Zagazig J. Agric. Res., Vol. 36 No. (4) 2009 789-801

EFFECT OF FROZEN STORAGE ON THE VOLATILE COMPONENTS OF TWO MANGO CULTIVARS

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Accepted 13 /8/2009

ABSTRACT: This study was carried out to isolate, identifaction of flavouring agent and effect of frozen storage for two of the most commonly grown mango varieties, i.e. Cobbania and Zebda. The volatile components were extracted by headspace collection method and analyzed using Gas Chromatography-mass Spectrometry.The obtained results revealed that 53 volatile components were fractionated and identified as responsible for characteristic flavor of fresh Cobbania variety. Meanwhile, 41 volatile components were identified in fresh Zebda pulp variety. Myrcene, ocimene and limonene were the most dominating volatile components identified in both varieties. It was also found that frozen storage greatly affected the volatile components responsible for the natural flavor of fresh fruits.The results showed a continual increase in the concentration of alcohols and aldehydes, ketones, esters and reduction in hydrocarbons and carbonyls at the end of frozen storage.

Key words: Mango, volatile components, Gas Chromatography, freezing, preservation.

INTRODUCTION

Flavor is described as the sensation produced by a material taken in the mouth, perceived principally by the senses of tast and also by the general pain, tactile and temperature receptors in the mouth flavor also denote the sum of the characteristics of the materials which produce the sensation (Hall, *et al.*, 1988).

Flavor study in different foods and drinks has been of increasing interest due to its relationship with

the quality of a food product. In the case of fruits, aroma is one of the most appreciated characteristics. Fruit flavor is particularly sensitive to compositional alteration. The volatile compounds that form the fruit flavor are produced through metabolic pathways during ripening, harvest, post-harvest and storage and depend on many factors related to the species, variety and type of technological treatment (Rizzolo *et al.,* 1992). Sometimes it is important to know the typical chromatographic pattern of fresh product in order to identify changes in volatile composition. The volatile components of fruit juices play a very important role in the overall acceptability of juices. Extensive studies had been done concerning the volatile components in different fresh fruit varieties. The mango is one of the first fruit to be cultivated by man. Compared to citrus and bananas, mangoes are the third most important crop in the tropics. Mango fruits are very much relished for their succulence, exotic flavor and delicious taste (Malo and Campblle, 1978). They are also an excellent source of dietary fibers, provitamin A and vitamin C.A fruit with many versatile properties has naturally found application for processing into several products (Singh, 1960, Hulme, 1971, Subramanyam *et al.,* 1975 and Ashraf *et al.,* 1981).

Mango is one of the now fruits, which can be processed at all storage of maturity into attractive and stable products for use all round the year mango fruits are produced principally in the developing countries of the tropics, with total world annual production of 34.185000 million tons (FAO, 2003).

Mango (*Mangifera Indica L.)* is one representative of the group of tropical fruits, becomes more and more importent on markets. The popularity of mangoes is increasing just because of their strong and pleasant aroma (Engel and Tressel, 1983). Mango belong to family *Anacardiaceae* in the *genus mangifera.* The family consists of 41 species of which the mango *(Mangifera Indica* L.*)* is the most important. It was know as a cultivated species from 4 to 6 thousand years at ago in Indian sub-continent it has spread to different parts of the world (Selvaraj and Pal, 1989).

In Egypt, mangoes are one of the most popular fruits. Mango trees are cultivated almost in all

area of Nile valley and around the dessert. Their cultivation is concentrated in sandy soil like in Sharkia and Ismailia governorates and new reclaimed areas. The annual production of mango was estimated to be 532.422 thousand tons produced from 115.529 fedans, with an average of 4.61 tons per feddan according to Anon, (2007).

There are several varieties grown in Egypt. The better known cultivars are Cobbania, Zebda, Pairi, Alphonso and Mabroka. Moreover Bielig and Askar (1974) investigated the aroma deterioration of orange juice during manufacture and storage. They found an increase in carbonyl compounds during the three months storage. On the other hand, Ahmed (1988) studied the change in the volatile components of strawberry during frozen storage at-18°C. The total aromatic components decreased after six months of frozen storage at-18°C. The percentage decrease or completely disappear during frozen at- 18°C and others reached higher concentration.

