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**Supplementary Material Available:** Four tables of the literature values of the components determined in the four species of fruit are given. References additional to those cited in the main body of the text are quoted (5 pages). Ordering information is given on any current masthead page.

## LITERATURE CITED

- Association of Official Analytical Chemists, "Official Methods of Analysis", 11th ed, Washington, D.C., 1970.  
 Association of Official Analytical Chemists, "Official Methods of Analysis", 12th ed, Washington, D.C., 1975.  
 Barakat, M. Z., El-Wahab, M. F. A., El-Sadr, M. M., *Anal. Chem.* **27**, 536 (1955).  
 Bickoff, E. M., *Methods Biochem. Anal.* **4**, 4 (1957).  
 Brodrick, H. T., Thomas, A. C., Van Tonder, A. J., Terblanché, J. C., South African Atomic Energy Board, PER Report No. 7, 1977 (ISBN 0 86960 6514).  
 Brodrick, H. T., Thomas, A. C., Visser, F. M., Beyers, M., *Plant Dis. Rep.* **60**(9) 749 (1976).  
 Bunnell, R. H., Driscoll, W., Bauernfeind, J. C., *Food Technol.* **12**, 536 (1958).

- Coetzee, W. H. K., Burger, I. J., *Food Ind. S. Afr.* **5**, 27 (1953).  
 Crosby, N. T., *Analyst (London)* **102**, 225-263 (1977).  
 Evered, D. F., *Analyst (London)* **85**, 515 (1960).  
 Fiske, C. J., SubbaRow, Y., *J. Biol. Chem.* **66**, 375 (1925).  
 Fox, F. W., "Studies on the Chemical Composition of Foods Commonly Used in Southern Africa", SAIMR, Johannesburg, 1966.  
 Hulme, A. C., "The Biochemistry of Fruits and Their Products", Vol. 1, Academic Press, London, 1970.  
 Hulme, A. C., "The Biochemistry of Fruits and Their Products", Vol. 2, Academic Press, London, 1971.  
 Lowry, O. H., Rosebrough, N. J., Farr, A. L., Randall, R. J., *J. Biol. Chem.* **193**, 265 (1951).  
 Saunders, R. M., *Anal. Chem.* **28**, 350 (1956).  
*S. Afr. Gov. Gaz.* **No. 3274**, 22 (1971).  
 Sumner, J. B., *J. Biol. Chem.* **65**, 393 (1925).  
 Thomas, A. C., Brodrick, H. T., South African Atomic Energy Board, PER Report No. 9, 1977 (ISBN 0 86960 6530).  
 Watt, B. K., Merrill, A. L., "Composition of Foods", Handbook No. 8, Consumer and Food Economics Research Division, Agricultural Research Service, USDA, Washington, D.C., 1975.  
 Wenkam, N. S., Miller, C. D., *Hawaii Agric. Exp. Stn., Bull. No.* **135** (1965).  
 WHO Press Release WHO/35, Sept. 7, 1976.

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## $\gamma$ Irradiation of Subtropical Fruits. 2. Volatile Components, Lipids, and Amino Acids of Mango, Papaya, and Strawberry Pulp

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An investigation of volatile components, amino acids, and fatty acids in irradiated and nonirradiated mango, papaya, and strawberry pulp samples was made. Capillary gas chromatographic analyses of sample extracts have revealed at least 137 mango volatiles, 85 papaya volatiles, and 124 strawberry volatiles. Examination of the gas chromatography profiles and peak ratios from integration data of samples at the same degree of ripeness show similar patterns, and no significant difference between the volatile profiles of irradiated and nontreated samples were established by peak-by-peak analyses of variance. It was further found that the free amino acid and total amino acid content of mango, papaya, and strawberry pulp remained unchanged by irradiation. The fatty acid composition of mango, papaya, and strawberry samples was similar in irradiated and control samples. It was also noted that the organoleptic qualities, volatile profiles, and lipid content of these fruits were highly dependent on the degree of maturity. This factor must be carefully considered in future comparative studies.

Irradiated papayas and strawberries were given recommendation for unconditional clearances for human consumption by an Expert Committee Meeting convened by FAO/IAEA/WHO ("Wholesomeness of Irradiated Food", 1977). Since mangoes have an apparent chemical similarity to strawberries and papayas, only limited feeding studies on mangoes have been commissioned by the International Food Irradiation Project (IFIP). However, it was recommended that these feeding studies be supplemented by analysis confirming chemical similarity between mangoes and the two fruits studied in detail.

Samples of irradiated and nonirradiated mango, papaya, and strawberry pulp were submitted to this Institute for study by the South African Atomic Energy Board, Pelindaba. The purpose of this investigation was to de-

termine if irradiation of the pulp caused significant differences in the lipid fraction, amino acid fraction, or in the total profile of volatile components of the various fruits. This study complements the compositional tables on irradiated and nonirradiated mangoes, papayas, strawberries, and litchis compiled by the South African Atomic Energy Board (Beyers et al., 1978).

