Chapter XI

Taste Changes in Fruits
Compounds of the odor fraction are very often products of special biochemical reactions, which are linked with ripening processes, or products of chemical reactions occurring during processing of the raw materials. They occur in high number, but in relatively low overall amounts. Compounds comprising the taste fraction are generally more closely related with the main metabolism of the raw material. They occur in much smaller numbers but generally in larger amounts in the milligram and gram range. Taste problems often coincide with general biochemical and nutritional aspects. It has been observed by Kolms that taste variation from system to system can be brought about by enzymes of the basic metabolism.

Foods having completely different compositions are related to many fruit flavors. They contain a nonvolatile basis, composed mainly of sugars and acids, in general organic acids, with a low pH between 3 and 4.

For taste sensations, sugars and acids take part in complex interactions. There is a range in composition with a medium sugar-acid ratio, which corresponds to the
quality judgment 'ripe'.

It can be said without much hesitation that sugar-acid system in citrus fruits contributes to the characteristic basic taste sensations in many fruits.

Ethylene is considered to be an important volatile compound responsible for initiation of the ripening process. According to Hulme et al., taste is centred in the balance between sugar and acid; phenolic compounds contribute both to flavour and taste, the astrigency of many of these compounds influencing the latter.

It has been recognized for many years that fruit continues to undergo chemical changes after harvest until finally spoilage occurs as it is attacked by fungi, yeasts or bacteria. The changes of fruit after harvest mainly include changes in respiration, water content, carbohydrates (sugar content) organic acids and pH. These changes considerably influence taste and odor qualities of the fruit under consideration.

Carbohydrate content alters significantly during ripening, during the climacteric, and during senescence changes. Green fruit (unripe) usually contains an abundance of starch, but is short on the soluble sugars that give ripe fruit its sweetness. On ripening, however, starches decrease and sugars increase in concentration. Since these changes have often
been observed (Table indicate increase in sugars), it has been assumed that the sugars are produced at the expense of the starch. Hülsme² and Bamell³ have conflicting views which indicate that the relation between starch and sugars in fruit is complex.

Acids decrease in many fruits during ripening or during storage. The fruits contain different organic acids in varying concentrations. For example in apple pulp and in pears, citric acid is in smaller amount, compared to amounts of malic acid. Changes in organic acids are of special interest, since these changes are related to metabolic processes.

There is an important role of inorganic substances in case of citrus fruit chemistry. The ash of the citrus fruit contains Fe, Mn, Ca, Zn, B, Sr, Ba, Sr, Al, Cr, Ti, Pb, Cu, Ni, Ag and also P, S, Cl, Br, I and F as reported by Roberts and Gaddum⁴, Rakienten et al.⁵ and Stevens⁶. Many of these elements are associated with enzyme systems and they are extremely important in the metabolism of fruit. Sometimes improper growth is a result of deficiency of some elements.

It is described by Harvey and Rygg⁷,⁸ that stored oranges and grape fruit at different temperatures showed changes in certain substances which could be temperature
related. In novel Granges, sucrose showed a slight loss (3%) of the original amount at 0°C but a large loss (47%) at 11°C. Reducing sugars changed much less than sucrose, but in the same direction. There was a loss of soluble solids with corresponding increase in easily hydrolysable polysaccharides. This may be correlated with the decrease in sweetness of the fruit. Of course, in the case of Washington Navel Oranges there was decrease in the bitter principles when stored at 26.7-32.2°C as reported by Rockland et al.\(^9\). The soluble solids of the orange juice increased but there was decrease in both reducing sugars and titratable acidity after 15 weeks' storage as reported by Trout\(^10\).

Compositional changes during growth and development:

In the case of bananas, Barnall\(^11\) has described certain changes in the pulp and peel of Gros Michel bananas sampled up to 130 days after emergence, which is well past the normal harvest time of 80-100 days. The dry matter increased steadily, reaching about 25% at normal harvest date. Starch accumulated for about 100 days and then hydrolysed extensively from 110 to 130 days. Sugar content was below 1% fr.wt. for 120 days and then increased to 4% at 130 days. Sucrose was the primary sugar in the early stages of development, with glucose and fructose predominating later.
Sucrose is the predominant sugar arising from starch hydrolysis in banana as reported by Poland et al. Acidity was high in the young fruits, fell steadily until 90-100 days, and then increased slightly.

