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# Biochemical Changes in Some Fruits at Different Ripening Stages

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*ABSTRACT*

*Soluble and insoluble proteins were decreased gradually in apricot whereas in mango the soluble protein increased and insoluble protein decreased during ripening. Fourteen amino acids could be detected in apricot and twelve in mango, and the percentage of each varied according to the degree of ripening.*

*Total and soluble carbohydrate were increased gradually in both apricot and mango fruits. Glucose, fructose and sucrose were determined in both fruits at all ripening stages, while xylose was found only in apricot. Certain volatile components were separated and identified in apricot, including aromatic aldehydes, esters, alcohols and ketones, while in mango thirty volatile components were identified, including* cis-*ocimene, myrcene, limonene, esters, aldehydes and terpenes.*

*Mango juice contained palmitic and oleic acids as major constituent fatty acids while the short chain fatty acids represented only 5% at the green* *mature stage and were decreased at other ripening stages. In apricot juice, myristic and oleic acids were the most abundant fatty acids, while the saturated short chain fatty acids comprised only 7% of the total fatty acids and decreased at the ripe and overripe stages.*

## INTRODUCTION

Apricot and mango fruits are among the most popular fruits in Egypt because of their attractive strong aroma and excellent flavour. Many attempts have been made to study the biochemical composition of such fruits at various maturity stages.

Casoli & Bellucci (1964) determined free and total amino acids for five varieties of apricots and found twelve free amino acids, while total amino acids were sixteen. Tang & Jennings (1968) identified the volatile component of apricot and showed that it includes myrcene, limonene, terpinolene, *trans*-2-hexanol, α-terpineol, acetic acid, geraniol, 2-methyl butyric acid, γ-octalactone and γ-decalactone. On the other hand, Popovskii *et al.* (1968) found that eight volatile fatty acids in apricot were identified, i.e. acetic, propionic, iso-butyric, iso-valeric, caproic and caprylic acids. The amounts of ethyl formate and acetate increased and iso-butanol and sec-butanol decreased during ripening. In mango fruits Bandyopadhyay & Gholap (1979) found that alphonso mango contained twelve flavour compounds including methyl acetate, *cis*-ocimene and β-pinene and several lactones. Tressl *et al.* (1983) found that mango contains the complete series of ethyl esters of the even-numbered fatty acids from $C_2$ to $C_{16}$ in relatively high amounts.

The aim of the present work is to study the biochemical changes in apricot and mango fruits, which may take place in protein, free amino acids, carbohydrates, sugars, volatile compounds and fatty acids at different maturity stages.

## MATERIALS AND METHODS

Apricot fruits (*Prunus armeniaca* var. *zibda*) and mango fruits (*Mangifera indica* var. *balady*) were obtained from a garden in Gharbeiah Governorate. The fruit samples were collected at three different stages, i.e. green mature (GM), ripe (R) and overripe (OR). The fresh samples were washed, dried, sliced into small pieces and finally divided into three parts.

The first part was dried at 70°C for determining protein and carbohydrates. The second one was extracted with 80% ethanol to determine soluble proteins, free amino acids and soluble sugars. The third part was used in preparing the juice. The ether extract of fruit juices were used in the determination of fatty acids and identification of volatile flavouring components only in the overripe stage in both fruits.

### Methods of analysis

The following methods were used for the analyses.

1. Soluble nitrogen was determined according to the method described by Mengel & Helal (1968).
2. Total nitrogen was determined according to the method described in AOAC (1970).
3. Free amino acids were determined according to the method described by Block *et al.* (1958).
4. Carbohydrate fractions were determined according to the method described by Mgnetski *et al.* (1959).
5. Free sugars were determined according to the method described by Dubois *et al.* (1956).
6. Lipids were extracted by diethyl ether according to AOAC (1970) and saponified with alcoholic potassium hydroxide (40%). The liberated fatty acids were methylated by diazomethane and the methyl esters, as well as volatile flavouring components, were analyzed by GLC (Varian 3700 gas liquid chromatograph equipped with dual flame ionization detector) using the method described by Tang & Jennings (1968). Peak identification was performed by comparing the relative retention time of each with those of standard materials. The peak area was measured by triangulation and the relative proportions of the individual compounds were therefore obtained by determining the partial areas in relation to total area.