## EXPERIMENTAL SECTION

**Cultivars.** Mangoes (*Mangifera indica* Linn.) Kent variety; papayas (*Carica papaya* Linn.) Papino variety (a type similar to the "Solo" variety grown in Hawaii); strawberries (*Fragaria ananassa* Linn.) Selekt variety.

**Source of Fruit.** Mangoes and papayas were supplied by the Letaba Co-operative, Tzaneen, Transvaal, while strawberries were supplied by the Glenwood Farm, Hartbeespoort, Transvaal.

**Irradiation.** The research "loop" of the commercial  $^{60}\text{Co}$  package irradiator (AECL, Ltd) at Pelindaba operating at a dose rate of ca. 0.80 kGy/h was used for all

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irradiations. Mango and papaya received 0.75 kGy dose while strawberry received 2.00 kGy radiation.

**Postirradiation Treatment.** The original consignment of mangoes (mango I) was irradiated as mature green fruit, stored at 13 °C for 21 days, removed to ambient temperature (20–24 °C), and allowed to ripen. The edible portions of the fruit were homogenized. The pulp was stored at –20 °C for 3 months before being submitted for study.

Because initial results indicated possible differing degrees of ripeness in control (nonirradiated) and irradiated pulp, the following method was used for a second consignment of mangoes (mango II) and for the papayas and strawberries. Untreated mangoes and papayas were allowed to ripen at ambient temperature. Strawberries were ripe on receipt and were processed within 5 h of harvesting. The ripe edible portions of the fruits were homogenized, the homogenate was equally divided, and one-half was irradiated. The frozen strawberry pulp was submitted for analysis within 3 days of irradiation. Mango and papaya were received as fresh pulp. The fruit pulps were analyzed immediately upon receipt.

**Organoleptic Evaluations.** Sensory judgements for possible difference between irradiated and nonirradiated pulp samples with respect to appearance, color, and odor were made by our laboratory staff at the time of investigation and in some cases by our experienced panel of 25 members. Comments on the results of these evaluations are included in the discussion.

**Headspace Analysis.** Fruit pulp (300 mL) was placed in a specially prepared headspace sampling flask with gas inlet and outlet valves attached. The system was thoroughly flushed with nitrogen and a stainless steel trap (0.32 × 20 cm) containing a 3-cm plug of Tenax-GC porous polymer was attached to the flask outlet. The pulp was stirred, the system was thermally equilibrated, and the headspace vapor was collected for 3 h from a nitrogen stream of 5 mL/min. The trap was then transferred to a gas chromatograph and heated, and the volatiles were back-flushed with nitrogen into the GC system.

**Vacuum Stripping.** Fruit pulp (50 mL) was placed in a simple freeze-drying apparatus, and both sample and collector were cooled with liquid nitrogen under vacuum. The pulp was allowed to warm gradually to room temperature while keeping the collector cold. The time required to complete the transfer of volatiles was 3 days and approximately 48 mL of aqueous solution was collected. This solution was then extracted three times with 10-mL portions of methylene chloride and the extract concentrated for GC analysis.

**Solvent Extraction (Ether).** Fruit pulp (150 mL) and 100 mL of diethyl ether were placed in a 250-mL glass flask and sealed with a glass stopcock. The mixture was mechanically shaken for 2 h at room temperature, transferred to a PTFE tube, and then centrifuged for 15 min at 9000 rpm at 10 °C. The ether layer was decanted and the process repeated three times. The ether extracts were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to approximately 25  $\mu$ L for GC analysis.

**Freon 12 "Bomb" Extraction.** Fruit pulp (300 mL) was extracted with dichlorodifluoromethane in a specially designed glass bomb apparatus in a manner previously described in detail (Blakesley and Loots, 1977).

**Gas Chromatography of Volatiles.** Chromatographic analysis of the volatile profile was done on a Perkin-Elmer Model 990 instrument using a flame ionization detector. The chromatograph was fully equipped for capillary column operation. Integration was accomplished by on-

line coupling to a Hewlett-Packard 3352B computer system. Conditions were as follows: Carbowax 20M glass capillary column, 50 m × 0.3 mm prepared by a static modification of our published method (Blakesley and Torline, 1975); injection temperature, 230 °C; column temperature, initial 40 °C, then programmed at 2 °C/min to 180 °C; detector temperature, 230 °C; nitrogen carrier flow, 1 mL/min.

**Statistical Evaluations of Volatile Profiles.** A peak-by-peak sorting routine and statistical comparisons of retention and integration data from replicate extracts and GC injections were done on our HP 5934A 32K disc-based computer system.

**Fatty Acid Analyses.** Fatty acid analyses were run by standard methods of this Institute. The moisture content of each sample was determined by a freeze-drying technique using 120 to 160 g of pulp.

