Preservation of Oil Palm Fruits: Nonoxidative Effects of Ionizing Radiation on Palm Olein and Crude Palm Oil

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ABSTRAK

Kesan sinaran-gama ke atas olein sawit telah dikaji. Sinaran dengan dos antara 0.1 hingga 1 MGy menyebabkan kerosakan ke atas asid lemak tak tepu tetapi hampir tidak ada kesan ke atas asid-asid lemak tepu. Kesan yang sama didapati pada sampel yang disimpan selama 1 dan 2 bulan pada suhu bilik. Sinaran pada 30 kGy juga merosakkan kandungan karotena di dalam minyak sawit mentah tetapi tidak mempengaruhi kandungan asid lemak bebas. Kajian ini mendapati sinaran-gama dapat digunakan untuk pengawetan tetapi tidak sesuai untuk tujuan pensterilan buah kelapa sawit.

ABSTRACT

The effect of gamma-irradiation on palm olein has been investigated. Irradiation doses (0.1 to 1 MGy) caused severe destruction of unsaturated but had little effect on saturated fatty acids. Similar effects were observed in irradiated samples stored for 1 and 2 months at room temperature. Radiation (up to 30 kGy) also caused severe destruction of carotenes in crude palm oil, but had no significant effect on the free fatty acid content. These findings indicate that gamma-radiation may be used for preservation but not for sterilization of palm fruits.

INTRODUCTION

One of the most important tasks of the palm oil producer is to produce high quality oil. Like other vegetable oils, palm oil is very susceptible to hydrolysis by the action of a Lipase enzyme which is found in palm fruit, fungi and microorganisms. The hydrolysis reaction causes fats to split into free fatty acids (f.f.a) and glycerol which lead to poor quality oil. A poor quality oil with more than 10% f.f.a. is sold as a regular grade, whereas good quality ones should have less than 5% f.f.a and marketed at a premium which would fetch much higher prices.

During harvesting, and especially when the palms get older and taller, the fruit bunches may suffer some bruising on falling to the ground. The damage may rupture the membranes which leads to the lipase gaining access to the fats. In a bruised and crushed fruit, the f.f.a content reaches 60% within a few hours, since the lipase starts acting as soon as the cell equilibrium is disturbed. The fungi not only attack the bruised or damaged fruits but also the ripe harvested ones on which they grow. As it is with most crops produced in the tropics, the fruits deteriorate within a few days after

harvest. The average shelf-life of ripe palm fruit is about 3 days. The problem is worst at the milling stage where the fruits are usually piled up for several days while waiting for processing. The bruised or over-ripe fruit may be covered and invaded by moulds or micro-organisms. The resulting oil will have a high f.f.a content, and poor quality oils are costly to refine. The fruit may also be damaged during transportation from the plantation to the mill. However, this problem is not critical in big plantations where a good transportation and harvesting system is provided. But it has a serious effect on small holders (small plantations) because the harvested fruits are usually left along the road-side for several hours or even days before being transported to the mill.

Clearly the bruising of bunches and fungal infection combined with delays between harvesting and processing are factors determining the quality of oil. In considering these problems, it is thought that radiation may be used to minimize the action of lipase. The fruit could be sterilised by radiation to reduce or to kill the micro-organism or fungi, deactivate enzymes and hence, extend the shelf-life of the ripe fruits in their harvested state. At present, there is no satisfactory method to overcome the problem. The only method being practiced is steam sterilization of the fruits at the processing stage. However, it is also known that radiation will damage the oil to some extent. Therefore, this research was conducted to investigate the non-oxidative effects of radiation on palm oil.

