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 γ 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 γ 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

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.

ACKNOWLEDGMENT

The authors are grateful to Austin Thomas and Marguerite Beyers of the South African Atomic Energy Board for irradiation of samples used in this investigation and to the National Food Research Institute, CSIR, for sponsoring this portion of the project.

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).
- Bieleski, 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).

Received for review December 29, 1977. Accepted August 25, 1978.

γ Irradiation of Subtropical Fruits. 4. Changes in Certain Nutrients Present in Mangoes, Papayas, and Litchis during Canning, Freezing, and γ Irradiation

Marguerite Beyers^{*1} and Austin C. Thomas

Mangoes, papayas, and litchis processed by canning, freezing, and γ 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

0021-8561/79/1427-0048\$01.00/0 © 1979 American Chemical Society

Chemistry Division, Atomic Energy Board, Private Bag X256, Pretoria, South Africa.

¹Seconded to the Atomic Energy Board from Citrus & Subtropical Fruit Research Institute, Nelspruit, South Africa.

incidence of food-bourne illness (Spicer, 1975).

Much research has been devoted to the question of whether food preservation by irradiation is hazardous to health. Cooked, irradiated foods have practically the same nutritive values as those subjected to classic treatments (del Val Cob and Sune, 1965), and vitamin losses in irradiated fresh fruit are no greater than those resulting from thermal processing (Dharkar and Savagaon, 1966). However, in spite of these similar side effects of preservation by irradiation and thermal processing, the irradiated process is still regarded with suspicion.

The purpose of this study is to compare changes in ascorbic acid and carotene, both essential nutrients, and sugar, which are present in relatively high concentrations, during the accepted processes of canning and freezing with those which occur in the presently largely unaccepted process of irradiation of the subtropical fruits, mangoes, papayas, and litchis.

EXPERIMENTAL SECTION

Source of Fruit. Fruits were supplied by the Letaba Cooperative, Tzaneen. The mangoes and papayas were mature-green on arrival, while the litchis were harvested at the edible-ripe stage. Tins of commercially canned fruit, originating from the Tzaneen area, were purchased at a retail outlet.

Prestorage Heat Treatments. Mangoes, Mangifera indica Linn. cv. Kent: 55 °C for 5 min and waxed. Papayas, Carica papaya Linn. (Papino papayas, a small fruit, similar to the "Solo" cultivar grown in Hawaii were used): 50 °C for 10 min and waxed. Litchis, Litchi chinensis Sonn. cv. Mauritius: 50 °C for 10 min. Fruits were heat treated to minimize fungal spoilage. A paraffin-based wax conventionally used on subtropical fruits was applied to reduce moisture losses from the skin. Heat treatment was carried out within 24 h of harvesting.

Processing. Fruits were irradiated within an hour of the heat treatment. The research "loop" of the commercial ⁶⁰Co irradiation unit (AECL Ltd) at Pelindaba, giving a dose rate of about 0.80 kGy/h, was used for all irradiations. The Fricke dosimeter was used to determine dose rates. Each irradiation treatment consisted of batches of 3, 7, and 20 fruits for the mangoes, papayas, and litchis, respectively, in two separate consignments to provide replicate experiments. Mangoes and papayas received total radiation doses of 0.75, 1.50, and 2.00 kGy, while litchis received 2.00, 3.00, and 3.50 kGy.

The mangoes and papayas were stored at ambient temperature $(20-24 \, ^\circ C)$ until the fruits softened. As the fruits ripened they were refrigerated until the rest of the consignment was ripe. Litchis were ripe on receipt and were refrigerated for about 24 h prior to thermal processing. All processing and chemical analyses on a consignment were done at the same time.

The experimental canning of the subtropical fruits closely followed commercial procedures.

Mangoes. (a) Twenty-four and 30 fruits were used in each of two consignments. The fruits were peeled, and the flesh was cut from the seeds and diced. The pieces were added to a 30% sucrose solution containing 0.5% citric acid preheated to 95 °C. (b) The temperature was adjusted to 80 °C and maintained for 5 min. Sterilized glass canning jars were hot-filled with fruit and syrup, closed, and sterilized at 95 °C for 35 min in a boiling water bath. After the jars were sealed they were allowed to cool and were stored at ambient temperature (20–24 °C) for 7 days.

