of phosphate. The solubilities of the products of these enriched samples are not above those obtained from untreated raw material. High solubilities were obtained in reactions with ground phosphate at 450 °C but there seem to be two factors involved. One is catalysis of the reaction causing the production of soluble phosphate. The other is connected with raising the temperature which lowers the solubilities and is due to grinding and not to particle size. It seems that further studies should be done by adding to the reaction mixture compounds that will cause formation of volatile fluorides.

LITERATURE CITED

Baniel, A. M., Bazevi, E. L., Blumberg, R., Lavie, S., Heimann, H. H., *J. Agric. Food Chem.* **13**(1), 88–91 (1965).
Pelly, I., Bar-On, P., **26**, 000 (1978).
Stavski, K., *Przem. Chem.* **49**(1), 19–21 (1970).

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# γ Irradiation of Subtropical Fruits. 3. A Comparison of the Chemical Changes Occurring during Normal Ripening of Mangoes and Papayas with Changes Produced by γ Irradiation

Austin C. Thomas and Marguerite Beyers*

Changes in the concentrations of ascorbic acid, carotenes, sugars, and titratable acidity were monitored in two mango and two papaya cultivars as the fruits ripened from mature green to the edible-ripe stage, both with and without γ irradiation with doses up to 2.0 kGy. Ascorbic acid and titratable acidity changes only slightly during ripening. Virtually no difference in the total sugar content could be observed between the irradiated and nonirradiated fruits. In most experiments an apparent increase in carotene content was produced by irradiation, but this was overshadowed by the much larger increase which occurred as a result of ripening. No significant change in the nutritional value of the fruits could be detected after irradiation. Natural variation and the physiological changes produced by ripening were greater than any radiation-induced changes.

The ability of ionizing radiation to bring about chemical change in substances exposed to them is well known, and in the treatment of foodstuffs by irradiation, chemical changes undoubtedly occur. Some vitamins, in particular, are highly reactive, and it has often been stated that irradiation causes a substantial loss of essential vitamins and a consequent loss of nutritional quality of treated foodstuffs (Khan et al., 1974a). However, at the relatively low doses applied to fruits, normally in the range 0.5–2 kGy, the magnitude of these changes is small, often less than natural chemical changes which occur in the fruit (e.g., ripening) and certainly much smaller than chemical changes brought about by conventional preservation methods (e.g., heating) (Lee et al., 1976), to which very little attention has been given.

The purpose of this study was to compare changes in the concentration of selected constituents which occur during the ripening processes of some subtropical fruits with possible changes produced by irradiation. The constituents monitored were ascorbic acid, total carotenes, and total sugars. Both of these vitamins are considered relatively unstable (Rao, 1962; Snauwert et al., 1973), whereas sugars, apart from water, are by far the most abundant group of compounds present in the fruits in question (ca. 8–15% w/w). Titratable acid was also monitored during the papaya ripening studies and in the second season of mango determinations.

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**Chart I**

| papayas | | mangoes | |
|---|---|---|---|
| Hortus Gold I | Dec 1975 | Zill I | Feb 1976 |
| Hortus Gold II | Aug 1976 | Zill II | Feb 1977 |
| Papinos I | Aug 1976 | Kent I | Mar 1976 |
| Papinos II | Oct 1976 | Kent II | Feb 1977 |

**Chart II**

| fruit | no./dose | total doses, kGy |
|---|---|---|
| papayas | | |
| Hortus Gold I | 5 | 0, 0.75, 1.50, 2.00 |
| Hortus Gold II | 12 | 0, 1.00, 1.50, 2.00 |
| Papino I and II | 30 | 0, 0.75, 1.50, 2.00 |
| mangoes | | |
| Kent I | 12 | 0, 0.75, 1.50, 2.00 |
| Kent II | 48 | 0, 0.75, 1.50, 2.00 |
| Zill I | 12 | 0, 0.75, 1.50, 2.00 |
| Zill II | 36 | 0, 0.75, 1.50, 2.00 |

## EXPERIMENTAL SECTION

**Source of Fruit.** All fruits were supplied by the Letaba Cooperative, Tzaneen. The timing of the various consignments of the fruits are as shown in Chart I.

Some variation occurred in the initial quality of the fruits obtained in Hortus Gold I, otherwise the fruits were received in a mature, green condition.

**Heat Treatments.** Fruits were heat treated and irradiated within 24 h of harvesting.

Papayas: 50 °C for 10 min and waxed. Mangoes: 55 °C for 5 min and waxed. The wax used was paraffin based

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and is conventionally used by the subtropical fruit industry to reduce skin wrinkling due to moisture loss.

**Irradiation.** Irradiations were carried out in the research "loop" of the commercial $^{60}$Co irradiation facility (AECL Ltd) at Pelindaba, at a dose rate of approximately 0.80 kGy/h. Dose rates were determined using the Fricke dosimeter. The number of fruits per irradiation treatment and the total dose are as shown in Chart II.

**Storage.** Fruits were stored at ambient temperature (20–24 °C) during the period of analysis. The first set of analyses were carried out within 1 to 2 h after irradiation. Subsequent analyses were done every second day except over weekends, when an analysis was done on Friday and the next one on Monday.

**Sampling Techniques.** *Papino Papayas.* The skin in the sampling area was swabbed with 70% aqueous ethanol. A pyramid was then removed from each fruit with a sterile knife. After removal of the peel and pips, the pyramids were chopped into small pieces. The pieces were thoroughly mixed and samples for the different chemical analyses were drawn from this mixture. The holes were filled with Vaseline and covered with a square of plastic previously dipped in 70% aqueous ethanol.