MATERIALS AND METHODS

Materials

Crude palm oil (CPO) was supplied by Trafford Edible Oil Refinery Ltd., Manchester. Boron trifluoride-methanol (14% w/v), standard fatty acid methyl esters-FAMES (C_8, C_{10}, C_{12}, C_{14}, C_{16}, $C_{1:6}$, C_{18}, $C_{18:1}$, $C_{18:2}$, $C_{18:3}$ and C_{20}) were purchased from Sigma Chem. Co. at a purity of 99%. The CPO and the standard FAMES were stored at –20°C to avoid deterioration. Activated carbon, n-hexane (AR), iso-ocatane (HPLC grade), and phosphoric acid (AR) were obtained from BDH Ltd. Activated earth (Fulmont) was provided by Laporte Industries Ltd., England. All other solvents were

of reagent grade and were used without furthe purification.

Preparation of Sample

Sample of palm olein was prepared from crude palm oil (CPO). Briefly: Sample of CPO (200 g) was treated with activated carbon (20 g) to remove carotenes, according to method of Ong et al. (1981). The activated carbon was then filtered using a sintered glass no. 3 filter and the oil was recovered after removal of solvent (diethyl ether) under reduced pressure in a rotary evaporator. The carotene-free oil was crystallised and fractionated into olein and stearin fractions at 2°C, according to method of Tan et al. (1981). The two fractions were then separated by filtration using a precooled sintered glass (no 3 filter) and washed with cold hexane. The oil was thus separated into a solid (stearin) and a liquid (olein). After removal of solvent by means of a rotary evaporator, the liquid palm olein was obtained and refined using 0.15% phosphoric acid (AR, 85 wt%) and 1.5% activated earth (fulmont) at 105°C (Zschau 1981; Shaw et al. 1981). The mixture was stirred for 30 mins and filtered to remove activated earth. These processes were carried out under nitrogen atmosphere. The oil obtained was stored in a glass bottle under nitrogen at –20°C until used.

Analysis of Fatty Acid Composition of Palm Olein

Fatty acid composition of palm olein was analysed as methyl ester derivatives. The esters were prepared according to IUPAC-method 2.301 (IUPAC 1979) and Morrison and Smith (1964). The esters were analysed using a gas chromatograph (Analytical-Instrument, model 92) provided with a flame ionization detector, coupled to a Spectra-Physics SPA4270 computerised integrator. A vitreous silica capillary column (25 m × 0.3 mm id) of BP20 with 0.5 µm film thickness (SGE Ltd) was used. The oven temperature was programmed from 130° to 240°C at a ramp rate of 7°C/min, after an initial isothermal period of 2 min. and was held for 10 min. after final temperature. The detector and injector port temperatures were 280°C and 250°C respectively. The flow rate of the carrier gas (nitrogen) was 60 cm³/min. The method was calibrated using a standard mixture of methyl

esters of known composition and a technique of internal normalization was used to quantify the sample.

Preparation of Sample for Irradiation

Samples of palm olein (20 g) were irradiated in small glass tubes (5.5 cm × 3.0 cm) with γ-rays using a ^{60}Co-gamma source at the University of Salford, England. The dose rate (65 Gy/min) was determined by Fricked Dosimetry using ferrous sulphate solution (Jayson *et al.* 1975). Samples were irradiated at room temperature and portions of irradiated samples (about 1 g each) were taken at various time intervals to give total doses between 0.1 to 1 MGy. The tubes were loosely stoppered so that the air could diffuse into the sample during irradiation. The fatty acid profile of irradiated samples was determined by gas chromatography fitted with a BP20 capillary column. Some samples were stored in the dark at 20°C for 1 and 2 months and their fatty acid composition were determined as before. The free fatty acid (f.f.a) content of palm olein was determined

immediately after irradiation according to IUPAC-method 2.201 (IUPAC, 1979). For the determination of f.f.a., the samples were irradiated up to 30 kGy.

The effect of γ-irradiation on carotene content of CPO was also investigated. Samples of CPO were irradiated and portions of irradiated samples were withdrawn at different intervals of time to give a total dose up to 100 kGy. A 1.5% solution of irradiated samples in isooctane (HPLC grade) was then prepared and the optical density at 446 nm was measured using a Pye-Unicam SP1800 spectrophotometer and a 1 cm silica cell.