### Statistical analysis

Analysis of variance for the completely randomized design was used and the LSD values were calculated for the various characters.

## RESULTS AND DISCUSSION

### Protein and carbohydrate fraction contents

The results given in Table 1 show a decrease in both total and insoluble protein of apricot and mango fruits during the different ripening stages.

**TABLE 1**
Protein and Carbohydrate Fractions of Apricot and Mango Fruits during Ripening

| *Ripening stage* | *Protein fractions (%)* | | | | *Carbohydrate fractions (%)* | | | *Free sugars (% of total carbohydrate)* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *S* | *I* | *T* | *S/I ratio* | *S* | *I* | *T* | *Glucose* | *Fructose* | *Sucrose* | *Xylose* |
| *Apricots* | | | | | | | | | | | |
| Green mature | 0·99 | 0·62 | 1·61 | 1·59 | 2·85 | 1·26 | 4·11 | 45·6 | 36·6 | 6·75 | 11·0 |
| Ripe | 0·73 | 0·52 | 1·25 | 1·40 | 4·06 | 1·52 | 5·58 | 40·3 | 41·4 | 7·15 | 10·1 |
| Overripe | 0·66 | 0·26 | 0·92 | 2·54 | 9·22 | 1·66 | 10·7 | 39·5 | 42·1 | 7·26 | 9·82 |
| *Mango* | | | | | | | | | | | |
| Green mature | 0·82 | 0·75 | 1·57 | 1·09 | 4·62 | 6·54 | 11·2 | 29·8 | 32·1 | 35·2 | — |
| Ripe | 0·87 | 0·53 | 1·40 | 1·64 | 10·9 | 4·22 | 15·2 | 46·0 | 28·5 | 19·2 | — |
| Overripe | 0·94 | 0·32 | 1·26 | 2·94 | 15·7 | 3·85 | 19·5 | 41·9 | 45·7 | 15·9 | — |

S = Soluble.
I = Insoluble.
T = Total.

However, soluble protein content in mango fruits showed a slight increase, whereas, in apricot fruits, it was decreased during the ripening stages. At the overripe stage, the soluble protein was more abundant, especially in mango fruits.

Our results are in good agreement with those obtained by Drawert *et al.* (1972).

## Carbohydrate fractions

Table 1 shows that the percentage of soluble and total carbohydrates were increased gradually in apricot and mango fruits according to the ripening stage. The insoluble carbohydrate showed a slight increase in apricot fruits, while in mango fruits, there was a marked decrease. Of the soluble sugars, glucose, fructose, sucrose and xylose were detected in apricots and their percentages varied according to the degree of ripening. At the green mature stage, glucose was the major sugar (45·6%) (Table 1), while at ripe and overripe stages fructose was the predominant one. Sucrose was nearly stable and fructose seems to increase gradually, while glucose and xylose decreased and reached their minimum values at the overripe stage.

In mango fruits, glucose, fructose and sucrose were detected at the three ripening stages. At the green mature stage sucrose was the major sugar followed by fructose and glucose in descending order, while at the ripe stage glucose was the predominant sugar. In overripe fruit, glucose and sucrose contents tended to decrease and fructose increased. These results indicate