*Hortus Gold Papayas.* In the case of the first consignment, a 2.5-cm hole was punched into each fruit on each sampling day with a cork borer. The cores were peeled and, after removing the pips, blended together. Samples for the chemical analyses were then taken from this homogenate. The holes were sealed by smearing Vaseline around the edges and placing a square of "parafilm" over the hole. These papayas collapsed after only a few days.

Sampling of the second consignment followed the pattern of the Papino papayas.

*Mangoes.* Sampling was carried out as described above for Papino papayas. Samples from all fruits in the same treatment were combined and placed directly into the liquid in which homogenation was carried out.

The mangoes withstood the injury of sampling very well and had a shelf-life equal to that of uninjured fruits stored under the same conditions. Any fruits which collapsed during the course of an experiment were discarded.

**Analytical Methods.** *Ascorbic Acid.* Two 15-g portions of papaya pulp or pieces or 2 × 10 g of mango pieces were weighed directly into 30 mL of 3% metaphosphoric acid reagent. The fruit–metaphosphoric acid mixture was blended for 15 s (papaya pulp) and 60 s (pieces) and diluted to 100 mL volumetrically with the acidic reagent. The suspended matter was centrifuged down and ascorbic acid determined in duplicate on the supernatant (Barakat et al., 1955).

*Carotenes.* Isolation of carotenes was effected by the method of Bickoff (1957), but using a 3.5-cm column. The recommended 7-cm column needed more than 25 mL to elute the pigment. Quantitative calculations were based on the method of Bunnell et al. (1958). Only one determination was carried out per day of analysis for the Hortus Gold pulp and first consignment of mangoes. Duplicate sampling was carried out in the case of all the other consignments.

*Sugars.* Hortus Gold pulp and the first consignments of mangoes: (a) Ten-gram portions of pulp or pieces were weighed into 30 mL of 80% neutral aqueous ethanol. The mixtures were maintained at 80 °C for 30 min to destroy invertase activity (Chan and Kwok, 1975). (b) The samples were homogenized, heated for the same period as before, and then diluted volumetrically to 100 mL with 80% ethanol. (c) Solids were filtered off through a fast filter paper. (d) The filtrate was subjected to chromatographic analysis (*S. Afr. Gov. Gaz.*, 1971). Only one ethanolic extract was made per fruit sampling.

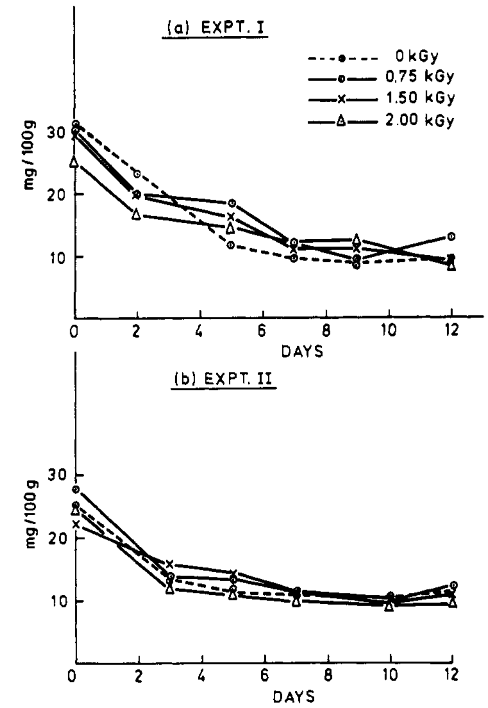


**Figure 1.** Ascorbic acid content: Zill mangoes.

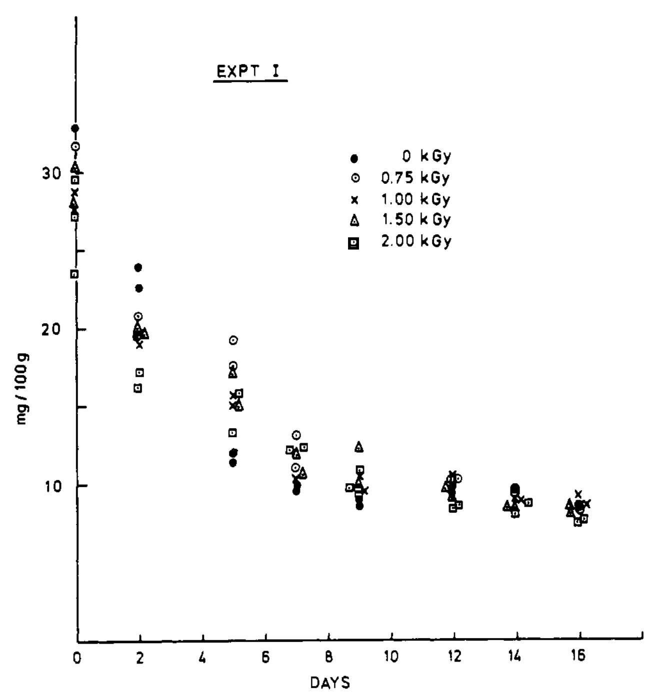


**Figure 2.** Ascorbic acid content: Zill mangoes.

Papino papayas and the second consignments of Hortus Gold papayas and of mangoes: Two 10-g portions of fruit pieces were treated as described above up to d. The filtrate was analyzed for sucrose and reducing sugars according to the method of Sumner (1925).