RESULTS AND DISCUSSION

The liquid palm olein used in the investigation was prepared from CPO. Throughout the experiments, nitrogen gas was maintained above the oil sample to minimize oxidation by atmospheric oxygen. A fatty acid profile of palm olein is shown in Table 1 while a gas chromatogram of their methyl esters is presented in *Figure 1*. The chromatogram shows three significant

TABLE 1

Fatty acid compositions of palm olein used in the investigation and comparison with those of PORIM[@]

Fatty acid	Symbol	Percentage of palm olein (wt %)	
		Present work	PORIM
SATURATED			
1. Lauric	C12:0	0.1 ± 0.01	0.1 – 0.6
2. Myristic	C14:0	0.9 ± 0.04	0.9 – 1.4
3. Palmitic	C16:0	39.7 ± 0.5	37.9 – 41.8
4. Stearic	C18:0	4.5 ± 0.3	4.0 – 4.8
5. Arachidic	C20:0	0.5 ± 0.04	0.3 – 0.8
MONOUNSATURATED			
6. Palmitoleic	C16:1	0.1 ± 0.01	0.1 – 0.3
7. Oleic	C18:1	42.7 ± 0.7	41.2 – 43.6
POLYUNSATURATED			
8. Linoleic	C18:2	11.3 ± 0.6	10.4 – 13.4
9. Linolenic	C18:3	0.3 ± 0.2	0.1 – 0.6
SATURATED (%)		45.6	
UNSATURATED (%)		54.4	

Values represent the mean of two separated determinations. Each determination consists of three set of data from three injections.

[@]PORIM : Palm Oil Research Institute of Malaysia.

peaks which represent three major fatty acids in palm olein, i.e palmitic (39.7 ± 0.5), oleic (42.7 ± 0.7) and linoleic (11.3 ± 0.6) acids. The rest are minor components, namely lauric, myristic, palmitoleic, stearic, linolenic and arachidic acids. The values obtained in this experiment are within the reported ranges (Tan *et al.* 1981; PORIM 1981).
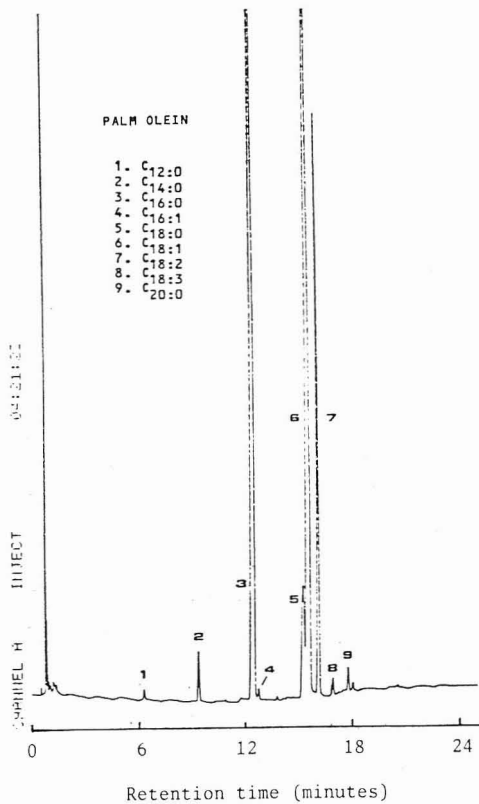

Fig. 1 Gas chromatogram of palm olein fatty acid methyl ester separated on a BP 20 capillary column (25m × 0.3mm id). Program: 130°(2 min.) to 240°C (10 min.) at 7°C/min. Carrier gas: N₂. Split ratio: 60:1.