**Fatty Acids in Papaya.** The dried samples were extracted with diethyl ether (3 × 65 mL) by shaking at room temperature for 3 h. The mass of the extracted lipids was determined after evaporation of the ether. Methyl esters were prepared by transesterification reactions using 0.025 M NaOCH<sub>3</sub> in dry methanol. The reaction mixtures were kept at 60 °C for 20 min and shaken every 3 min in a Heidolph mixer.

After formic acid neutralization of excess NaOCH<sub>3</sub>, the esters were extracted into hexane. Analysis at this stage indicated incomplete esterification, so the mixtures were refluxed 2 min in excess 14% BF<sub>3</sub>/methanol reagent. Reextraction and removal of solvent provided suitable samples for GC analysis. The results appear in Table II.

**Fatty Acids in Mango.** Triglycerides were extracted from 100 g of the original consignment of mango pulp (mango I) into diethyl ether (4 × 60 mL). Centrifugation at 5000 rpm was necessary to separate the solvent from the pulp. The combined ether extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed by evaporation. Esterification was accomplished using the NaOCH<sub>3</sub>/methanol procedure described above.

The second consignment of mango (mango II) was extracted in the manner as described for papaya. The lipid material was saponified and esterified according to modifications (Van Wijngaarden, 1967) of the Metcalfe et al. (1966) procedure.

The lipids were refluxed in 2 mL of 0.5 M methanolic NaOH until the fat globules went into solution (ca. 5 min). Two milliliters of 14% BF<sub>3</sub>/methanol reagent was added, and reflux continued for 2 min followed by the addition of 1.5 mL of heptane and an additional 1-min reflux. Then 2 mL of saturated NaCl solution was added and, after mixing, the heptane layer containing the methyl esters was removed for analysis. The results for mango I and mango II are listed in Table I.

**Fatty Acids in Strawberry.** Extraction of lipids into diethyl ether was accomplished in the same manner as described for papaya. Saponification and esterification were done using the BF<sub>3</sub>/methanol procedure as described for mango II. The results appear in Table III.

**Gas Chromatography of Fatty Acids.** Chromatographic analysis for the fatty acids was done on a Hewlett-Packard Model 5750 instrument using flame ionization detectors. Integration was accomplished by on-line coupling to a Hewlett-Packard 3352B computer system. Conditions were as follows: Dual glass column operation 2.3 m × 2 mm packed with 4% DEGS on Chromosorb G and a 6-cm precolumn containing 5% DEGS (Analabs) on Chromosorb G; injection temperature, 240 °C; column temperature, isothermal at 185 °C; detector temperature,

**Table I. Fatty Acid Composition: Mango (g of Fatty Acid/100 g of Fatty Acids) (c = Control,  $\gamma$  = 0.75 kGy)**

fatty acid	I <sup>a</sup>		II <sup>b</sup>	
	c	$\gamma$	c	$\gamma$
capric acid	0.1	0.1		
lauric acid	0.3	0.2	0.4	0.4
<i>myristic acid</i> <sup>c</sup>	3.1	3.7	4.5	4.4
pentadecanoic acid	0.3	0.3	0.4	0.4
palmitic acid	26.3	25.1	19.8	21.7
palmitoleic acid	10.9	10.7	17.0	17.7
heptadecanoic acid	0.3	0.3	0.5	0.4
stearic acid	0.5	0.5	0.6	0.6
<i>oleic acid</i>	24.5	19.3	19.8	20.8
<i>linoleic acid</i>	5.6	7.1	5.3	5.6
<i>linolenic acid</i>	25.9	28.5	29.3	26.7

<sup>a</sup> Control and irradiated pulp at different degrees of ripeness. <sup>b</sup> Control and irradiated pulp at the same degree of ripeness. <sup>c</sup> Italics indicate significant difference detected.

250 °C; nitrogen carrier flow, 20 mL/min.

**Amino Acid Analyses.** Amino acid analyses were run by standard procedures of this Institute.

Extractions of free amino acids were done by a modification of the method of Bielecki and Turner (1966). Two milliliters of 12:5:3 methanol-chloroform-water was added to accurately weighed (ca. 200 mg) pulp samples. This mixture was homogenized 1 min in a Whirlimixer and centrifuged, and the clear liquid was decanted. This process was repeated on the solid residue, and the decants were combined. The residue was saved for subsequent extraction.

The combined decants were added to 1 mL of chloroform and 1.5 mL of water, shaken in the Whirlimixer, and centrifuged to break the emulsion. The supernatant aqueous layer was separated and saved.

The solid residue from the methanol-chloroform-water extraction was then extracted three times with 2-mL portions of 80% ethanol by the homogenation, centrifugation, and decantation procedure. The ethanolic extracts were combined and added to the supernatant aqueous layer above. The clear solution was then evaporated under vacuum at 35 °C, dried under vacuum with P<sub>2</sub>O<sub>5</sub>, and dissolved in 2.0 mL of pH 2.2 buffer solution. Suitably sized aliquots were then taken for analysis.