**TABLE 2**
Free Amino Acids of Apricots and Mango Fruits during Ripening (mg/100 g)

| *Free amino acid* | *Apricots* | | | *Mango* | | |
|---|---|---|---|---|---|---|
| | *Green mature* | *Ripe* | *Overripe* | *Green mature* | *Ripe* | *Overripe* |
| Glycine | 12·7 | 18·2 | 14·1 | 7·65 | 5·45 | 7·88 |
| Alanine | 6·01 | 8·45 | 60·2 | 16·8 | 10·8 | 13·6 |
| Valine | 1·02 | 1·96 | 2·35 | — | — | — |
| Aspartic | 25·1 | 19·6 | 20·2 | 4·12 | 8·55 | 6·84 |
| Glutamic | 16·6 | 15·2 | 14·0 | 3·52 | 8·66 | 10·8 |
| Arginine | 3·64 | 2·18 | 0·68 | 0·67 | 8·16 | 4·22 |
| Lysine | 3·55 | 7·22 | 4·22 | 3·42 | 7·86 | 4·35 |
| Leucine | 5·62 | 5·08 | 5·42 | — | — | — |
| Threonine | 2·86 | 3·84 | 2·75 | 7·52 | 11·4 | 9·64 |
| Serine | 10·8 | 3·22 | 10·9 | 1·66 | 1·20 | 2·08 |
| Cysteine | 0·78 | 0·94 | 0·82 | — | — | — |
| Tyrosine | 6·45 | 5·22 | 4·65 | 10·9 | 11·3 | 16·4 |
| Phenylalanine | — | — | — | 4·65 | 3·80 | 2·55 |
| Methionine | 0·45 | 0·64 | 2·65 | 1·32 | 2·60 | 1·22 |
| Histidine | 1·08 | 1·60 | 0·90 | 4·65 | 3·88 | 2·46 |
| TFAA | 96·6 | 93·5 | 90·1 | 75·9 | 83·6 | 82·0 |

that the soluble sugars are changed by enzymatic effects during the ripening stages.

Table 2 illustrates the free amino acids of apricot and mango during the whole ripening process. Fourteen amino acids could be detected and determined in apricot. Generally, aspartic acid was the major amino acid followed by glutamic acid and glycine. It is noteworthy that the total free amino acids decreased slightly at the maturity stage. Many workers have reported the presence of the same amino acids in Egyptian apricots (Casoli & Bellucci, 1964).

In mango fruits, twelve amino acids could be detected (Table 2) while valine, leucine and cysteine were absent at all ripening stages. This finding is completely different from that of Asker (1973), who found that valine and leucine were the major amino acids. The absence of valine and leucine during the three ripening stages and the gradual decrease in phenylalanine content may be due to the variety, climate or ecological factors (environmental conditions) or the incorporation of these amino acids in the synthesis of other compounds, i.e. volatile components (Drawert *et al.*, 1972). The amounts of other amino acids varied according to the ripening stages.

Volatile compounds in the overripe apricot and mango fruits are illustrated in Tables 3 and 4. In the case of apricot many components were identified, i.e. aromatic and aliphatic aldehydes, esters, alcohols and ketones. Methyl benzoate, methyl cinnamate, β-phenyl ethyl acetate and benzyl acetate were all present and probably contribute to the fruity aroma as reported by Tang & Jennings (1968). β-ionone, which contributes to the fruity aroma, comprises 3·16%. Among the terpene derivatives linalyl acetate was the highest in percentage, followed by α-terpineol and linalool, respectively. However, the fragrant flavour components (as ester com-

**TABLE 3**
Volatile Components of Apricot Juice

| *Peak No.* | *(tr)* | *Components* | *Percentage* |
|---|---|---|---|
| 1 | 1·5 | Amyl acetate | 2·76 |
| 2 | 2·2 | 3-Methyl butanol | 0·63 |
| 3 | 2·6 | Pentanal | 0·42 |
| 4 | 3·3 | 3-Hexanol | 4·40 |
| 5 | 4·3 | Ethyl butyrate | 16·8 |
| 6 | 5·6 | Hexanal | 0·94 |
| 7 | 6·9 | Heptanal | 7·70 |
| 8 | 7·5 | Linalyl acetate | 11·5 |
| 9 | 8·0 | 2-Hexanol | 6·45 |
| 10 | 9·1 | Methyl hexanoate | 2·38 |
| 11 | 10·0 | Octanal | 0·52 |
| 12 | 10·6 | 2-Methyl-1-pentanol | 13·2 |
| 13 | 12·5 | Linalool | 0·40 |
| 14 | 13·6 | Nonanal | 1·05 |
| 15 | 15·0 | 1-Heptanol | 0·88 |
| 16 | 16·3 | Decanal | 0·31 |
| 17 | 17·4 | Methyl octanoate | 0·79 |
| 18 | 19·0 | Hendecanal | 0·33 |
| 19 | 20·7 | *n*-Octanol | 0·25 |
| 20 | 21·6 | Methyl benzoate | 6·08 |
| 21 | 22·6 | Benzyl acetate | 1·27 |
| 22 | 23·4 | β-Phenyl ethyl acetate | 0·65 |
| 23 | 24·6 | Dodecanal | 0·55 |
| 24 | 26·3 | β-phenyl ethylalcohol | 0·58 |
| 25 | 28·1 | α-Terpineol | 0·88 |
| 26 | 28·1 | Benzyl alcohol | 2·28 |
| 27 | 30·6 | β-Ionone | 3·16 |
| 28 | 31·7 | Methyl cinnamate | 3·60 |
| 29 | 34·5 | 3-Heptanone | 0·64 |
| 30 | 36·4 | 3-Octanone | 4·75 |
| 31 | 40·4 | Myristaldehyde | 0·67 |
| 32 | 42·8 | Unknown | 2·69 |