It is believed that the peroxidation which occurs at low doses and a direct interaction between radiation and oil components are responsible for the destruction of fatty acids in irradiated samples. Some polyunsaturated fatty acids, and especially the ω6 acids, namely linoleic and arachidonic acids and the ω3 such as linolenic acid are known as Essential Fatty Acid

(EFA). They have important nutritional consequences and therefore must be provided in the diet. The destruction of these acids by ionizing radiation is a great disadvantage if radiation is to be used for palm fruit preservation or sterilization. The impact of high energy radiation produces initially excited triglyceride molecules and/or ionic triglyceride molecules, followeed by homolytic cleavage which occur randomly at the carbon-carbon bonds in the fatty acid moiety to produce various compounds, Scheme 1.

$$
\begin{array}{l}
CH_2 - O \wr C \wr CH_2 \wr CH_2 \wr (CH_2)_x - CH_3 \\
| \\
CH - O - OR_2 \\
| \\
CH_2 - O - OR_3
\end{array}
$$
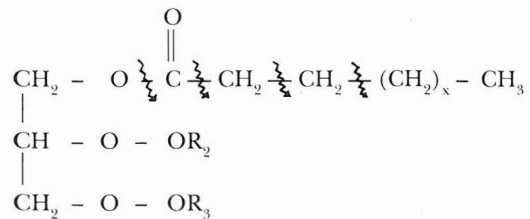
Scheme 1

The changes of fatty acid content in palm olein after irradiation are given in Table 2. Neither the saturated nor the unsaturated fatty acids decreased significantly at low irradiation doses. Only small changes were observed in saturated components, namely lauric, muristic, palmitic, stearic and monounsaturated oleic acids at 0.1 MGy. These components, as expected, were very resistant to radiation. Furthermore, palm olein contains a relatively high concentration of natural vitamin E which protects against peroxidation (peroxidation leads to formation of hydroperoxides and subsequent decomposition of the hydroperoxides destroys fatty acids). The highly unsaturated fatty acids, however, were very sensitive and readily destroyed by irradiation. The linoleic acid was significantly reduced after irradiation with 0.1 and 1 MGy whilst linolenic acid was completely destroyed at 1 MGy (*Figure 2*). Generally, most saturated components are increased as a function of irradiation dose whereas unsaturated components decreased with increasing total dose. These results are in good agreement with those reported by Takyi (1981), Kavalam (1969) and Hammer *et al.* (1979).

Samples irradiated with 0.4 MGy and stored for 2 months at room temperature showed a small decrease in linoleic acid but a large reduction in linolenic acid content. The

TABLE 2

Fatty acid compositions of irradiated and unirradiated palm olein as determined by GC.
Dose rate 65 Gy/min.

Fatty acid	Fatty Acid Composition (WT %)					
	unirrd p/olein	0.1MGy	0.18MGy	0.4MGy	0.67MGy	1.0MGy
SATURATED						
1. C12:0	0.1	0.2	0.2	0.2	0.2	0.2
2. C14:0	0.9	1.0	1.2	1.0	1.1	1.0
3. C16:0	39.7	42.3	42.1	43.8	47.6	48.6
4. C18:0	4.5	4.4	4.5	4.9	5.6	6.3
5. C20:0	0.5	0.4	0.5	0.6	0.6	0.7
MONOUNSATURATED						
6. C16:1	0.1	0.3	0.2	0.3	0.4	0.4
7. C18:1	42.7	40.5	41.1	41.4	39.7	39.6
POLYUNSATURATED						
8. C18:2	11.3	10.6	9.9	7.8	4.8	3.3
9. C18:3	0.3	0.3	0.2	0.2	0.1	–
SATURATED (%)	45.6	48.3	48.5	50.5	55.1	56.9
UNSATURATED (%)	54.4	51.4	51.4	49.7	45.0	43.3

Values reprersent the mean of two separate derminations.
" – " indicates not detectable.