*Titratable Acidity.* Two 10-g portions of fruits were weighed into ca. 30 mL of water. The mixture was homogenized and then heated for 60 min at 80 °C. After dilution to 100 mL the homogenate was centrifuged and 50 mL of the supernatant was then titrated potentiometrically with 0.01 N NaOH (AOAC, 1975).

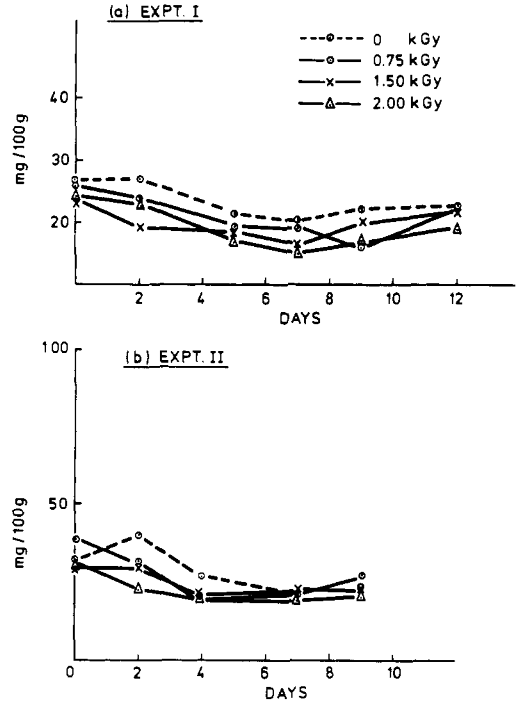


**Figure 3.** Ascorbic acid content: Kent mangoes.

The sensitivity and precision of the analytical methods are discussed in part 1 of this series.

## RESULTS AND DISCUSSION

**Ascorbic Acid.** *Zill Mangoes* (Figures 1 and 2): Mean values of ascorbic acid contents of fruits given the various treatments are shown in Figures 1a and 1b, as the fruits ripen. It is clearly seen that ascorbic acid concentration decreases by a factor of 2.5 to 3 during the ripening period, *irrespective of treatment.*

Figure 2 gives individually determined values for one experiment, from which it may be seen that no consistent, dose-dependent effect can be detected. The limits of error also decreased with increasing degree of ripeness of the fruit. This is perhaps predictable due to the inevitable variation of maturity of green fruit, which decreases as the fruits ripen. Any apparent difference between irradiated and control samples (Figure 1a and 1b) is not statistically significant.

*Kent Mangoes* (Figure 3): The ascorbic acid content of Kent mangoes decreased to a much smaller extent than in the case of Zill mangoes. Values of irradiated samples tended to be lower than the values for the controls, but the lowering of values cannot be correlated with the magnitude of the radiation dose applied nor are the differences (except for day 2) statistically significant.

*Papino Papayas* (Figures 4a and 4b): A slight increase in ascorbic acid occurred with ripening in the first consignment, but the opposite trend was shown in the second consignment. Individual values show a wide range of variation but this variation cannot be correlated to dose.

Figure 4c gives values of ascorbic acid in four different consignments, measured when the fruit was at the edible-ripe stage. Irradiation, even to 2 kGy, evidently has little effect on the ascorbic acid content (Kovâcs and Tengumnuay, 1972; Moy et al., 1971).

*Hortus Gold Papayas* (Figure 5): The results obtained in the first consignment (Figure 5a) showed a large variation in ascorbic acid levels, but this variation cannot be correlated to radiation dose. The more reliable data given in Figure 5b shows that no significant difference occurs in the levels found in the different treatments.