For the determination of total amino acids, accurately weighed pulp samples were hydrolyzed with 2 mL of 6 N HCl under vacuum at 110 °C for 22 h. The hydrolysates were dried with NaOH/P<sub>2</sub>O<sub>5</sub> under vacuum and taken up in 2.0 mL of pH 2.2 buffer solution. After centrifuging, suitable aliquots of the clear mixture were used for analysis. The samples were analyzed on a Beckman Model 120C amino acid analyzer calibrated with Pierce standard solution (Batch 07105-7). Integration of the resulting chromatograms and calculation of the results were done on-line with the Hewlett-Packard 3352B computer system. The results appear in Table IV.

## RESULTS AND DISCUSSION

**Volatile Components.** Irradiated and control samples of mango I pulp were subjected to sensory evaluation for appearance, color, and odor immediately upon receipt. Significant differences were found. The method of head-space analysis was employed to obtain a GC profile of volatile compounds. The results indicated a significant difference between samples as expected from the organoleptic data. Unfortunately, only relatively few compounds were detected (ca. 20) and it became apparent that another sampling technique would be necessary for a

detailed study of the volatile pattern.

We then attempted a vacuum stripping procedure. We were impeded here by the high water content of the distillate. Methylene chloride extraction of the aqueous distillate provided GC samples less satisfactory than the head-space technique.

Direct extraction of the fruit pulp by normal liquid-liquid or liquid-solid techniques was not convenient because of the consistency of the pulp and the formation of emulsions.

We were finally able to obtain suitable extracts using Freon 12 as a solvent in a specially designed glass "bomb" extractor (Blakesley and Loots, 1977). Chromatographic analysis of samples obtained in this manner were shown to be acceptable for this study on the basis of the number of peaks observed and on the reproducibility of the ratios of relative peak abundances from replicate extractions.

Significant differences between GC profiles of the irradiated and control mango pulp samples were obvious. It was suspected, however, that the degree of ripeness between the fruit samples might vary substantially due to the sample preparation technique. This would, of course, have a profound effect upon the organoleptic quality and on the GC volatile profile.

To investigate this possibility we obtained another set of pulp samples (mango II) at the same stage of ripeness, half freshly irradiated and half control. These samples did not show differences organoleptically. We immediately extracted the samples using the "bomb" technique and obtained chromatograms in which we could observe at least 137 volatile components. The extract itself retained an excellent mango aroma.

Three replicate extractions of both the irradiated and control samples were prepared and four to six replicate chromatograms were run on each extract. The retention and integration data were sorted with the aid of specially prepared computer software to create a composite chromatogram of each sample. Figure 1 shows a computer printed line-graph representation of the composite chromatogram for the control mango sample while Figure 2 shows the similar representation for the irradiated mango sample.

Inspection of the chromatograms indicate that the overall profiles are remarkably similar. Detailed inspection of the integration data shows minor differences in some peak ratios; however, these differences are about the same as observed in replicate extractions of identical samples. A peak-by-peak analysis of variance over all of the integration data did not indicate any significant differences in the profiles. It is therefore concluded that no significant change in the volatile profile of mango fruit pulp was detected by the methods described in this investigation.

Papaya and strawberry pulp samples were extracted by the "bomb" method. The consistency of the oily residue necessitated the addition of a few microliters of pentane for convenience in GC analyses. Liquid-liquid extraction with diethyl ether was also done on both fruit pulps. In this case centrifugation was necessary to recover the solvent from the pulp. The ether extracts, though exhibiting suitable and reproducible GC profiles, were organoleptically judged not to have as "good" a fresh fruit aroma as did the Freon extracts. It was assumed that the Freon extracts provided a better example of the true volatile patterns.

Replicate extracts and replicate chromatograms of control and irradiated papaya and strawberry were prepared and analyzed in the same manner as described for mango. The line-graph representations of the composite