saturated and monounsaturated components content, however, were not significantly changed during the same period of storage. In general, the total composition of satured components were increased whereas the unsaturated ones were decreased in samples stored for one and two months, Table 3. It is difficult to correlate the destruction of unsaturated fatty acids with storage times. It seems that the conditions of the experiment played a vital role. Irradiation in aqueous media, for instance, where the concentration of soluble oxygen is high, will increase the oxygen-exposed surfaces. This permits faster reactions of the radiation-induced radicals with oxygen which accelerate the destruction of polyunsaturated fatty acid with the formation of peroxide and its breakdown products. In this study, the oil was irradiated as it was, more or less in its natural form. Due to its high viscosity, low oxygen content and high percentage of saturated fatty acids, it may limit the destruction of unsaturated fatty acids upon storage. Therefore, it might be expected that post-irradiation storage has very little effect on the free fatty acid composition of irradiated palm olein.

Formation of Free Fatty Acid

The free fatty acid (f.f.a) content is the fundamental parameter controlling the quality of palm oil. From the refiners' point of view, palm oil with high f.f.a is highly undesirable because it means losses due to high refining cost and low market prices. Oil with more than 10% f.f.a is marketed as ordinary grade, and thus fetches a low price. Therefore the change in f.f.a in irradiated palm oil is a very important factor, if radiation is to be applied for preservation or sterilization of palm fruits. In this investigation, the palm olein samples were irradiated up to sterilization doses. The formation of f.f.a was determined immediately after irradiation (*Figure 3*) and reported as percentage of palmitic acid (MW 256). Each value represents the average of a duplicate determination.