El-Nemr, (1995) investigated the changes in flavoring constituents of mango pulp during frozen storage. They found an increase in the concentration of alcohols and esters and reduction in hydrocarbons and carbonyls at the end of frozen storage.

The present study amis to investigate the changes in flavor constituents and off-flavor arising for two mango pulp cultivars during freezing storage at-20°C for 3 and 9 months.

MATERIALS AND METHODS

Materials

Mango Fruits

About 100Kg of ripe fruits of Zebda and Cobbania varieties were used in this investigation. They were obtained from a private farm in El-Sowa (Sharkia governorate, Egypt).

Methods

Preparation of Mango Pulp

Mango fruits were, washed cut into halves, the seed removed, peeled and dried and juice was mechanically extracted pulp.The pulp was extracted and homogenized using the method described by Askar, *et al.* (1981).

The extracted pulp was divided into suitable portions filled in plastic containers and stored

at-20°C for 3 and 9 months. The samples were allowed to thaw at 20°C for 10 hr befor being analysed.

Extractions of Volatile Components

The aroma components of mango pulp, were isolated according to the method described by Umano *et al.* (1995) using head space extraction in a closed bottle as follows: 100 ml of juice was placed in a 1L Wolf bottle equipped with magnetic stirrer-Nitrogen gas was allowed to pass through the bottle from nitrogen generator at a rate of 20 ml/min. the volatiles were trapped in gas washing cylinders filled with 150 ml diethyl ether and cooled with ice at 4°C. The process was continued for 2.5 hrs. the mixture of diethyl ether and volatiles in each cylinder was collected, dried over anhydrous sodium sulphate and evaporated at 40°C by rotary evaporator to 5ml, then transferred into 10ml vial and re-evaporated under a stream of nitrogen gas to volatiles were identified using the GC/MS system. This extract was kept in amber glass bottles at -18°C were identified using the GC/MS system

Gas Liquid Chromatographic Technique

Gas liquid chromatographic technique (GlC) was carried out for each Kind of juice using a dual flame ionization detector –PYE-unicam Instrument. The chromatograph was filled with SE-30 stainless steel column (108mx 3mm) packed with supelcois phase (3%methyl silicon) coated in supelcoport (100/120 mesh). Column oven temperature of injector and decetor were, 25°C and 300°C airflow rates were 60, 30 and 300 ml/min respectively. Peak identification time for each peak with those of standard chromatogram and the quantitative determination was based upon the area under peaks.

Gas Chromatography (GC) - Mass Spectrometer (MS) System

Varian gas chromatography (Walnut Greek, California, USA). DB-5 capilly column (J and W Scientific USA), 30 meter length and 0,25 mm thickness was used. Column temperature was programmed from 60 to 220°C at rate of 5°C/min. Injection temperature was 220°C. Helium was the carrier gas at a flow rate1.0 ml/min and the column head pressure was 10-15 PS mass spectrometries. Finnigon mat SSQ7000 (Thermo Inst., USA) mass spectrometer. Mass standard library (Nist Software Package National Institute for standerd Technology, USA) was used.

The estimation was carried out in Central Laboratories for Services, National Center of Research, Dokki, Giza.

RESULTS AND DISCUSSION

Effect of Frozen Storage on the Flavour Components of the Two Mango Cultivars

The results of qualitative and quantitative analysis of volatile flavor components of the two mango cultivars during freezing storage (-20°C) for 3 and 9, months are summarized in Table (1-2).

So, the changes in the volatile components of Cobbania and Zebda mango pulp durring frozen storage at-20°C for 3 and 9 months were determined qualitatively and quantitatively by GLC/MS technique. Results in Table 1,2 showed that most of the hydrocarbons fraction was decreased for the frozen storage at -20°C after 3, 9 months. Moreover, this decrement was higher for the fresh mango pulp than frozen storage was reported by Macleod *et al.* (1988), in this concept, the predominate compound, α-terpinolene decreased sharply after frozen storage, Ahmed (1988) and Sallam, *et al.* (1996).