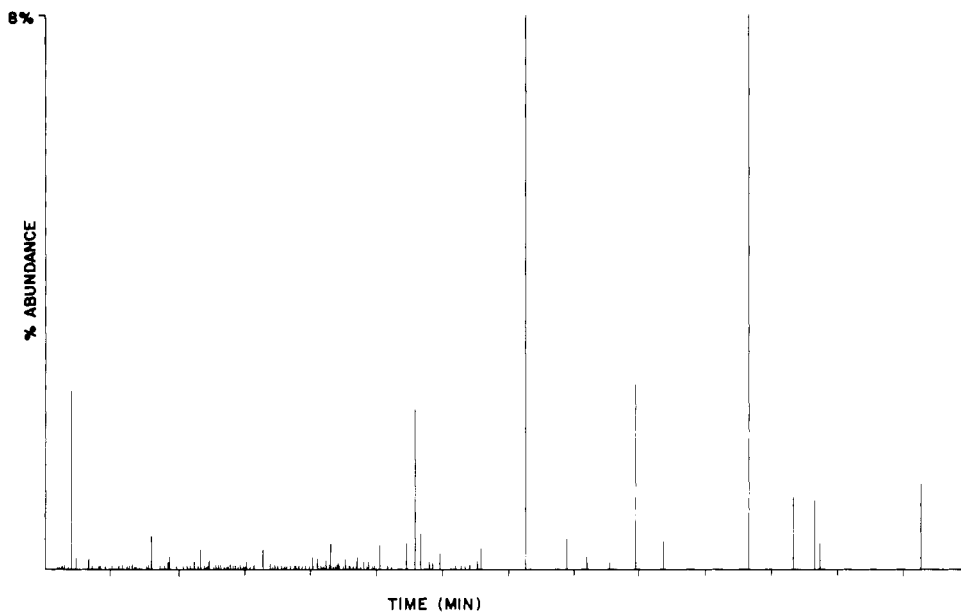


Figure 1. Computer drawn line-graph representation of the composite GC volatile profile from the control sample of mango II fruit.

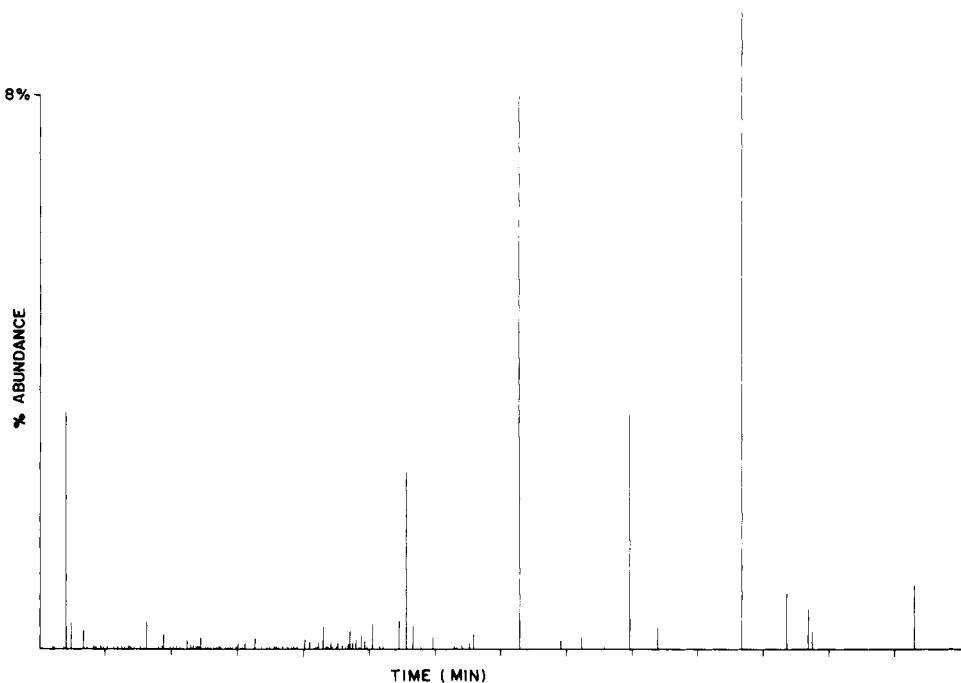


Figure 2. Volatile profile from irradiated mango II fruit.

chromatograms of control and irradiated strawberry appear in Figures 3 and 4. Similar representations for control and irradiated papaya are shown in Figures 5 and 6, respectively.

At least 124 strawberry and 85 papaya volatiles were detected. Examination of the composite chromatograms again indicates similarity before and after irradiation. Peak-by-peak analyses of variance over the integration data gain indicate that the minor profile differences observed can be attributed to within sample variation rather than between sample variation. Thus, it was concluded that no significant volatile profile changes were detected before and after irradiation of strawberry or papaya fruit pulps.

**Fatty Acids.** The results of fatty acid analyses on control and irradiated samples of mango I and mango II fruit pulps appear in Table I. The results from analyses of samples of papaya and strawberry are in Tables II and

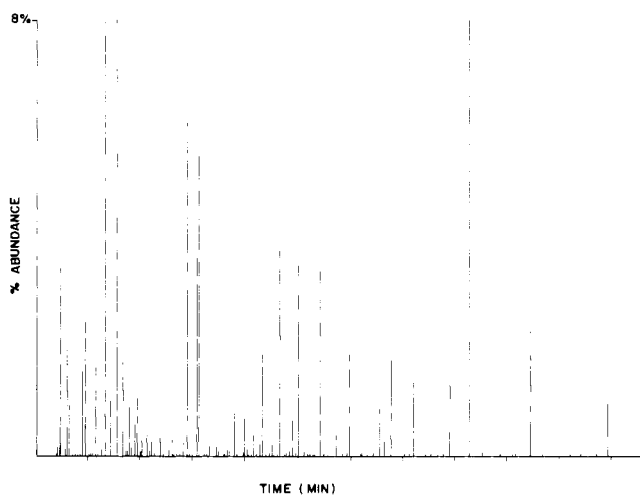


Figure 3. Volatile profile from control strawberry fruit.