Radiation may induce the formation of f.f.a through the following mechanism: cleavage of the C-O bond of an excited triglyceride
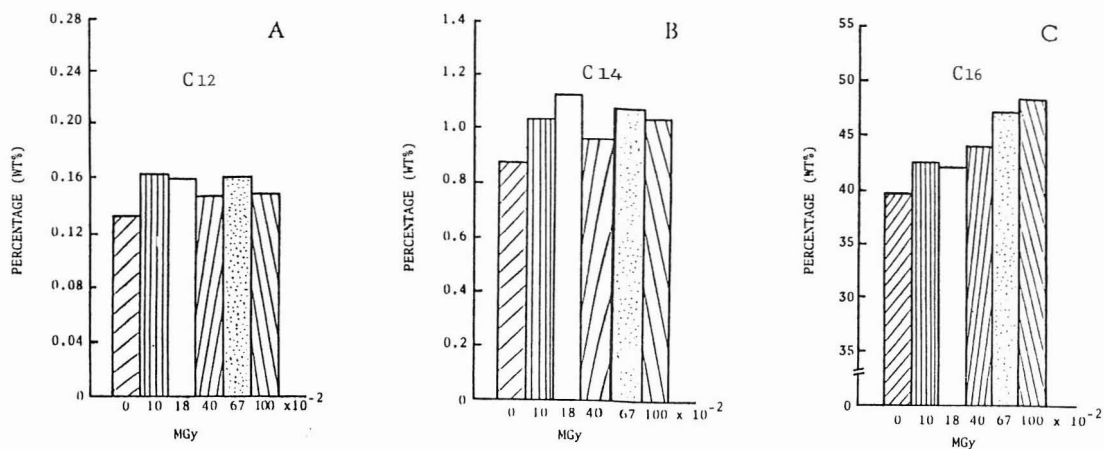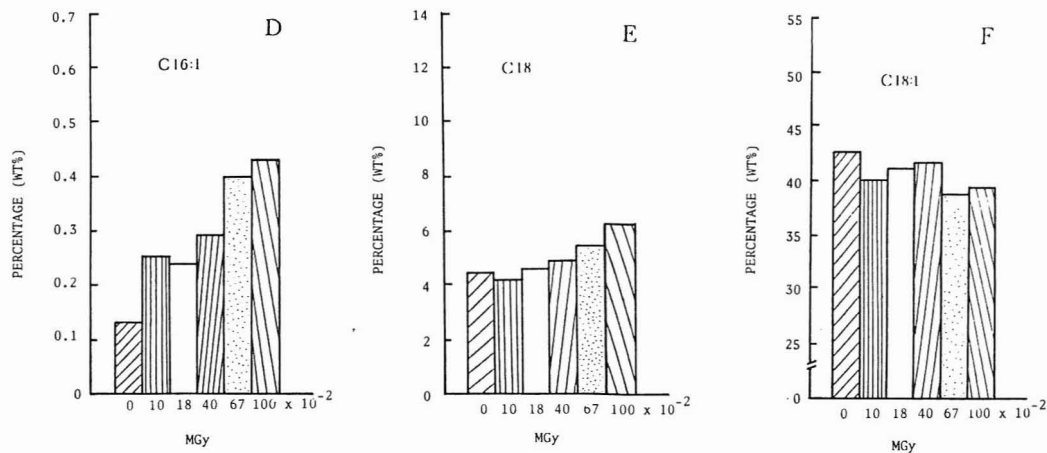
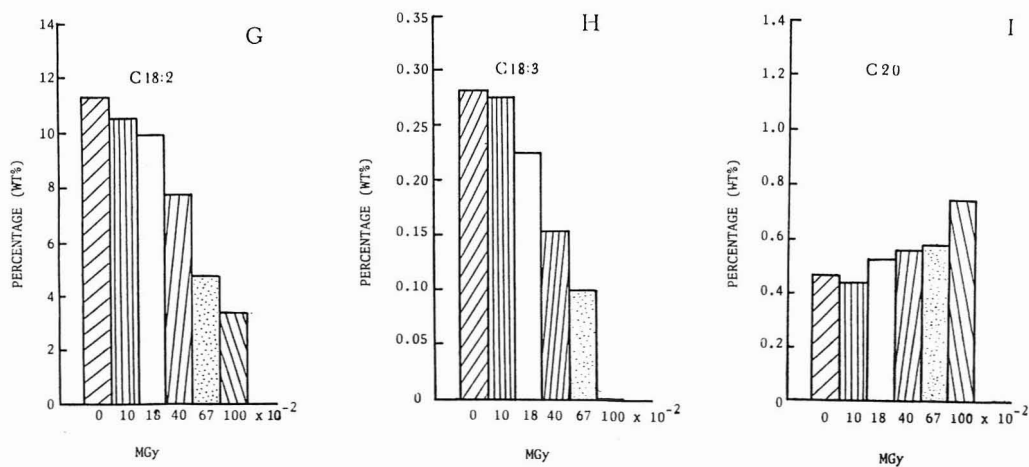Figure 2. (Continued)

Figure 2. (Continued)

Fig. 2 (A - I) : Effect of gamma-irradiation on the proportions of fatty acids in irradiated palm olein. Total dose: 0.1 to 1 MGy at dose rate 65 Gy/min.

TABLE 3

Post-irradiation effect of gamma-irradiation on fatty acid composition
of irradiated palm olein (wt %). Samples stored at room temperature (21°c)
after irradiation with 0.1 and 0.4 MGy. Dose rate 65 Gy/min.

| Fatty Acid	Unirrd. (Control)	Just after irrd.	0.1 MGy		0.4 MGy	
			1 month	2 months	1 month	2 months
SATURATED						
1. C12:0	0.1	0.2	0.2	0.2	0.2	0.2
2. C14:0	0.9	1.0	1.1	1.1	1.0	1.0
3. C16:0	39.7	42.3	42.3	42.4	43.8	43.8
4. C18:0	4.5	4.4	4.4	4.4	5.0	5.0
5. C20:0	0.5	0.4	0.5	0.6	0.6	0.6
MONOUNSATURATED						
6. C16:1	0.1	0.3	0.3	0.3	0.3	0.3
7. C18:1	42.7	40.5	40.6	41.1	41.4	41.4
POLYUNSATURATED						
8. C18:2	11.3	10.6	10.4	9.7	7.7	7.6
9. C18:3	0.3	0.3	0.2	0.2	0.1	0.0
SATURATED (%)	45.6	48.3	48.5	48.7	50.6	50.6
UNSATURATED (%)	54.4	51.4	51.5	51.3	49.5	49.3