The alcohol-soluble nitrogen pulp changes markedly during development. The period of nitrogen depletion corresponds to the period of most rapid expansion of the fruit, and Steward et al. suggested that the rapidly growing fruit utilizes nitrogen reserves for protein synthesis faster than they can be replenished. Total soluble nitrogen in the peel followed the same general trends as in the pulp, although its content was much lower.

The ripening of banana is certainly hastened by ethylene produced within the fruit and it has been shown by Young et al., Tapson and Robinson that ripening can be delayed for weeks or months by holding the green fruit in an atmosphere of 10% oxygen, 5-10% CO₂ or a combination of low O₂ and high CO₂. This is very useful for controlled atmospheric storage for the longer voyages usually by sealing the fruit in polyethylene bags of selective permeability. This indicates that respiratory and compositional changes in biochemistry of banana can be artificially controlled.

The most striking chemical changes which occur during the post harvest ripening of the banana, are the hydrolysis of
starch and the accumulation of sugars. About 20-25% of the pulp of the fresh green fruit is starch. In the week or so from initiation to completion of ripening, starch is almost completely hydrolysed, only 1-2% remaining in the fully ripe fruit.

Sugars, normally 1-2% in the pulp of green fruits of banana, increases to 15-20% in the ripe pulp. Total carbohydrate decreases 2-5 during ripening, presumably as sugars are utilized in respiration as reported by Essecke.

Here is a direct evidence of the fact that polymeric carbohydrates like starch degrade into mono-disaccharides like glucose, fructose or sugars during the ripening hence flat or no taste to sweet taste is directly linked with the sites available for hydrogen bonding from the molecules of the fruit to interact with the site on the tongue. In addition the cycle of changes involved in the enzymatic hydrolytic breakdown of the nucleotides to give acids, sugars and soluble compounds which are responsible for varieties of taste, such as sweet, sour and bitter all found together in foods. The same is true in citrus fruits, too. In addition, a large number of substances are formed which provide different flavours. The list of the substances is quite high for each food item, e.g. tea, coffee, butter, milk etc. The
substances belong to the group of alcohols, esters, aldehydes, terpenes, and many others.

It is known that severe chilling tends to a breakdown of ripening processes. This explained in a way that as if certain cells do not receive the 'signal' which initiates ripening, Murata and Ku suggested that chilling may cause inhibition of certain key respiratory enzymes, resulting in accumulation of ethanol and acetaldehyde, which further interfere with the normal metabolic pathways.

In case of oranges 75-80% of the total soluble solids of orange juice are sugars. The changes in the sugar content of valencia oranges were studied by Stahl and Camp. The reducing, nonreducing and total sugars increased as fruit continued to ripen on the tree. Similar results were found with grapefruit and tangelo orange by Harding and Fisher and Harding and Sunday. Curl and Veldhuis concluded that the principal sugars in Florida valencia orange juice were sucrose, glucose and fructose which occurred in an approximate ratio of 2:1:1. McCready et al. using paper chromatography, identified these three sugars to be the main ones in the juices of grapefruit, lemon, tangelo and orange. There appears to be no definite trend in sugar
concentrations in the maturing grape fruits, but there is generally an increase in reducing sugars with maturity 28.

A positive correlation between vitamin C and soluble solids of juice of Valencia oranges is shown by Sites and Reitz 29. It is likely that vitamin C, sugars and citric, malic and oxalic acids must have some interconversions by way of biochemical enzymatic activity.

Oberbacher and Vines 30, 31, 32 found evidence for the occurrence of ascorbic acid oxidase in immature oranges. Marsh Seedless Grapefruit was found to have highest ascorbic acid oxidase activity, while lemon and lime were very low in this enzyme. Thus ascorbic acid appears to have some role in the metabolism.

Martin et al. 33 compared the chemical changes of grapefruit in storage with those left on the tree. They concluded that changes in acid and soluble solids taking place in grapefruit during storage are similar to those in fruit left on the tree, but they proceed at a slower rate.

According to Bulmer 34 the period of maturation lasts from veraison to the state of ripeness. During the 40-50 days of this period, grapes continue to swell, store carbohydrates and lose their acidity. Tannin synthesis increases as the skin becomes more coloured and the characteristic aroma develops. Actually, bitter sour
sweet are the changes taking place during many of the citrus fruits.