**TABLE 4**
Volatile Compounds of Mango Juice

| *Peak No.* | *(tr)* | *Components* | *Percentage* |
|---|---|---|---|
| 1 | 2·9 | Butanol | 0·89 |
| 2 | 3·6 | Myrcene | 6·23 |
| 3 | 4·3 | *iso*-Butyl acetate | 0·94 |
| 4 | 4·9 | Butyl acetate | — |
| 5 | 5·6 | Hexanal | 1·38 |
| 6 | 6·0 | Unknown | 1·44 |
| 7 | 6·8 | Isoamyl acetate | 0·68 |
| 8 | 7·5 | Heptanal | 4·87 |
| 9 | 8·0 | Limonene | 1·82 |
| 10 | 9·0 | Hexyl acetate | 0·64 |
| 11 | 10·0 | Linalool | 2·18 |
| 12 | 11·0 | *cis*-Ocimene | 39·3 |
| 13 | 12·9 | 1-Hexanol | 2·18 |
| 14 | 13·9 | Nonanal | 2·65 |
| 15 | 15·0 | Methyl-hexanoate | 0·52 |
| 16 | 16·0 | Benzaldehyde | 1·82 |
| 17 | 16·3 | Unknown | 2·42 |
| 18 | 17·0 | Methyl octanoate | 1·13 |
| 19 | 18·5 | 2-Furfural | 1·82 |
| 20 | 19·9 | 5-Methyl furfural | 2·05 |
| 21 | 21·5 | Ethyl octanoate | — |
| 22 | 22·5 | 2-Acetyl furan | 5·86 |
| 23 | 23·3 | Phenyl acetaldehyde | 5·34 |
| 24 | 24·2 | Phenyl ethyl acetate | — |
| 25 | 25·0 | α-Terpineol | 3·20 |
| 26 | 26·2 | Phenyl ethyl alcohol | 1·42 |
| 27 | 27·2 | Unknown | 0·68 |
| 28 | 28·7 | Benzyl alcohol | 0·50 |
| 29 | 30·2 | 3-Heptatanone | 6·02 |
| 30 | 31·7 | Ethyl decanoate | — |
| 31 | — | — | — |
| 32 | — | — | — |

pounds) have the highest percentage. On the other hand, aliphatic aldehydes are at much lower concentrations than esters. Aldehydes such as 3-methyl butanal, pentanal and hexanal are derived by β-oxidation of fatty acids. The types of ketones commonly found in apricot juice were 3-alkanones such as 3-heptanone and also derived from β-oxidation and decarboxylation of fatty acids. Lipparini & Cavana (1975) reported that apricot contains 0·04–0·10% diacetyl, 0·05–0·13% acetone and 8–21% of 2–3 dibutylene glycol.

In mango, thirty compounds were separated with different concentrations as shown in Table 4. Among these components, twenty-four compounds were identified including esters, aldehydes, alcohols and hydrocarbons. The results are similar to those obtained by Hunter *et al.* (1974). Table 4 shows that *cis*-ocimene and myrcene were the major compounds in the over-ripened mango juice. The same results were obtained by Tressl *et al.* (1983). Alcohol, terpineol and linalool had the highest concentrations, with the total esters representing about 3·8%. The two alcohols terpineol and linalool were also identified by Abo-Elenein *et al.* (1983). Furan derivatives seem to have some role in producing the characteristic sugar sweetness of mango and are found in considerable amounts in mango juice. As is well known, furan derivatives are produced by Maillard reactions and may give the brown colour which is observed in the pulp of the mango fruits (Tang & Jennings, 1968).