Values represent the mean of duplicate analyses.
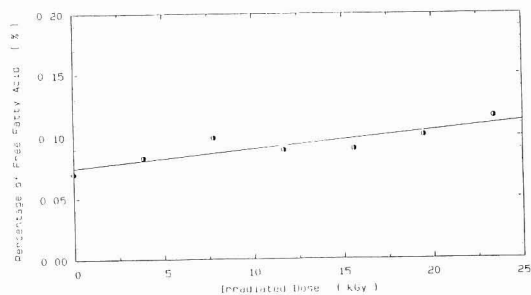
Fig. 3 *Effect of gamma-irradiation on the formation of free fatty acid in irradiated palm olein. Dose rate 65 Gy/min.*

molecule due to impact of γ-radiation on palm olein produces an acyloxy-free radical which abstracts a hydrogen atom to form the free fatty acid, Scheme 2.

At preservation doses which are less than 1 kGy (Kader 1986) there was no detectable change in f.f.a content and less than 0.2% were formed at doses up to 30 kGy which are proposed for sterilization (Webb 1985; Diehl 1977). This result showed that sterilization doses
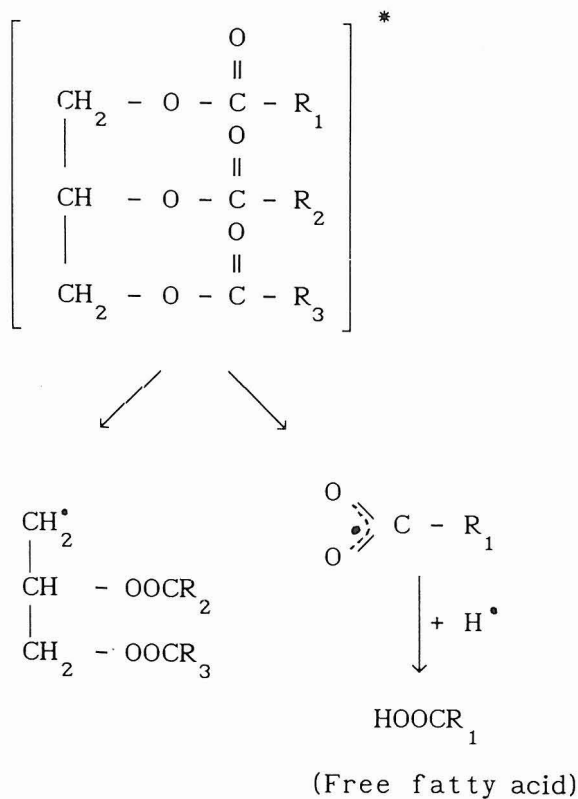
Scheme 2. Scission at the acyloxy-methylene bond.

has no significant effect on f.f.a content of irradiated palm olein. From this point of view, radiation can therefore, be applied to preserve and sterilize palm fruits.