The reduction in α-terpinolene caused the deterioration in aroma because this compound is considered as one of the main contributors to the odor quality of mango juice (El-Nemr and Askar, 1986).

Moreover, a part of this component probably has been converted to α-terpinolene and terpinen – 4- 01 which could lead to an unfavorable aroma and fishy flavor (El-Nemr, 1985), Moreover, ß-ocimene were also decreased in the some pattern as α-terpinolene. Reduction in this compound means loss of flavor components as reported by Bielig and Askar (1974), Abo El-Neil (1984) On the other side it could be observed from the results in Table 1 & 2 that, was a sharp decrease in all volatile fractions after frozen storage at-20°C for 3, 9 months probably due to freezing preservation, especially of the hydrocarbons fractions.

Finally, the decrease in the volatile components in both Cobbania and Zebda could be mainly due to chemical and /or enzymatic reactions, or probably due to changes in the natural configuration of any of the inherent aromatic compounds leading to the formation of other components not previously found

Table 1. Volatile flavor components of Cobbania manago pulp fresh and frozen storage at - 20°C after 3,9 months

Constituents	R_t (min)	Fresh Cobbania	Concentration % Storage period (months)	
			3	9
Hydrocarbons:				
Delta -3- careen	6.14	0.88	0.20	0.25
Myrcene	6.62	26.12	15.12	13.50
α-Terpinene	7.18	0.20	-	-
Limonene	7.42	9.25	10.15	7.75
β-phyllandrene	8.06	0.002	-	-
β- Ocimene	8.65	12.95	11.30	8.70
γ-terpinene	9.11	0.30	-	-
α-pinene	9.76	0.15	-	-
β-pinene	10.04	0.10	-	-
α-Terpinolene	10.81	6.00	4.25	2.50
Tetradecane	11.92	-	0.11	2.50
α-Humulene	12.65	0.88	-	-
Hexadecane	13.37	0.35	-	0.15
Octadecane	13.48	0.07	-	-
α-Copaene	14.05	-	-	-
Heptanene	14.37	0.20	-	-
Nonane	15.77	-	-	-
p-Cymene	15.85	0.03	-	-
β-Caryophyllene	16.14	8.50	6.50	4.30
Esters:				
Ethyl acetate	18.67	0.01	-	-
Ethyl butanoate	19.26	7.25	-	2.50
Butyl acetate	21.93	0.14	-	-
(z)-3-hexenyl acetate	23.57	0.38	-	-
Methyl ethyl butan oate	24.91	0.11	-	-
Ethyl myristate	25.63	0.14	-	-
Ethyl linoleate	26.60	0.18	-	-
Ethyl palmitate	29.07	0.45	5.50	0.70
Ethyl-3–hydroxyl butanoate	30.38	-	-	-
Amyl acetate	31.05	-	-	-

Table 1: Cont.