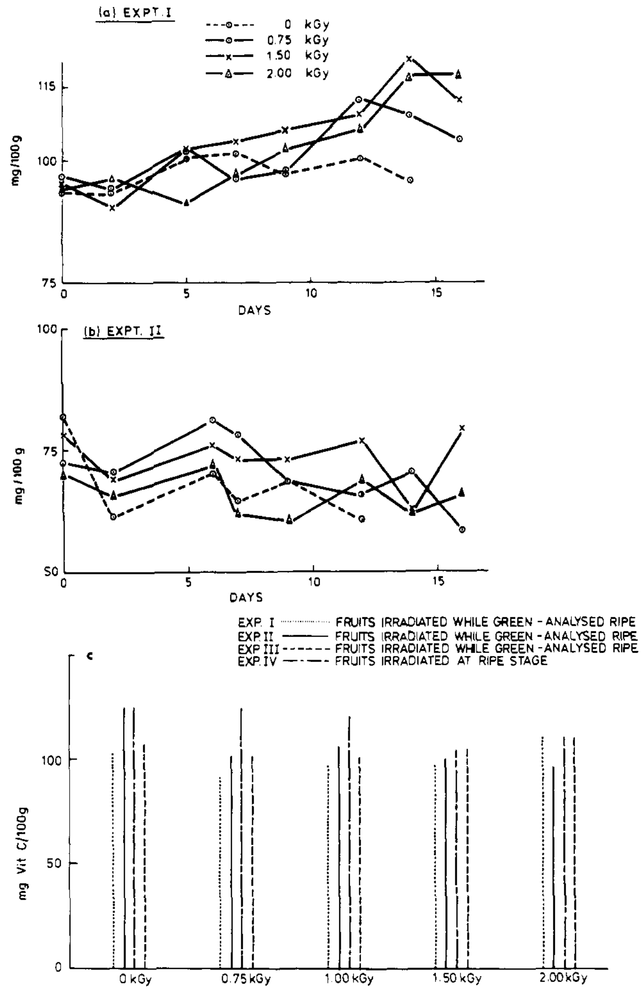


**Figure 4.** Ascorbic acid content: Papino papayas.

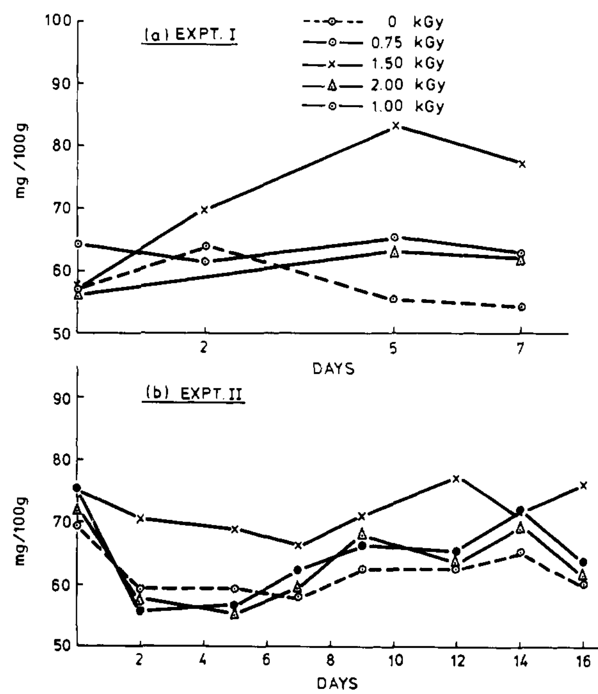


**Figure 5.** Ascorbic acid content: Hortus Gold papayas.

In the experiments described above, there is no evidence of any loss in nutritional quality with respect to ascorbic acid as a result of irradiation, even at the relatively high dose of 2.0 kGy. Of the four types of fruit examined, only