Effect of Radiation on Carotenes

Palm oil is rich in carotenes and they are responsible for the orange-red colour of CPO. An average concentration ranging from 500 to 800 ppm is observed in palm oil from various geographical origins (Goh *et al.* 1985; Cornelius 1977). Carotenes show a strong absorbtion at three wavelengths, 418, 446 and 470 nm. The destruction of carotenes by radiation was monitored at 446 nm, the strongest absorbtion of the three. The UV absorbtion spectra of irradiated and unirradiated carotenes in isooctane are shown in *Figure 4*. Optical densities of irradiated solutions were converted to a 1% solution and expressed as $E_{446}^{1\%}$. The concentrations of carotenes in ppm were then obtained by multiplying this factor by 383 (a universal factor) which is based on the molar extinction coefficient of pure β-carotene (Swoboda 1981).
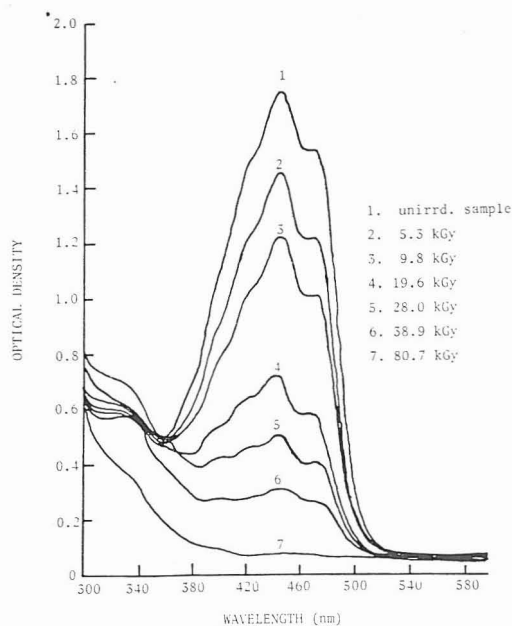
Carotenes are very sensitive to radiation. Its concentration was reduced significantly with increasing irradiation dose. Nearly 50% of carotenes were destroyed after irradiation with 15 kGy which is less than the recommended dose range for food sterilisation (30 – 50 kGy) (Diehl 1977). Within the range of sterilisation doses, about 80% destruction occurred and almost 100% destruction at doses greater than 80 kGy (*Figure 5*). This result suggests that radiation is not suitable to replace steam sterilisation which is traditionally used to sterilize palm fruits to deactivate enzymes and prevent a rapid rise in f.f.a. Application of higher doses (above sterilization dose) is very limited, as it causes great damage to carotenes. This is very important as carotenes have a significant value. Besides acting as photooxidation inhibitors in palm oil, carotenes have both economic and nutritional values. Being a precusor of vitamin A, it is a highly valued product and if extracted and marketed may bring extra revenue and benefits to the palm oil industry.
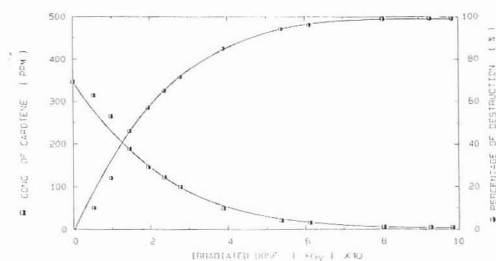
Fig. 5 *Destruction of carotene by gamma-radiation in crude palm oil.*

However, these results have shown that radiation may be suitable for palm fruits preservation since this process involves much lower doses between 1 to 10 kGy. Infact, a dose of 10 kGy is much higher than the dose needed for preservation under practical conditions. In U.S, under a newly approved regulation (April 1986) only doses up to 1 kGy are permitted for preservation of fruit and vegetables (Kader 1986). Under this condition, the preservation of palm fruits by radiation seems promising. At such doses, only a minor destruction of carotenes occurs-less than 5%. In fact, lost of caro-

Fig. 4 *Changes of carotene content in crude palm oil with irradiation doses. Dose rate 65 Gy/min.*

tenes by radiation at 1 kGy is very small and less than those caused by freezing and heat treatment (Bayer *et al.* 1979).

At present, the factor(s) responsible for the destruction of carotenes is not known. The gradual disappearance of carotenes with increasing dose indicates that the production of this factor is dose dependent. Radiation must cause the production of species (peroxides?, free radicals? say) and it could be that these species cause the destruction of carotene.

CONCLUSION

Radiation may be used for preservation of palm fruits since doses for this purpose have no significant effect on f.f.a and carotene contents of palm oil. It is not suitable for sterilization of palm fruits if carotenes are desirable. However, if radiation is used for this purpose on an industrial scale, it is important to find doses which minimize carotene losses but produce a high quality oil.

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