Alcohols:				
1-Butanol	50.92	0.11	3.15	8.50
2- methyl propan -1-01	61.77	0.55	1.45	6.70
Methyl-3-buten-2-01	37.95	0.098	0.50	3.50
1- Hexanol	40.81	1.32	3.80	10.50
α- Terpineol	42.73	0.15	-	-
Geraniol	38.40	0.06	-	-
(z)-3- Hexene-1-01	72.91	-	0.50	0.91
2-Heptadecan- 01	10.45	0.45	0.70	0.80
Linalool	11.03	2.95	1.30	0.50
Benzyl alcohol	28.97	-	3.50	1.50
Acids:				
Butyric acid	19.60	0.39	0.30	-
Acetic acid	32.16	0.01	0.02	0.04
Benzoic acid	36.24	0.005	0.001	-
Headecanoic acid	36.36	-		
Aldehydes & ketones:				
Hexanal	48.77	0.12	1.55	3.50
2-Heptanone	58.22	2.90	1.70	0.80
2-Hexenal	15.07	1.24	1.15	0.70
β- ionone	31.64	0.15	-	-
Heptanone	34.34	-	-	-
Furfural	34.96	3.50	4.95	7.30
5-hydroxy methyl furfural	14.46	3.95	6.15	14.70
Decanal	14.55	-	1.70	2.80
Pheyl acetaldehyde	58.22	0.004	0.07	0.08
Citral	74.46	0.001	-	-
Benzaldhyde	60.35	-	0.50	0.90
Methyl cinnamic aldhyde	65.98	-	0.55	0.70
Lactones:				
γ- Octalactone	21.04	0.91	0.90	0.80
Δ- Octalactone	25.37	0.63	0.65	0.70
γ- Butyrol lactone	66.71	0.18	0.80	0.90
Decalactone	35.41	0.41	0.40	0.80
Δ- Caprolactone	36.82	0.91	0.31	0.65
γ- Caprolactone	30.10	1.02	1.70	1.30
Miscellaneous:				
Acetoin	72.62	0.39	0.31	0.50
Methyl anthranilate	9.50	0.01	0.07	0.09
4- venyl phenol	37.71	0.005	0.003	0.08

Table 2. Volatile flavor components of Zebda mango fresh and frozen storage at -20°C after 3, 9 months

Constituents	R_t (min)	Fresh Zebda	Concentration % Storage period (months)	
			3	9
Hydrocarbons:				
Delta -3- carene	6.14	0.75	0.40	0.30
Myrcene	6.62	24.55	14.30	8.60
α-Terpinene	7.18	0.65	0.11	0.15
Limonene	7.42	14.18	11.20	8.15
β-phyllandrene	8.06	-	-	0.70
β- ocimene	8.65	11.22	9.75	6.70
γ-Terpinene	9.11	0.95	-	0.15
α-pinene	9.76	0.15	-	-
β-pinene	10.04	0.10	-	-
α-Terpinolene	10.81	5.00	4.16	2.80
Tetradecane	11.92	-	-	-
α-Humulene	12.65	1.44	0.25	0.30
Hexadecane	13.37	0.55	-	-
Octadecane	13.48	0.70	-	-
α-Copaene	14.05	0.92	-	-
Heptanene	14.37	0.07	-	-
Nonane	15.77	-	-	0.70
p-Cymene	15.85	-	-	-
β-Caryophyllene	16.14	6.33	4.95	3.40
Esters:				
Ethyl acetate	18.67	0.54	-	-
Ethyl butanoate	19.26	13.22	-	1.77
Butyl acetate	21.93	-	-	-
(z)-3-hexenyl acetate	23.57	-	-	-
Methyl ethyl butanoate	24.91	-	-	-
Ethyl myristate	25.63	-	-	-
Ethyl linoleate	26.60	-	-	-
Ethyl palmitate	29.07	-	-	-
Ethyl -3 – hydroxyl butanoate	30.38	0.03	-	-
Amyl acetate	31.05	0.07	-	-

Table 2. Cont.