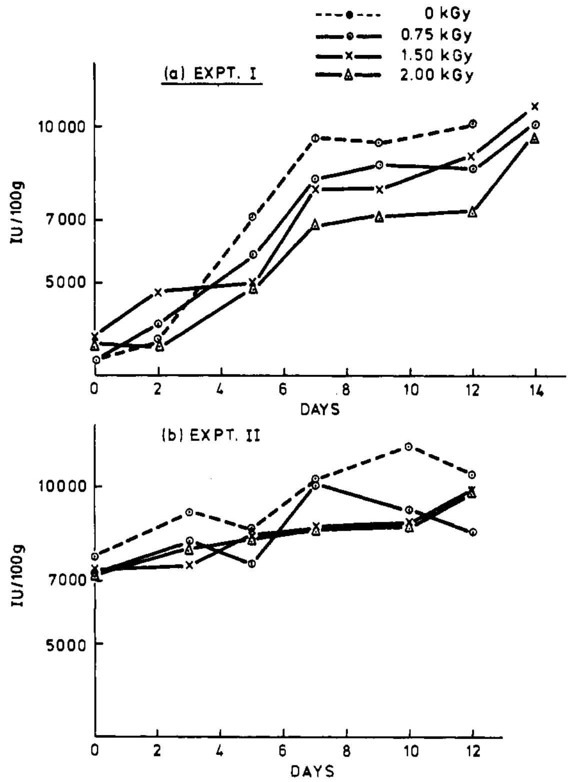


**Figure 6.** Carotene content: Zill mangoes.

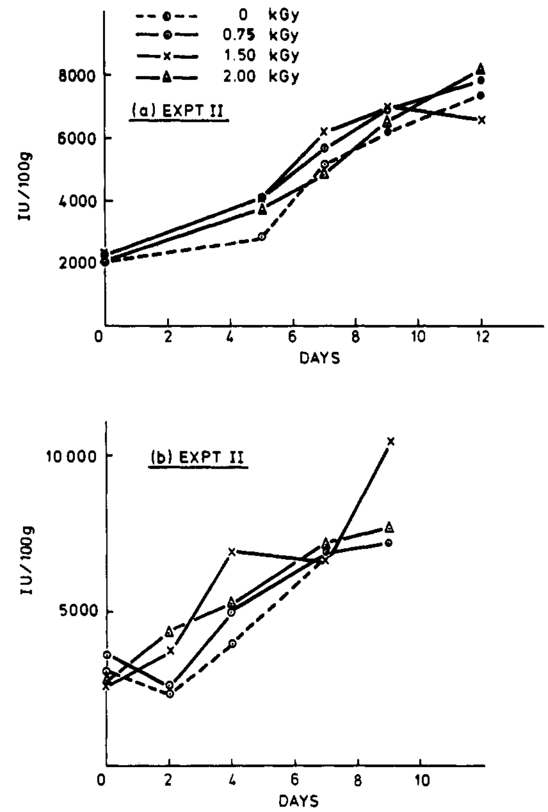


**Figure 7.** Carotene content: Kent mangoes.

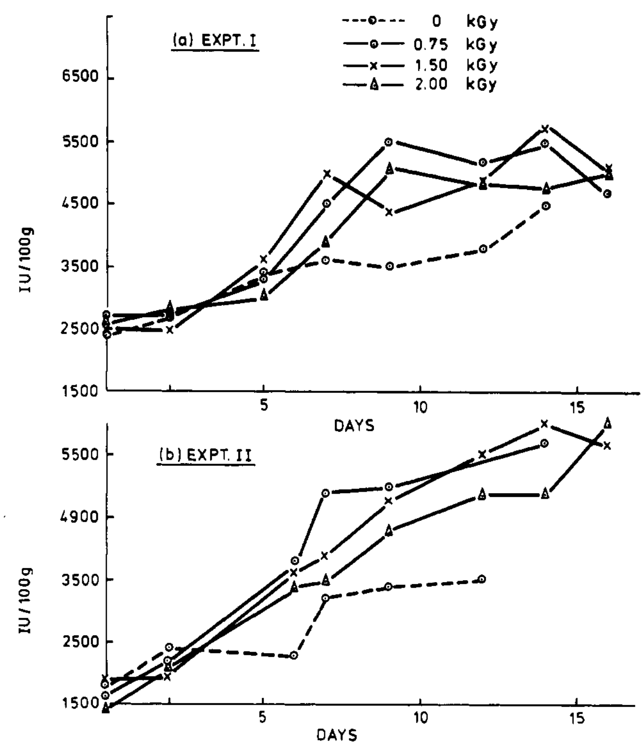


**Figure 8.** Carotene content: Papino papayas.

the Zill mango showed a significant change in ascorbic content during ripening. The decrease which occurred in this cultivar was common to all treatments and was not related to radiation dose.

**Carotenes.** *Zill Mangoes* (Figure 6): The most marked effect was the expected large increase which occurred during ripening. This is particularly pronounced in Figure 6a, showing an increase from 2500 to 10 000 IU/100 g. Irradiation produced no significant change in the initial carotene content and, although values for irradiated samples lagged slightly behind those of the controls, final values of around 10 000 IU were measured in all treatments. This behavior of the carotene content probably reflects the slight delay in ripening brought about by irradiation.

*Kent Mangoes* (Figure 7): Carotene content increased roughly fourfold with ripening in both consignments. Values obtained for all treatments behave in the same manner, but those of the irradiated treatments indicate a slight, apparent *increase* in carotene content (ca. 10%) at all stages of maturity. On the other hand, in shelf-life studies on mangoes it has been consistently observed that irradiation results in a slight delay in ripening, and accordingly, in color development (Kahn et al., 1974b). It seems likely, therefore, that the apparent increase in carotene content due to irradiation is due to increased extractability which may result from the radiation treatment rather than an increased synthesis of this constituent. Statistical analysis shows no significant difference between treatments.

*Papino Papayas* (Figure 8): The same increase of carotene content occurs with ripening of Papinos as was found in mangoes. Again, values for irradiated fruits show an apparent *increase* in carotene content, but there is no consistent dose-related trend and therefore probably not due to irradiation.

*Hortus Gold Papayas* (Figure 9): The variation in initial carotene levels shown in Figure 9a is almost certainly due to the variation in the degree of maturity of the fruits obtained for this experiment. In the ripe fruits the variation is much smaller and is not related to radiation dose. Initial carotene values in the second experiment show little variation, but large fluctuations occur during ripening. The fluctuations are not, however, consistent with the radiation dose applied.

The carotene content of both mangoes and papayas increases greatly during ripening, in cases by almost 400%. Irradiation appears to increase the carotene values slightly