Table 5 shows the fatty acid composition of oil samples of apricot and mango juice during the ripening stages, in which nine predominant fatty acids with different chain length were found. Myristic acid in apricot and palmitic acid in mango were the more abundant saturated fatty acids while oleic acid in both was the principal unsaturated fatty acid, followed by

**TABLE 5**
Fatty Acids (%) of Apricot and Mango Juice during Ripening

| *Fatty acids* | *Apricots* | | | *Mango* | | |
|---|---|---|---|---|---|---|
| | *Green mature* | *Ripened* | *Over ripened* | *Green mature* | *Ripened* | *Over ripened* |
| *Saturated FA* | | | | | | |
| $C_8$ | 1·49 | 0·74 | 0·83 | — | — | — |
| $C_{10}$ | 3·22 | 0·86 | 1·06 | 1·24 | 1·08 | 0·82 |
| $C_{12}$ | 3·17 | 0·92 | 0·64 | 3·30 | 0·92 | 1·72 |
| $C_{14}$ | 43·2 | 48·6 | 46·3 | 0·82 | 0·88 | 0·78 |
| $C_{16}$ | 10·0 | 15·6 | 15·0 | 49·3 | 55·0 | 57·0 |
| $C_{18}$ | 3·78 | 2·25 | 3·48 | 2·20 | 2·88 | 2·70 |
| Total | 64·9 | 68·7 | 67·3 | 56·9 | 60·8 | 63·7 |
| *Unsaturated FA* | | | | | | |
| $C_{18:1}$ | 20·8 | 15·7 | 20·0 | 26·2 | 21·3 | 22·9 |
| $C_{18:2}$ | 10·3 | 10·6 | 7·52 | 11·6 | 10·9 | 8·18 |
| $C_{18:3}$ | 4·07 | 4·91 | 4·81 | 5·39 | 7·06 | 5·82 |
| Total | 35·2 | 31·3 | 32·3 | 43·1 | 39·2 | 36·9 |
| TS/TU | 1·84 | 2·20 | 2·10 | 1·32 | 1·55 | 1·71 |

linoleic acid during all the ripening stages. The concentration of myristic acid ranged from 43·2% to 46·3% and palmitic acid from 49·3% to 57·0% through the ripening stages, while oleic acid ranged from 20·8% to 15·7% in apricot oil and from 26·2% to 21·3% in mango oils. On the other hand, the short chain saturated fatty acids, i.e. $C_8$,$C_{10}$ and $C_{12}$, constituted 7% and 5% of total fatty acids in apricot and mango oil, respectively. It is noteworthy that the amounts of the lower fatty acids (from $C_8$ to $C_{12}$) were decreased at ripe and overripe stages and this may be due to the volatile and water-soluble properties of these fatty acids.

The results indicated that the amount of linoleic acid was decreased, accompanied by a noticeable increase in the amounts of palmitic or myristic acids in both apricot and mango oils; this may be due to the conversion of some $C_{18:2}$ to saturated fatty acid, enzymatically. The percentage of total saturated fatty acids ranged from 64·9% to 67·3% in all ripening stages, while the percentage of total unsaturated fatty acids ranged from 35·6% to 32·3%. Due to ripening the amount of total saturated fatty acids increased or the degree of saturation was increased as evidenced by the increase in total saturated/total unsaturated ratio (TS/TU ratio). Our results are in agreement with those obtained by Matto & Modi (1970).

Finally, we can conclude that, initially, the fruits are highly acidic. The acidity decreases gradually with the approach of harvest maturity. The reduction of acidity during ripening plays a great part in the sugar:acid balance and consequently, in influencing the taste and flavour of the fruits. Also, the composition of constituent fatty acids varies, depending on the degree of maturity. Otherwise, the lipids have been linked with colour and flavour development during ripening. There is a correlation between the flavour and the ratio of palmitic to palmitoleic acid. If this ratio was more than 1 this meant a wild aroma, while less than 1 gave a strong aroma. Also, a detailed knowledge of the sterol composition may be helpful in identifying the presence of synthetic additives during manufacture. So, the results obtained may help technologists to determine the best stage of ripening to enhance the final products and to elucidate the changes which occur during the production of these fruits.

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