Alcohols:				
1-Butanol	50.92	0.28	2.90	8.15
2- methyl propan -1-01	61.77	-	1.30	5.80
Methyl-3-buten-2-01	37.95	-	0.30	3.10
1- Hexanol	40.81	0.005	3.90	9.40
α- Terpineol	42.73	0.32	-	-
Geraniol	38.40	0.05	-	-
(z)-3- Hexene-1-01	72.91	0.51	0.30	0.95
2-Heptadecan- 01	10.45	-	0.60	0.70
Linalool	11.003	1.55	1.20	0.80
Benzyl alcohol	28.97	-	2.25	1.90
Acids:				
Butyric acid	19.60	0.07	-	-
Acetic acid	32.16	-	-	0.07
Benzoic acid	36.24	0.05	0.03	0.01
Hexadecanoic acid	36.36	0.08	-	-
Aldehydes & Ketones:				
Hexanal	48.77	-	1.30	2.90
2-Heptadecane	58.22	-	1.15	0.90
2-Hexenal	15.07	-	1.30	0.40
β- ionone	31.64	0.20	-	-
Heptanone	34.96	0.15	-	-
Furfural	34.96	2.15	2.75	6.50
5-hydroxy methyl furfural	14.46	4.65	5.30	13.80
Decanal	14.55	0.20	0.70	0.90
Phenyl acetaldehyde	58.22	-	0.06	0.09
Citral	73.46	-	-	-
Benzaldhyde	60.95	0.01	-	-
Methyl cinnamic aldhyde	65.98	0.004	-	-
Lactones:				
γ- Octalactone	21.04	0.22	0.10	0.80
Δ- Octalactone	25.37	0.13	0.19	0.25
γ- Butyrol lactone	66.71	-	-	-
Decalactone	35.41	0.37	0.40	0.8
Δ- Caprolactone	36.82	-	-	-
γ- Caprolactone	30.10	0.95	0.90	0.60
Miscellaneous:				
Acetoin	72.62	0.15	-	-
Methyl anthranilate	9.50	0.11	-	-
4- venyl phenol	37.71	-	-	-

b ıt consequently appeared, ii dicating continuous changes in tl e final aroma and/ or the final fl ıvor and acceptability of such N ango varieties on prolonged fi ɔzen storage Macleod *et al.* (: 988).

Moreover, the aldehydes, esters a ıd alcohols showed the some tr ɔnd increasing such as 1-butanol, 1 hexanal, 2-methyl propan -1-01, α terpinolene, (z)-3-x ene- 1-01, ß-ic none, hexanol, heptanone, d ɔcanal, citral, and benzaldhyde, in th e stored samples than the fresh ju ice.

Moreover, the production of 2, 5· dimethyl 2-H-furanone (in fr ɔzen Cobbania in the stored) and 5· hydroxy methyl furfural in fr ɔzen Cobbania and Zebda. The ir crease in the furan derivatives w ıich accompanied by the brown c(lor is attributed to the reaction b(tween reducing sugars and a ı ıino acids during storage or re lated to the degradation of as corbic acid Aboul Eneine *et al.* (1983). Results in Table 1 & 2 a] pear also that, the furfural was fc und in the fresh mango pulp, but in small quantity, and increased a ı er frozen storage at-20°C for 3, 9 nonths El-Nemr (1995).

In general, the changes in the flavor of mango pulp during frozen storage were due mainly the reduction in the principle flavor compounds and the formation and increasing in furfural, hexanal, 1-butanol, hexanol and methyl butanate which caused terpinyl, aged fermented rancid aroma and off flavor for the product. These undesirable falvors due to enzymatic and microbial activity.

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تأثير التخزين بالتجميد على مركبات النكهة فى صنفين من المانجو

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جرى هذا البحث بغرض فصل وتعريف ودراسة تأثير الحفظ بالتجميد على مركبات النكهة لصنفين من أصناف المانجو هما الكوبانية والزبدية.

تم إستخلاص مركبات النكهة الطيارة فى المانجو الطازج وذلك باستخدام طريقة الفراغ القمى Headspace ثم التعرف عليها باستخدام جهاز التحليل الكروماتوجرافى الغازي GLC المرتبط بجهاز تحليل طيف الكتلة (GC/ MS). حيث أمكن فصل والتعرف على ٥٣ مركبا طياراً من ثمار صنف الكوبانية على حين أمكن فصل والتعرف على٤١مركبا طياراً من ثمار صنف الزبدية الطازجة. كما وجد أن مركبات الميرسين والأوسيمين والليمونيين هما المركبات السائدة فى كل من الصنفين. ولقد وجد أن التجميد والتخزين بالتجميد يؤثران تأثيرا واضحا على مركبات النكهة لكل من الصنفين.

أوضحت النتائج زيادة مستمرة فى تركيز الكحولات والألدهيدات والكيتونات والأسترات ونقص فى المركبات الهيدروكربونية والكربونيلية فى نهاية التخزين.