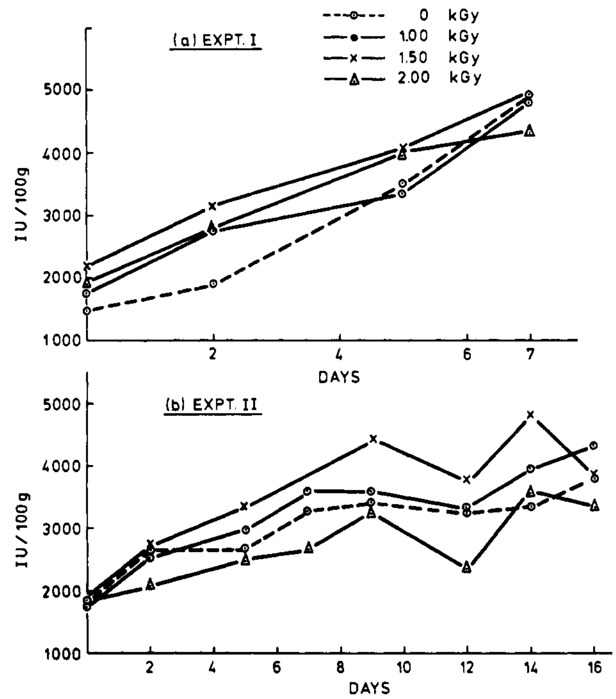


**Figure 9.** Carotene content: Hortus Gold papayas.

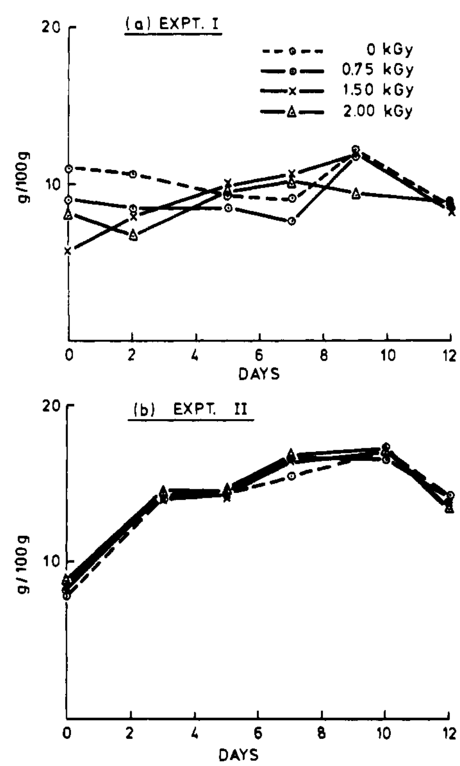


**Figure 10.** Sugar content: Zill mangoes.

in most cases. It is not known whether this is due to the irradiation making the carotenes more readily available for measurement or whether it stimulates the formation of the compounds. In any case, irradiation certainly does not cause any measurable loss of carotenes at the doses applied (Moy et al., 1971; Pablo et al., 1972).

**Sugars.** *Zill Mangoes* (Figure 10): Some variation between individual values of sugar content occurred in the first consignment, but this was almost certainly due to random variation between fruits as no consistent trend is evident with respect to ripening or radiation dose. In the second consignment, very consistent values were obtained,

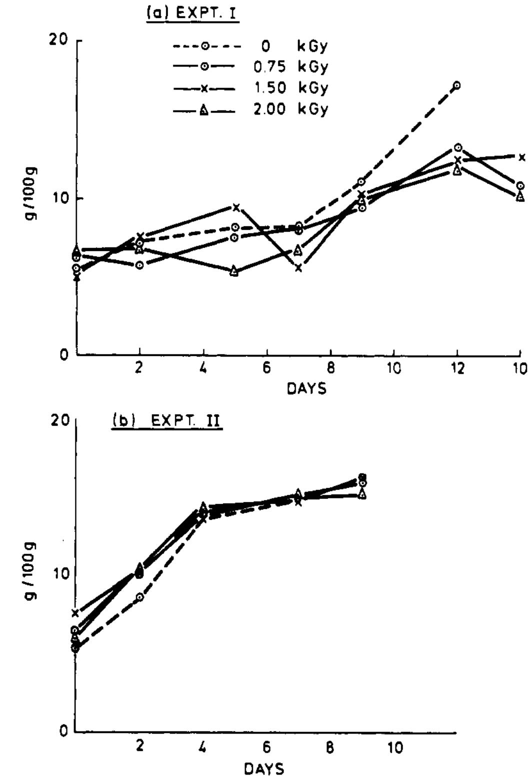


**Figure 11.** Sugar content: Kent mangoes.

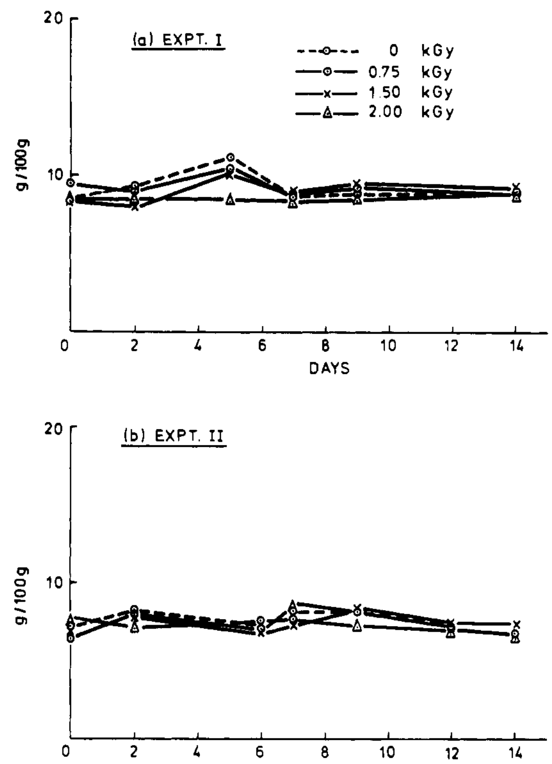


**Figure 12.** Sugar content: Papino papayas.

showing an approximate doubling of sugar content but with hardly any difference between treatments.

*Kent Mangoes* (Figure 11): In both consignments of Kent mangoes, as with the second consignment of Zill, the sugar content roughly doubled during ripening. Apart from slight variation between treatments, no significant effect was observed due to irradiation (Leley et al., 1943).

*Papino Papayas* (Figure 12): Unlike the results obtained for mangoes, apart from a slight fluctuation in