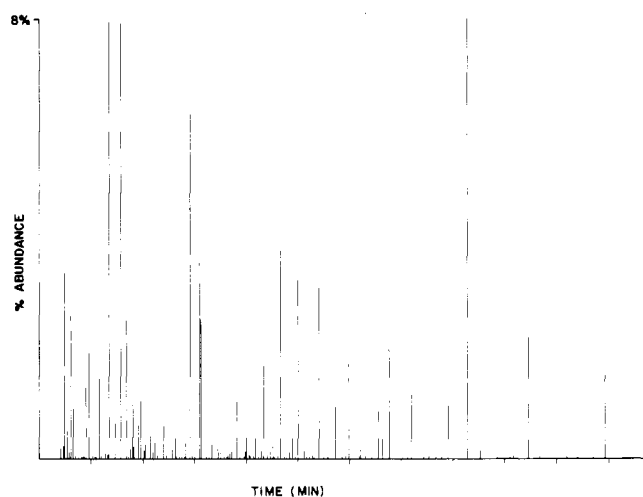


Figure 4. Volatile profile from irradiated strawberry fruit.

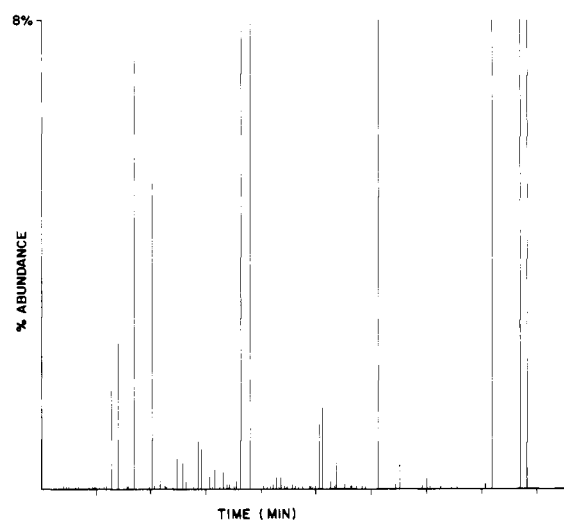


Figure 5. Volatile profile from control papaya fruit.

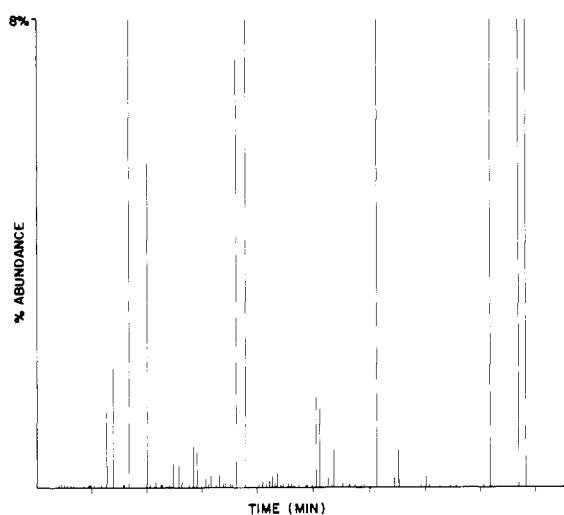


Figure 6. Volatile profile from irradiated papaya fruit.

III, respectively. Ackman (1972) has estimated the probability of error in the gas chromatographic analysis of fatty acids over different compositional ranges. These values have been used as a basis for comparison for the fatty acid patterns of the samples under investigation here. In the cases where differences between control and irradiated samples exceeded the estimated ranges, the specific fatty acids and their compositions are indicated in the

Table II. Fatty Acid Composition: Papaya (g of Fatty Acid/100 g of Fatty Acids) (c = Control,  $\gamma$  = 0.75 kGy)

fatty acid	c	$\gamma$
lauric acid	1.3	1.1
myristic acid	8.3	7.6
palmitic acid	27.2	27.5
palmitoleic acid <sup>a</sup>	18.6	17.8
stearic acid	1.4	1.5
oleic acid	13.0	13.2
linoleic acid	3.2	3.1
<i>linolenic acid<sup>b</sup></i>	18.8	21.5
total lipids, g/100 g of pulp	0.035	0.039
moisture, g/100 g of pulp	86.8	86.9

<sup>a</sup> Contains both 16:1  $\omega$ 7 and 16:1  $\omega$ 9. <sup>b</sup> Italics indicates significant difference detected.