Papayas. Two consignments consisting of 35 and 40 fruits each were peeled, freed of pips, and diced. The cubes were steeped in 1% CaCl₂ solution for 5 min, drained, and

Table I. Influence of Irradiation, Freezing, and Canning on Ascorbic Acid, Carotene, and Sugars of Some Subtropical Fruits

		% of control (100%)			
analysis	fruit	fresh irradiate d	frozen	exptly. canned	
ascorbic acid	mangoes	83-89	14-37	67	
	papayas	101-114	58-100 ^a	45	
	litchis	83-94	12 - 42	63	
carotene	mangoes	86-103	100	102	
	papayas	94-97	69-71	53	
total sugars	mangoes	102-141	55-62	59	
	papayas	88-91	84	368	
	litchis	81-107	123	274	

^a Frozen under nitrogen.

dropped into a preheated (95 °C) 42% sucrose solution containing 0.92% citric acid. The procedure as described for mangoes from b was followed, but fruits were sterilized for 45 min.

Litchis. Two consignments, each consisting of one 5-kg carton, were used. Stoned and peeled segments were added to a 30% sucrose solution preheated to 90 °C. The procedure described for mangoes from b was again followed, but sterilization for only 20 min was necessary.

Ripe mango and papaya flesh were homogenized in a Waring blender for 60 s and small portions of about 100 g were immediately frozen to -15 °C. The frozen papaya pulp was kept under nitrogen. Litchis were frozen intact. Pulping of litchis led to an abnormally high ascorbic acid loss of 46% (Chan et al., 1975a).

Analytical Methods. Ascorbic Acid. Two 15-g portions of fresh or frozen pulp were weighed directly into 30 mL of 3% metaphosphoric acid reagent. After homogenization the mixture was diluted volumetrically to 100 mL with metaphosphoric acid reagent and the suspended matter centrifuged down. Two 10-mL samples of the supernatant from each replicate were then analyzed for ascorbic acid according to the method of Barakat et al. (1955).

Carotenes. Carotenes were extracted from 10-g portions of mango or papaya pulp using the method recommended by Bickoff (1957), but using a 3.5-cm column. The longer 7-cm column needed more than 25 mL to elute the carotenes. The method of Bunnell et al. (1958) was used for the quantitative calculations.

Sugars. Ten-gram portions of fresh or frozen pulp were weighed into 30 mL of 80% aqueous ethanol neutralized for 1 h over $CaCO_3$ and immediately placed in a water bath at 80 °C for 30 min to destroy invertase activity (Chan et al., 1975b; Chan and Kwok, 1975). The heated mixture was then blended for 2 min in a stainless steel cup of a Waring blender. The homogenate was again heated for 30 min at 80 °C, allowed to cool, and diluted to 100 mL volumetrically. The diluted homogenate was filtered through a fast filter paper and analyzed chromatographically as described in the South African Government Gazette (S. Afr. Gov. Gaz., 1971).

A third consignment of frozen and canned mangoes was tested for sugar content using the photometric method of Sumner (1925) on the ethanolic extracts.

The accuracy of these methods of analysis is evaluated in part 1 of this series.

RESULTS AND DISCUSSION

Ascorbic Acid. In Figure 1 the mean ascorbic acid values are depicted for fruits subjected to three different irradiation treatments, frozen for 6 to 12 weeks, or canned experimentally and commercially. This figure and Table I show that, at most, irradiation causes a 17% loss of

Table II. Block Analysis of Variance^a

analysis	figure	fruit	F test	t test	comments
ascorbic : acid	1	mango	*	+	1. control: irradiation; control: experimental canning; differences NS
					 experimental canning, irradiation, freezing: differences NS; freezing 1.5 m SL 1.50 kGy; freezing 3 m SL irradiation
		papaya	**	+	 control: irradiation, differences NS; canning, freezing 3 m SL control; freezing 1 m (under N): control, differences NS
					2. canning, freezing 3 m SL irradiation
		litchis	**	+	1. control: irradiation, differences NS; canning, freezing SL control
					2. freezing 3 m SL all treatments except freezing 1.5 m; freezing 1.5 m: canning, differences NS; freezing 1.5 m SL irradiation; canning: irradiation, differences NS
carotene	2	manga	NS	NA	SE madiation, caming. madiation, differences to
carotene	4	mango			
4 - 4 - 1	•	papaya	NS	NA	
total 3 sugar	3	mango	NS	NA	
		papaya	* *	+	irradiation: freezing: control, differences NS; experimental canning SH all other samples
		litchis	NS	NA	

^a NS, nonsignificant; (*) significant difference, P = 0.01; (**) significant difference, P = 0.05; (+) t test applied to find differences; NA, t test not applicable; SL, significantly lower; SH, significantly higher.

