet taste (least sensitivity), as described by deMan (1990). However, bitterness may be desirable in certain types of food and especially in beverages or drinks such as coffee or tea. Compounds that are responsible for the bitter sensation may greatly affect one's flavour perception, due to the close relationship between the bitter and sweet taste sensations at different concentrations (Lindsay, 1996; Heath, 1994). Basically, the compounds that are responsible for the bitter sensation can be distributed into 3 classes: alkaloids, glycosides, and peptides. Caffeine that is present in coffee is one of the compounds that are found in the class of alkaloids, as shown in Figure 3. However, there are also some other bitter-tasting chemical compounds which fall beyond these classifications. They are quassin and limonin (Heath, 1994).

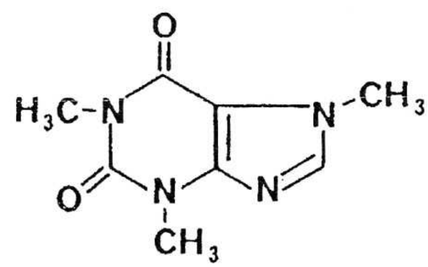

Figure 3 Structure of caffeine (Lindsay, 1996)

Limonene (shown in Figure 4) is a bittering agent that is present significantly in citrus fruit, especially bitter orange (*Citrus auranticum*). This bittering agent has resulted in serious economic consequences, due to the occurrence of an undesirable bitter sensation in fresh and processed citrus fruit (Lindsay, 1996).

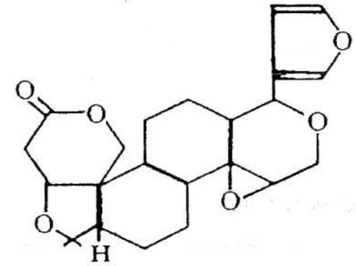

Figure 4 Structure of limonene (Heath, 1994)

7. Flavor Enhancer

MSG, a common abbreviation that is familiar to everyone can be easily found printed on the packaging of a processed food such as instant noodle. This compound, monosodium glutamate (MSG), as shown in Figure 4, is widely used in the food industry only for one reason- it owns strong flavor-enhancing properties. This is why it is also known as the flavor enhancer. There are also some other compounds such as trichlomic acid and ibotenic acid, maltol or 5'-inosine monophosphate which possess the same properties as MSG (deMan, 1990; Lindsay, 1996). These flavor-enhancing compounds, in themselves have little or no taste or odor at all. They have a unique characteristic which is to modify or enhance the existing flavor of a food. Furthermore they can change the mouth feel and induce a sensation of fullness or satisfaction (Heath, 1994). However, the actual mechanism of how these flavor enhancer work still remains a mystery (Lindsay, 1996).

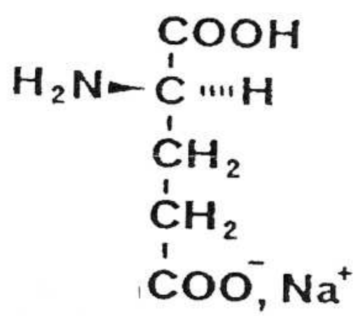

Figure5 Structure of monosodium glutamate (MSG) (Lindsay, 1996)

8. Flavor Inhibitor and Modifier

Both flavor inhibitors and modifiers are very similar to flavor enhancers, where these substances also possess a unique property, which is the ability to modify the perception of taste qualities. Compounds which have this ability are gymnemagenin that is found in the leaves of tropical plant – *Gymnema sylvestre* and a protein that is contained in the miracle fruit – berries of West African shrub (*Synsepalum dulficum*). Gymnemagenin (shown in Figure 5) is also known as a flavor inhibitor, whre it can suppress or decrease the ability to taste sweetness and bitterness. While the protein that is found in the miracle fruit is known as taste modifying protein. It has tha ability to change the perception of sour to sweet sensation (deMan, 1990).

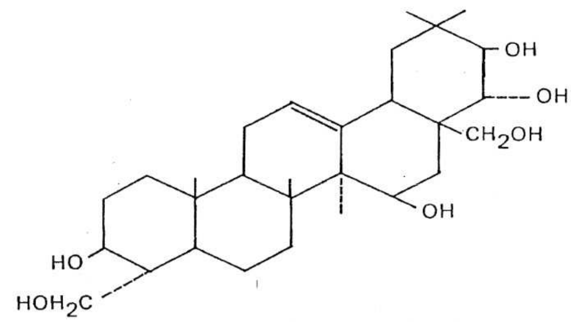

Figure 5 Structure of gymnemagenin (deMan, 1990)

9. Pungency

Pungency is a taste sensation that contributes a hot, sharp and stinging feeling in the mouth. Pungency is a quite common taste sensation, can be perceived in several spices or vegetables such as ginger, pepper, or capsicum. Compounds that are responsible for this taste sensation not only contribute to the oral effect, but also to aroma. Capsaicin (XIII) is the pungent compound that is present in capsicum. It is also known as a capsaicinoid, which is a vanillylamide of monocarboxylic acids. While the pungent compounds, which are found in ginger, are called gingerols. They comprise of a group of phenylalkyl ketones and are able to contribute aromas (Lindsay, 1996).

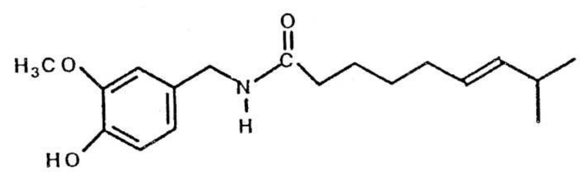

Figure 6 Structure of capsaicin

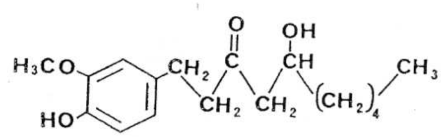

Figure 7 Structure of gingerol

10. Astringency

Astringency is considered as one of the less defined flavor taste sensations. It manages to give a dry feeling in the mouth, along with a coarse puckering of the oral tissue. Astringency is perceived when the responsible compounds, which are tannin or polyphenols associated with protein in the saliva, stimulate the receptor buds on the tongue. These two substances have a unique characteristic, which is the ability to give both bitter and astringent taste sensation. This is why sometimes people get confused with the astringency and bitter taste sensation. Astringency may be desirable or undesirable in food flavors. For example, it is desirable in tea, but too much of astringency will be undesirable in wines (Lindsay, 1996).

11. Cooling

Cooling sensation is encountered in food materials which are able to contribute a mint like flavor perception. The primary food materials that provide the cooling effect are peppermint, spearmint, and wintergreen. The common natural occurring substance that is responsible for the cooling sensation is menthol (Lindsay, 1996).

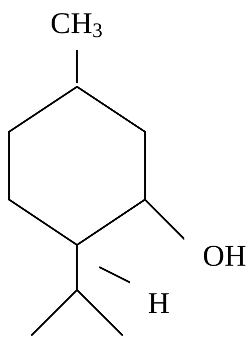

Figure 7. Structure of menthol (Lindsay, 1996)

CONCLUSION

Flavor is a complex sensation once a person ingests foods. The mechanisms of flavor formation in fruits are more complex than that of in vegetables. As consequences, the fruits have various sensation of flavor. In addition, vegetables do not have ripening period as fruits, in which the flavor precursors may develop, but instead, it develops the flavor during cellular disruption (cutting, breaking, chewing, and cooking processes). Study on flavor is challenging as the appealing of foods arises from the flavor.

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