Table III. Fatty Acid Composition: Strawberry (g of Fatty Acid/100 g of Fatty Acids) (c = Control,  $\gamma$  = 2.00 kGy)

fatty acid <sup>a</sup>	c	$\gamma$
palmitic acid	5.7	5.0
palmitoleic acid	0.5	0.4
stearic acid	1.3	1.4
oleic acid	19.4	19.8
linoleic acid	41.6	41.4
linolenic acid	29.8	30.5
arachidic acid (icosanoic)	1.0	1.0
icosanoic acid	0.6	0.5
total lipid, g/100 g of pulp	0.078	0.082
moisture, g/100 g of pulp	93.4	93.4

<sup>a</sup> No significant differences detected.

respective tables by italics. In all of the analyses, the acids were identified by their GC retention and by their ECL values (equivalent chain length).

The fatty acid analysis of mango I revealed a significant difference in the levels of myristic, oleic, linoleic, and linolenic acids. It has been established that during the ripening process of mango fruit an increase in the triglyceride content is accompanied by significant changes in the ratios of fatty acids (Bandyopadhyay et al., 1973a,b). These changes occur primarily in the unsaturated acids, palmitoleic, oleic, linoleic, and linolenic. Unfortunately, obtaining comparative ratios of acids was not possible since samples of irradiated and nonirradiated fruit at various stages of ripeness were unavailable at the time. However, these results lend evidence to the suspicion that the control and irradiated mango I samples were indeed at different degrees of ripeness. This suspicion was confirmed by analysis of samples of mango II known to be at the same degree of ripeness. The fatty acid patterns are very similar with only the unstable linolenic acid showing a significant difference.

Unexpected problems were encountered during preparation of methyl ester derivatives of papaya for analysis. Both the  $\text{BF}_3$ /methanol procedure (Metcalf et al., 1966) and the transesterification procedure gave only partially esterified products. Complete esterification was only accomplished by a combination of these methods. The reason why the papaya lipids resisted esterification by standard methods is not known.

It is evident from Table II that the total lipid content of papaya is very low. The fatty acid patterns of control and irradiated papaya samples are very similar with the only detected significant difference being again in the unstable linolenic acid.

No significant differences were observed in the fatty acid patterns of control and irradiated samples of strawberry pulp.

Table IV. Amino Acid Composition (g of Amino Acid/100 g of Pulp) c = Control, γ = 0.75 kGy (mango, papaya), γ = 2.00 kGy (strawberry)

amino acids	A. mango				B. papaya				C. strawberry			
	c		γ		c		γ		c		γ	
	free	total	free	total	free	total	free	total	free	total	free	total
essential acids												
histidine	T <sup>b</sup>	0.007	T	0.008	0	0.006	0	0.005	0.001	0.007	0.001	0.008
lysine	0.0003	0.021	T	0.022	0.002	0.022	0	0.020	0	0.019	0	0.022
phenylalanine	0	0.010	0	0.010	0	0.010	0	0.009	0	0.014	0	0.015
tryptophan		not determined										
methionine	0	0.004	0	0.003	0	0.002	0	0.003	0	0.006	0	0.006
threonine	0	0.013	0	0.014	0	0.012	0	0.012	0	0.019	0	0.020
leucine	0.0001	0.021	0.0001	0.023	0.002	0.018	0	0.018	0	0.023	0	0.025
isoleucine	0.0001	0.010	T	0.011	0.001	0.009	0.001	0.009	0.001	0.012	0.001	0.013
valine	0.0003	0.015	0.0003	0.013	0.001	0.011	0.001	0.011	0.002	0.015	0.002	0.017
semiessential												
arginine	0.0017	0.012	T	0.011	0.002	0.011	0.002	0.009	0	0.015	0	0.019
tyrosine	T	0.005	T	0.005	0	0.006	0	0.006	0	0.006	0	0.008
cystine	0	T	0	T	0	0	0	0	0	0	0	0
glycine	0.0002	0.015	0.0001	0.016	0.007	0.020	0.007	0.020	0.001	0.018	0.001	0.019
nonessential												
serine	0.0028	0.016	0.0027	0.014	(0.023) <sup>a</sup>	0.017	(0.022) <sup>a</sup>	0.015	(0.084) <sup>a</sup>	0.025	(0.083) <sup>a</sup>	0.026
glutamic acid	0.0029	0.046	0.0028	0.047	0	0.037	0	0.035	0.014	0.112	0.013	0.120
aspartic acid	0.0025	0.031	0.0023	0.028	0.003	0.055	0.002	0.056	0.010	0.151	0.009	0.150
alanine	0.0054	0.022	0.0058	0.023	0.003	0.015	0.002	0.015	0.017	0.035	0.017	0.035
proline	0	0.010	0	0.007	0	0.011	0	0.011	0	0.013	0	0.019

<sup>a</sup> See Discussion. <sup>b</sup> T = traces only.