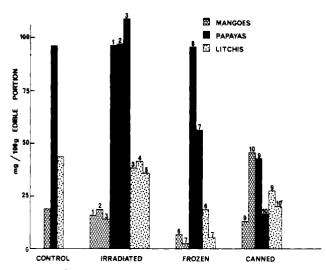


Figure 1. Comparison of the influence of the processing methods on the ascorbic acid concentration. Irradiation treatments: (1) 0.75 kGy, (2) 1.50 kGy, (3) 2.00 kGy, (4) 2.50 kGy, (5) 3.00 kGy. Periods for which fruits were frozen: (6) 1.5 months, (7) 3 months, (8) 1 month. Heat processing: (9) experimental, (10) commercial.

ascorbic acid in irradiated mangoes and litchis, which is well within the accepted levels for the more conventional processing methods (Ross, 1960). The same fruits suffered 86–88% reduction in this vitamin after storage at -15 °C for 12 weeks. Papayas were frozen under nitrogen which could account for the relatively low loss of 42%. Canning of mangoes and litchis was less detrimental to the vitamin content of these fruits than freezing, with losses of 33 and 35%, respectively, but the vitamin concentration was halved during the heat processing of papayas. The high values of the commercially canned mangoes can only be attributed to added vitamin. Values in the other commercially canned fruits, however, were lower (Abd-Allah and Zaki, 1974).

Analysis of variance of the ascorbic acid content (Table II) indicated no significant differences between the control and irradiation treatments. A significant depression of ascorbic acid levels was noted for the frozen samples of all fruits. An exception was the papaya sample which was frozen under nitrogen. Canning of papayas and litchis significantly lowered the concentration of this vitamin.

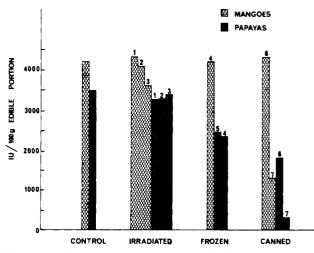


Figure 2. Effect of the processing methods on the carotene concentrations. Irradiation treatments: (1) 0.75 kGy, (2) 1.50 kGy, (3) 2.00 kGy. Periods for which fruits were frozen: (4) 3 months, (5) 1 month. Heat processing: (6) experimental, (7) commercial.

Carotene. Carotene in mangoes was not affected to any great extent by any of the processes applied experimentally (Gardezi and Tremazi, 1966). Statistical analysis shows no significant differences between treatments, but more than two-thirds of this pigment was destroyed during commercial canning (see Figure 2).

Papayas retained about 95, 70, and 27% carotene after irradiation, freezing, and canning, respectively (see Table I), which again is not of statistical significance.

Sugars. The total sugar content of irradiated mangoes was 2–41% higher than that of the control, while the frozen and canned fruits retained 58 and 72% of this nutrient, respectively, but none of the differences were statistically significant (Figure 3).

Irradiation and freezing influenced sugars in papayas to about the same degree, viz. 11% reduction with irradiation and 16% reduction after freezing. A huge increase of 386%, the only significantly elevated sugar concentration, occurred in the experimentally canned fruit as a result of added sugar.