In the case of grape fruit, it is noted that at veraison, within 10 days or so, the sugar content increases by a factor of 6 or 7\(^3\). Ibertea Gayon\(^3\) has shown that immature grapes can readily synthesize carbohydrates from malic acid. This has been established by measuring C\(^{14}\) radioactivity after introducing C\(^{14}\)-malate into the berries.

\[
\text{COO} \quad \text{NAD}^+ \quad \text{NADH} \quad \text{COO}^- \quad \text{ATP}^+ \quad \text{ADP}^3- \quad \text{COO}^- \\
\text{HO} \quad \text{C} \quad \text{H}_2 \quad \text{C} = 0 \quad \text{CO}_2 \quad \text{CO}_2 \quad \text{C} - \text{PFO}_3^2- \\
\text{Ca}_2 \quad \text{Ca}_2 \quad \text{COO}^- \quad \text{Phospho-enol pyruvate} \\
\text{COO} \\
\text{L-malate} \quad \text{Oxalacetate} \\
\text{Carbohydrate synthesis from L-malic acid}\(^3\)\]

This appears to be the first proof of the conversion of malic acid to sugars in the grape and goes some way to explain the decrease in acid and increase in sugars observed.
during ripening. Of course, there are many other acids present in the fruit.

It is also reported by Hardy that the high percentage of C-14 found in organic acids only a few hours after supplying immature grapes with labelled sugars indicates that most of the malate and tartarate in the berries originates from glucose and fructose, translocation from the leaves is also possible. Hardy considered that malic acid and tartaric acids are not biochemically related. This indicates how citrus fruits differ in their sweet-sour taste and two fruits of any variety can be considered to have the same composition so far as the taste is concerned because this is an enzyme controlled process.

The following series of changes explain formation of tartaric acid from glucose.

\[
\text{glucose} \xrightarrow{Ox} \text{5-gluconic acid} \rightarrow (\text{aldehyde of glycollic acid}) \xrightarrow{\text{oxidation}} \text{tartaric acid} \leftarrow (\text{aldehyde of tartaric acid})
\]

Mechanism of formation of tartaric acid from glucose.

Introduction of labelled compound of nitrogen into immature grape berries generally results in a rapid synthesis of amino acids, labelling being maximal when the
times of exposure are short (45 minutes to 3 hours). The amino acids lose their radioactivity rapidly since they are intermediary compounds in many metabolic reactions, particularly in the formation of organic acids and carbohydrates.

It is known that ascorbic acid increases during the growth of the grape berry, remains at a constant level during maturation and tends to decrease during ripening.

In case of mango, Leley and co-workers found starch to increase from 1 to 13% in the fruit during growth. After picking, starch was hydrolysed in 3 days. Regarding the acidity, Wardlaw and Leonard made a careful study and observed that a rise and fall in acidity during development are similar to that obtained for other fruits. Singh et al. and Mukerjee also observed similar pattern in acidity changes. Nonreducing and total sugars increase gradually showing a slight fall during ripening, while reducing sugars remain more or less constant throughout the period of development. There is a continuous accumulation of starch up to maturity and this falls during ripening.

The ascorbic acid content is considerably greater in the green, young fruit than in ripe fruit. Matto and Hody working with the alfonso mango variety found 250 mg/100 g fresh pulp in the unripe fruit, 90 mg in partially ripe and 165 mg in the ripe fruit.
A comparison of the Indian Mango with those from Florida suggests that green, unripe fruits of the Indian varieties contain much less sugar than the Florida fruits but that, when ripe, the sucrose content of the Indian varieties is higher (exception of the Neelan variety). Increase in soluble solids during ripening reflects conversion of starch into sugar. Increase in sucrose and decrease in acid seem to be the only biochemical criteria available for the assessment of ripeness.

Leale et al. found the starch content of Alphonso mangoes to be 14% of the fresh weight at harvest. According to Diallo, mango is one of the fruits to contain reserve polysaccharide at harvest. During subsequent ripening of the fruit, sucrose rose from 5.8 to 14.2% of the fresh weight, while pH rose from 3.0 to 5.2. Total acidity varies from 0.71 to 0.13 (as citric acid).

Pattabhiraman et al. considered from the chromatographic study of the odoriferous compounds of the mango fruit that carotene modified the overall aroma carboxyl compounds and alcohols appeared to be involved in the aroma contribution.