An important observation is that the lipid fraction of all three fruit pulps contained a relatively high proportion (20 to 30% of total fatty acids) of linolenic acid (9,12,15-octadecatrienoic acid). This acid is the main fatty acid of linseed oil which is known for its drying properties. The acid occurs in many plant species, but due to instability it is not favored as a component of edible oils. The relative ease of oxidation of linolenic acid tends to reduce the keeping quality of these products (Eckey, 1954).

The presence of linolenic acid in the fruit pulps investigated is useful to measure any possible oxidative decomposition which may have resulted from  $\gamma$  irradiation. Only small changes in the linolenic acid content of irradiated and control papaya and mango samples were observed. In strawberry, which received the highest radiation dose, the linolenic acid content was virtually unchanged.

**Amino Acids.** The results of analyses of free amino acids and total amino acids in control and irradiated samples of mango, papaya, and strawberry pulps are listed in Table IV. Unfortunately, tryptophan could not be determined due to its destruction in acid media in the presence of carbohydrates.

In the papaya and strawberry samples, the relative absorbances for free serine at two wavelengths (399 and 570 nm) were not characteristic of this acid. This indicated that another substance coeluted with serine and explains the unusually high value obtained. From past experience we believe this interfering substance to be asparagine. In the total amino acid determination, asparagine would be hydrolyzed to aspartic acid and thus would not interfere with the total serine determination.

It is apparent from the results that no significant differences between the free and total hydrolyzed amino acid compositions of mango, papaya, or strawberry pulps were detected after  $\gamma$  irradiation.

#### CONCLUSIONS

It is concluded that the GC volatile patterns were not significantly changed during the irradiation of mango, papaya, or strawberry fruit pulp in the samples submitted to this Institute. It was further found that the free amino

acid content and the total amino acid content of mango, papaya, and strawberry pulp were not changed by irradiation. The fatty acid composition of these fruit pulps was similar in irradiated and nonirradiated samples.

Linolenic acid, which is considered relatively easy to oxidize, was present in all three fruit pulps. It is significant to note that the linolenic acid ratios were only slightly changed during irradiation of mango and papaya and remained unchanged during irradiation of strawberry.

Finally, it should be noted that for comparative studies on the irradiation of fruits, the degree of ripeness between control and irradiated samples must be considered and should be as nearly identical as possible.

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#### LITERATURE CITED

- Ackman, R. C., *Prog. Chem. Fats Other Lipids* **12**, 165 (1972).  
 Bandyopadhyay, C., Gholap, A. S., *J. Agric. Food Chem.* **21**, 496 (1973a).  
 Bandyopadhyay, C., Gholap, A. S., *J. Sci. Food Agric.* **24**, 1497 (1973b).  
 Beyers, M., Thomas, A. C., Van Tonder, A. J., *J. Agric. Food Chem.*, previous paper in this issue (1978).  
 Bielecki, R. L., Turner, N. A., *Anal. Biochem.* **17**, 278 (1966).  
 Blakesley, C. N., Torline, P. A., *J. Chromatogr.* **105**, 385 (1975).  
 Blakesley, C. N., Loots, J., *J. Agric. Food Chem.* **25**, 961 (1977).  
 Eckey, E. W., "Vegetable Fats and Oils", Reinhold, New York, N.Y., 1954.  
 Metcalfe, L. D., Schmitz, A. A., Pelka, J. R., *Anal. Chem.* **38**, 514 (1966).  
 Van Wijngaarden, D., *Anal. Chem.* **39** 848 (1967).  
 "Wholesomeness of Irradiated Food", Report Joint FAO/IAEA/WHO Expert Committee, Technical Report, Series 604, WHO, Geneva, 1977 (ISBN 92 4 120604 7).

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## $\gamma$ Irradiation of Subtropical Fruits. 4. Changes in Certain Nutrients Present in Mangoes, Papayas, and Litchis during Canning, Freezing, and $\gamma$ Irradiation

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Mangoes, papayas, and litchis processed by canning, freezing, and  $\gamma$  irradiation were analyzed for their ascorbic acid, carotene, and sugar content. Both experimentally and commercially canned fruits were used as well as samples frozen for up to 3 months and irradiated with doses at least 1.25 kGy higher than those recommended for commercial irradiation. Chemical changes due to irradiation were generally small, amounting to losses of between 0 and 15%. In comparison, changes due to freezing and heat processing were considerable; losses in the order of 50 to 70% were recorded.

Food preservation by thermal processing, as in canning and freezing with salt, sugar, nitrates, nitrites, sodium benzoate, and sulfur dioxide as additives, has long been

an acceptable form of food processing. It is accepted that these methods lead to destruction of essential nutrients (Lund, 1975; Adsule and Roy, 1974). On a worldwide basis, normal components of natural food products and natural contaminants such as microbial toxins and other poisons such as selenium and mercury derivatives have produced greater known injury to man than any category of toxic chemical produced in processing of foods by heat or ionizing radiation (Spicer, 1975). Food additives have also made a substantial, though lesser, contribution to the total

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