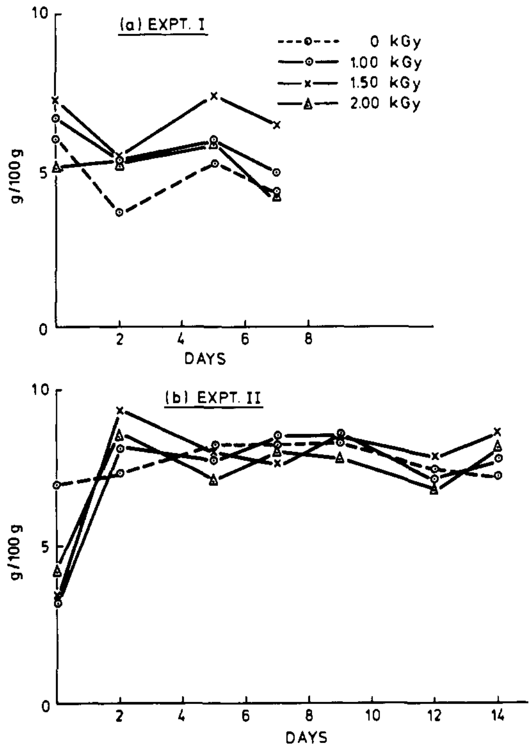


**Figure 13.** Sugar content: Hortus Gold papayas.

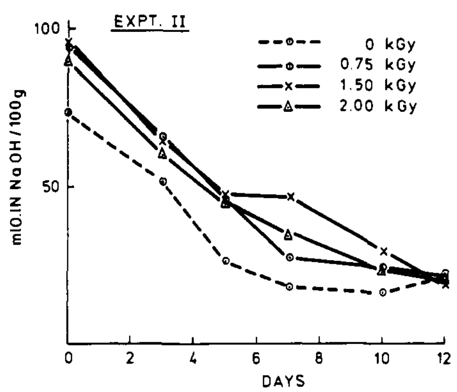


**Figure 14.** Titratable acidity: Zill mangoes.

values, little change occurs in the total sugar content of Papinos due to ripening or irradiation.

*Hortus Gold Papayas* (Figure 13): Figure 13a shows little change in sugar content with ripening and no trend consistent with radiation dose applied. The more consistent results obtained for the second consignment show an initial sharp increase in sugar content, particularly in treated fruits, but thereafter the values for all treatments remain essentially static with little differences between treatments. Apart from day 0 in Figure 13b, little change in total sugar concentrations occur during ripening or as a result of irradiation.

Some variation occurred between treatments in the first consignments of three of the fruits under investigation. These variations are random and are not related to radiation dose applied. Using the improved experimental method for sugar determination as described earlier for the second consignments of the fruits, far more consistent results were obtained and little difference was observed between treatments. It can only be concluded from these results that irradiation has a negligible effect on the total sugar content of these fruits.

**Titratable Acidity.** *Zill Mangoes* (Figure 14): Titratable acidity falls rapidly with ripening, from about 90

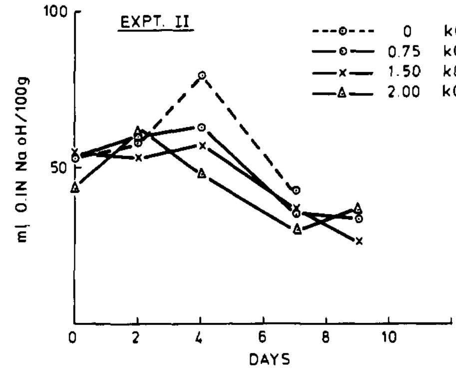


**Figure 15.** Titratable acidity: Kent mangoes.

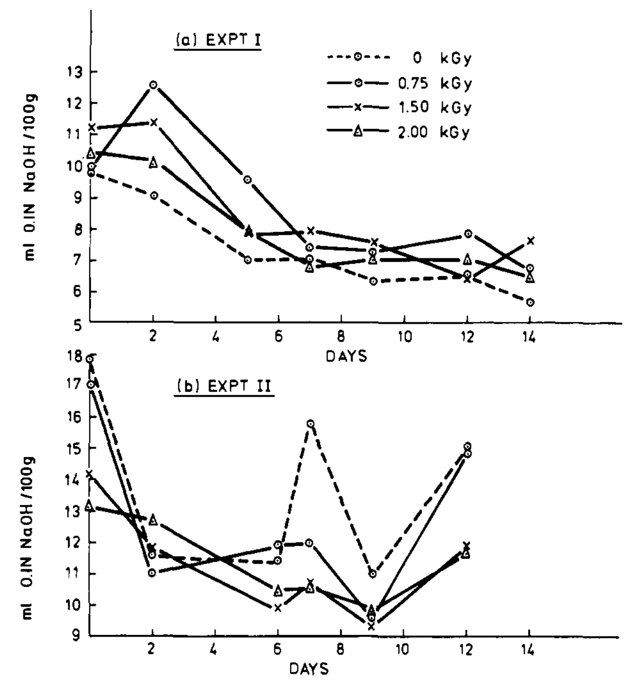


**Figure 16.** Titratable acidity: Papino papayas.

mL to only 20 mL of 0.1 N NaOH/100 g of pulp. The values for the nonirradiated fruit are consistently lower than values for irradiated samples, but all the values converge in the ripe fruit at 12 days storage. This behavior again may reflect the delayed ripening produced by irradiation, but there is no significant difference in the values obtained (Dennison and Ahmed, 1967).

*Kent Mangoes* (Figure 15): Unlike the Zill mangoes, Kent mangoes exhibited a peak in acidity after 2–4 days which is more noticeable in the nonirradiated fruits. Although statistical analysis shows significant differences between some treatments at 2 and 7 days, these differences are not consistent with radiation dose.

*Papino Papayas* (Figure 16): In general, titratable acidity appears to decrease with ripening, but with some fluctuation in individual values. No significant difference is caused by irradiation and no consistent effect is attributable to the radiation treatments.

*Hortus Gold Papayas* (Figure 17): As for the Papino papayas, acidity generally decreases with ripening. Fluctuating values obtained for the various treatments are entirely random and show no dependence upon radiation dose.