Modi and Patwa showed that ripe mangos are ten times richer in carotene and than partially ripe ones, while unripe,
green mangos do not contain even traces of carotene. Increase in carotene was accompanied by decrease in acid content and in increase in sugar.

In fact, highly complex biochemical changes must be taking place in the mango fruit, especially during ripening phase.

Some experimental study is made in the laboratory which shows the change in pH, titratable acids and sugar content in some fruits.

Table gives data about acidify, pH and sugars for some ripe and unripe fruits.
## Table 10-A

<table>
<thead>
<tr>
<th>Fruit</th>
<th>pH</th>
<th>Titratable acidity</th>
<th>Total sugar</th>
<th>Sugar acidity ratio</th>
<th>pH</th>
<th>Titratable acidity</th>
<th>Total sugar</th>
<th>Sugar acidity ratio</th>
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<tbody>
<tr>
<td>Mango</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>A. Alfonso</td>
<td>1.9</td>
<td>4.5</td>
<td>2.7</td>
<td>0.60</td>
<td>4.4</td>
<td>0.20</td>
<td>14.49</td>
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<td>B. Pirio</td>
<td>2.4</td>
<td>2.7</td>
<td>2.1</td>
<td>0.77</td>
<td>4.2</td>
<td>0.31</td>
<td>12.70</td>
<td>41.04</td>
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<td>C. Potapuri</td>
<td>3.1</td>
<td>1.3</td>
<td>7.5</td>
<td>4.29</td>
<td>4.4</td>
<td>0.30</td>
<td>13.61</td>
<td>45.45</td>
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<td>Apple</td>
<td>3.7</td>
<td>0.3</td>
<td>6.6</td>
<td>8.1</td>
<td>3.7</td>
<td>0.5</td>
<td>11.9</td>
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<td>Guava</td>
<td>4.3</td>
<td>0.3</td>
<td>5.0</td>
<td>6.5</td>
<td>4.2</td>
<td>0.6</td>
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<td>Plum</td>
<td>-</td>
<td>2.0%</td>
<td>11.0</td>
<td>5.5</td>
<td>-</td>
<td>1.7%</td>
<td>19.4</td>
<td>11.2</td>
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<td>Tomato</td>
<td>75.1</td>
<td>1.2</td>
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<td>4.2</td>
<td>83.3</td>
<td>4.5</td>
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<tr>
<td>Pineapple</td>
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<td>7.5</td>
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<td>1.7</td>
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<td></td>
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</tr>
<tr>
<td>Grapes</td>
<td>3.3</td>
<td>12.5</td>
<td>13.0</td>
<td></td>
<td>4.2</td>
<td>39.0</td>
<td>20.1</td>
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<tr>
<td>Berries</td>
<td>3.0</td>
<td>24.1</td>
<td>6.1</td>
<td></td>
<td>4.0</td>
<td>12.9</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>Non citrus fruits</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>Banana</td>
<td>4.2</td>
<td>4.3%</td>
<td>4.2</td>
<td></td>
<td>5.7</td>
<td>10.9%</td>
<td>13.7</td>
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<tr>
<td>Chiku</td>
<td>5.7</td>
<td>0.2</td>
<td>4.9</td>
<td></td>
<td>5.7</td>
<td>0.2</td>
<td>10.8</td>
<td></td>
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</table>
In most of the citrus fruits studied, it is observed that there is increase in pH and sugar content while decrease in titratable acids. Increase in pH and sugar content increases the sweetness of the fruits. Increase in sugar to titratable acid ratio also enhances the taste and flavour property during ripening process. Physical properties like colour and hardness directly reflect these changes.

Data in table indicate increase in pH and sugars while decrease in titratable acidity. This is in line with the observations made by Leley et al. Decrease in acidity results in the change of taste from sour to sweet sugar acid ratio increases during ripening process. Flavor changes during ripening are very significant. External color of the fruit. Softness and the flavor of the fruit are easily marked. Spectroscopic and chromatographic analyses of the fruits have indicated that these are esters and carbonyl compounds. This has shown that in mango odour is associated with carotenoids.

It is also noticed by Laxminarayan and Subramanyam that CO₂ injury is results in mango fruits stored for 21 days under 10% and 15% CO₂ atmosphere and ripened in 7 days
at room temperature.

Color of the fruit becomes very pale yellow and yellow in patches. Fruits become very soft and off flavour results. Decarboxylation in ripening fruit is accelerated under CO₂ atmosphere.