The various processing methods did not affect the sugar content of litchis significantly. Elevated values were also

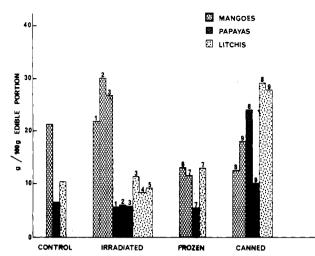


Figure 3. Total sugar content of fruits subjected to the processing methods. Irradiation treatments: (1) 0.75 kGy, (2) 1.50 kGy, (3) 2.00 kGy, (4) 2.50 kGy, (5) 3.00 kGy. Periods for which fruits were frozen: (6) 1.5 months, (7) 3 months. Heat processing: (8) experimental, (9) commercial.

recorded for canned litchis (274%; Table I). Frozen litchis had a surprisingly high sugar content of 13.12 mg %, 23% higher than the control fruits. Radiation-processed litchis showed fluctuating values from 81 to 107% of the control.

CONCLUSION

In the three subtropical fruits studied, chemical changes due to irradiation were generally small, amounting to losses of between 0 and 15% of the three constituents measured. In comparison, heat processing caused more extensive losses. In one instance, that of a commercially canned sample of papayas, a 90% loss of carotenes was measured. Freezing was responsible for the greatest reductions in ascorbic acid concentrations.

The idea that any food can be free of toxins is a misconception, and efforts to consume only foods with low toxin levels can even lead to malnutrition (Jukes, 1977). The small degree of chemical change produced by irradiation as compared to other processing methods will be accompanied by a proportional reduction in possible toxin production resulting from such chemical change. Indeed, exhaustive multigeneration animal feeding studies on a wide variety of irradiated foodstuffs have failed to show any adverse effects attributable to the consumption of relatively large proportions of the irradiated foods in the

diet (Food Irradiation Information Supplement, 1976).

Extension of the marketable life of foodstuffs by irradiation should, in view of the mildness of the treatment with respect to chemical change, be the preferred method of treatment. The recommendations of a joint FAO/ IAEA/WHO Expert Committee ("Wholesomeness of Irradiated Food", 1977), which reviewed detailed wholesomeness observations on a number of radiation-processed foods, are a welcome step forward in recognizing the safety of this food preservation process.

ACKNOWLEDGMENT

The Atomic Energy Board is thanked for permission to carry out this research. Thanks are due to E. A. Bosch, F. M. Ferreira, H. C. le Roux, and A. Jacobsz for experimental assistance.

LITERATURE CITED

- Abd-Allah, M. A., Zaki, M. S. A., Nahrung 18, 207 (1974).
- Adsule, P. G., Roy, S. K., J. Food Sci. Technol. 11, 269 (1974).
- 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).
- Bunnell, R. H., Driscoll, W., Bauernfeind, J. C., Food Technol. 12, 536 (1958).
- Chan, H. T., Kuo, M. T. H., Cavaletto, C. G., Nakayama, T. O.
- M., Brekke, J. E., J. Food Sci. 40, 701 (1975a). Chan, H. T., Kwok, S. C. M., J. Food Sci. 40, 770 (1975).
- Chan, H. T., Kwok, S. C. M., Lee, C. W. Q., J. Food Sci. 40, 772 (1975b).
- del Val Cob, M., Sune, N. O., "Food Preservation by Irradiation" Evolution and Present Status in the World, Report J.E.N. 158-51/I 15, Madrid, 1965, AEC-tr-6690,p 16.
- Dharkar, S. D., Savagaon, K. A., J. Food Sci. 31, 22 (1966).
- Food Irradiation Information Supplement, No. 6, International Project in the Field of Food Irradiation, Karlsruhe, West Germany, 1976.

Gardezi, S. A. H. Z., Tremazi, S. A., *Pak. J. Sci.* 18, 198 (1966). Jukes, T. H., *Food Technol.* 31, 40 (1977).

- Lund, D. B., in "Nutritional Evaluation of Food Processing", Harris, R. S., Karmas, E., Ed., Avi Publishing Co., Westport, Conn., 1975, Chapter 9.
- Ross, E., Hawaii Farm Sci. 9, 3 (1960).
- S. Afr. Gov. Gaz. No. 3274, 22 (1971).
- Spicer, A., Br. Med. Bull. 31, 220 (1975).
- Sumner, J. B., J. Biol. Chem. 65, 393 (1925).
- "Wholesomeness of Irradiated Food", Joint FAO/IAEA/WHO Expert Committee Technical Report, Series 604, WHO, Geneva, 1977 (ISBN 92 4 120604 7).

Received for review December 29, 1977. Accepted August 28, 1978.