In general, decrease in titratable acidity occurred over the ripening period of the fruits examined. Marked fluctuations in individual values occurred in some experiments but these appeared random and cannot be

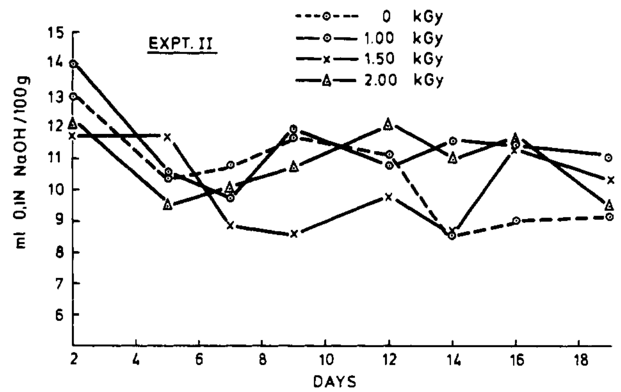


**Figure 17.** Titratable acidity: Hortus Gold papayas.

correlated with irradiation treatments.

CONCLUSION

The concentrations of ascorbic acid, carotenes, sugars, and titratable acidity have been monitored in two mango and two papaya cultivars as the fruits ripened from mature green to the edible-ripe stage, both with and without irradiation to doses up to 2.0 kGy.

Ascorbic acid and titratable acidity contents changed only slightly during ripening of the fruits and natural variation was greater than any change which may have been brought about by radiolysis. Virtually no difference in total sugar content could be observed between the irradiated and nonirradiated fruits in the five experiments using the revised analytical technique. In the earlier determinations random fluctuations were observed. In most of the experiments, irradiation produced an apparent *increase* in carotene content, but this was overshadowed by the much larger increase which occurred as a result of ripening.

There is, therefore, no evidence to support the theory that irradiation of these fruits causes any significant change in their biosynthesis of nutrients during ripening. In fact, any radiation-induced changes which do occur are too small to be detected against the background of natural variation of the various constituents, and by the changes in the content of these constituents produced during the physiological changes which take place in these fruits during ripening.

ACKNOWLEDGMENT

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LITERATURE CITED

Association of Official Analytical Chemists, "Official Methods of Analysis", 12th ed, Section 22.061, 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).
Bunnell, R. H., Driscoll, W., Bauernfeind, J. C., *Food Technol.* **12**, 536 (1958).
Chan, H. T., Kwok, S. C. M., *J. Food Sci.* **40**, 770 (1975).
Dennison, R. A., Ahmed, E. M., *J. Food Sci.* **32**, 702 (1967).
Khan, I., Sattar, A., Ali, M., Muhammed, A., *Food Sci. Technol.* **7**, 25 (1974a).
Khan, I., Sattar, A., Ali, M., Muhammed, A., *Lebensm.-Wiss. Technol.* **7**, 25 (1974b).
Kovâcs, J., Tengumnuay, Ch., *Acta Aliment. Acad. Sci. Hung.* **1**, 213 (1972).
Lee, C. Y., Downing, D. L., Iredale, H. D., Chapman, J. A., *Food Chem.* **1**, 15 (1976).
Leley, V. K., Narayano, N., Daji, J. A., *Indian J. Agric. Sci.* **13**, 291 (1943).
Moy, J. H., Akamine, E. K., Brewbaker, J. L., Buddenhagen, I. W., Ross, E., Spielmann, H., Upadhya, M. D., Wenkam, N., Helber, D., Dollar, A. M., Hanovka, M., McClish, G. A., in "Disinfestation of Tropical Fruits by Gamma Irradiation", Vienna, Austria IAEA No. STI/PUB/299, Hawaii University, Honolulu, 1971, pp 43–57.
Pablo, I. S., Manalo, J. A., Cardeno, T. A., *Philipine J. Nutr.*, 113 (1972).
Rao, B. S. N., *Radiat. Res.* **5**, 683 (1962).
Snauwert, F., Tobback, P. P., Anthonissen, A., Maes, E., in "Radiation Preservation of Food", Proc. Symp. Bombay, Nov 1972, IAEA, Vienna, 1973, p 29.
*S. Afr. Gov. Gaz.* **No. 3274**, 22 (1971).
Sumner, J. B., *J. Biol. Chem.* **65**, 393 (1925).

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# Fate of [$^{14}$C]Trifluralin in Soil

Tomasz Golab,* William A. Althaus, and Harlan L. Wooten

The degradation of trifluralin was investigated in field soil over a 3-year period. A 2-month laboratory investigation was also performed using field soil flooded with water. Twenty-eight transformation products were isolated and identified in these studies. None of the isolated transformation products exceeded 3% of the initially applied trifluralin. After 3 years, less than 1.5% of the applied trifluralin could be detected in soil, 4% was distributed among numerous transformation products, and 38% remained as soil-bound residues. $\alpha,\alpha,\alpha$-Trifluorotoluene-3,4,5-triamine, a degradation product of trifluralin, appeared to be a key compound in the formation of soil-bound residues.

Trifluralin ($\alpha,\alpha,\alpha$-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) is a preemergence herbicide used for control of a wide variety of grass and broadleaf weeds in many agronomic and horticultural crops (Alder et al., 1960; Soper et al., 1961). The fate of trifluralin has been investigated in soil and plants (Probst et al., 1967; Golab et al., 1967) and in artificial rumen fluid and ruminant animals (Golab et al., 1969). Probst et al. (1975) and Helling (1976) have reviewed the results of numerous investigations on the fate of trifluralin under various physical and biological conditions.

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