Irradiation Bleaching of Palm Oil, Palmolein, and Palm Stearin

Sir:

The color of palm oil is basically due to carotenoid pigments. In practice, palm oil bleaching is accomplished by heating the oil until the desired color is achieved; all extra color is removed (1). It is believed that during heating, carotenoid molecules break down, thereby reducing the number of double bonds and rendering the molecule colorless. It has been reported (2) that for carotenoids to appear yellow, all nine conjugated double bonds must remain intact. If any double bond is removed/reduced/oxidized, the molecule will lose the yellow color. This phenomenon has been utilized for the bleaching of palm oil.

For all of the following studies, 50 g each of red palm oil, palmolein, and palm stearin were placed separately in glass Petri dishes (20 cm diameter), and the fat was spread uniformly. Six replicates of each experiment were run. In the first study the dishes were kept under the midday sun for 4 h (11:30 A.M. to 3:30 P.M.). The samples were then kept in the dark until the next day's exposure. During exposure, the temperature was recorded as between 28 and 32°C. Complete bleaching (total removal of color) was achieved for all three samples after 8 h. Another set of dishes was kept under an IR lamp. The distance between sample and lamp was 15 cm, and the lamp diameter was 12 cm. Complete bleaching was achieved in all three samples after 2 h. Next, the oils in Petri dishes were exposed to UV light (<280 nm) for a period of 5 h. The distance between the sample and the UV source was 22 cm. UV irradiation did not yield bleached oil. The next condition was microwave treatment; this was conducted with a BPL Sanyo micro/convection Model 900T microwave oven with a power supply of 230 AC 50 Hz (single phase), a microwave power consumption of 1350 W, a microwave energy output of 900 W, and a microwave frequency of 2450 MHz. One hundred percent power was used for the experiments. Fats in the Petri dishes were kept in the microwave oven for 5–30 min, but no significant decrease in color was found. Finally, 50 g of each oil was placed separately in 250-mL beakers and heated to 180°C on a hot plate. Twenty minutes of heating showed a marginal decrease in color. However, total color disappeared after 30 min of heating.

In commercial practice, adsorption refining is used to bleach edible oils but not palm oil. Palm oil is bleached by heating the oil, whereby β-carotene is destroyed/modified and loses its color. Irradiation, a novel process, might be able to replace heat bleaching of palm oil to achieve similar or better bleaching results; this should reduce the formation of artifacts. Of the five treatments tested for bleaching palm oils (solar, IR, and UV irradiation; heat and microwave treatments), two, i.e., microwave treatment and UV irradiation, had no effect. Solar irradiation, IR irradiation, and heat treatment achieved complete discoloration for all three samples within 8 h, 2 h, and 30 min, respectively. UV and microwave irradiation, it appears, do not produce sufficient heat energy or bond vibration to affect bond cleavage; hence, they were not effective. Since palm oil bleaching by solar and IR radiation is unconventional, it is necessary to assess the changes occurring in the oil and the advantages to be gained before they are recommended for industrial use.

Irradiated and heat-treated samples of palm oil, palm stearin, and palmolein were fractionated into nonpolar and polar fractions using column chromatography (3). These bleached samples were weighed and loaded on the columns in hexane. The nonpolar (I) fractions were eluted with hexane and the polar (II) fractions with diethyl ether. The percentages of the two fractions obtained are given in Table 1. As bleaching was not achieved in UV-irradiated and microwave-treated samples, they were not fractionated. It appeared that TAG broke down during heating to form nontoxic MAG, DAG, and FFA. But excessive heating/irradiation also may lead to formation of toxic oxygen-containing (or oxy) components, which are nutritionally undesirable. Degradation was maximal in heat-bleached oils and minimal in oils bleached by solar irradiation.

TLC (4) of fractions I and II obtained from controls and from samples bleached by solar irradiation, IR irradiation, and heat treatment was carried out using hexane/diethyl ether (60:40 vol/vol) as the mobile phase and perchloric acid as the visualizing agent. The first fraction for all samples, including the control, gave a single spot after heating, at R_f 0.96. This spot corresponded to TAG as confirmed by running a standard. However, β-carotene merged with TAG in the unbleached control sample.

The second fraction of the unbleached control sample gave two spots, at R_f 0.5 and 0.2, for phytosterols and FFA, respectively, as confirmed by comparing the R_f values with reference standards. The second fraction obtained from solar-, IR-, and heat-bleached oils gave two additional spots, at R_f 0.31 and 0.43, corresponding to oxy-compounds generated during bleaching. The results are given in Table 2. The second fraction

TABLE 1
Polar and Nonpolar Fractions Obtained from Unbleached and Irradiation-Bleached Oils

Sample	Av. % nonpolar fraction	SD	Av. % polar fraction	SD
Control (unbleached) oils	96.1	0.20	3.4	0.03
Solar irradiation-bleached oils	86.2	0.2	13.0	0.10
IR irradiation-bleached oils	83.7	0.19	15.0	0.14
Heat-bleached oils	76.3	0.21	22.6	0.08

Paper no. J10580 in *JAOCS 81*, 517–518 (May 2004).

TABLE 2
Detection of Oxygenated Compounds[a] in the Polar Fraction by Derivative TLC and IR Absorption Frequency

	Derivative TLC			IR absorption frequency (cm^{-1})		
Bleaching treatment	DNPH (for >C=O) orange spot at R_f 0.43	Iodine-starch (for –C–O–O–) blue spot at R_f 0.31	$(NH_4)_6Mo_7O_{24}$ (for –OH) violet spot at R_f 0.32	>C=O (1720–1735)	–C–O–O– (820–890)	–OH (3200–3400)
Control (unbleached) oil	–	–	–	Nil	Nil	3200 (vb)
Solar irradiation-bleached oil	+	0	+	1720 (s)	Nil	3340 (b)
IR irradiation-bleached oils	+	0	0	1730 (s)	Nil	3350 (b)
Heat-bleached oil	0	–	0	1735 (s)	Nil	3350 (b)

[a] DNPH, dinitrophenyl hydrazone; s, sharp; b, broad; vb, very broad. +, present; –, absent; 0, present as faint or very faint spot.

obtained from the control (unbleached) oil did not form dinitrophenyl hydrazone (5), iodine-starch (6), or ammonium molybdate (6) derivatives, indicating the absence of free carbonyls, peroxides, and hydroxyl derivatives, respectively.

IR spectra of fraction II lacked peaks between 1720–1735 and 820–890 cm^{-1}. A very broad hump observed at 3200–3400 cm^{-1} may be due to moisture in the oil fraction becoming associated with glyceride molecules through hydrogen bonding. Solar-, IR-, and heat-bleached fractions contained carbonyl and hydroxyl derivatives, as they gave positive color spots on TLC. IR spectra confirmed the results obtained by TLC, as peaks were observed at 1720–1735 cm^{-1} for free carbonyls and 3200–3400 cm^{-1} for hydroxyl functionalities in free and associated forms. It has been reported (7) that 48 h of irradiation by intense sunlight, shady sunlight, indoor light, direct sunlight, and UV light break down β-carotene to the extent of 70, 36, 44, 40, and 40%, respectively, resulting in decreased absorption at 450 nm. It has been indicated that during heat and/or light irradiation, the initial breakdown of the carotenoids occurs through formation of epoxides (8). The epoxides lead to the formation of aldehydes, ketones, apocarotenals, and furanoids. Further oxidation and reoxidation would seem to occur from the end of the molecule rather than through scission of the chain. Ionizing radiation rapidly decolorizes solubilized β-carotene, whereas dried-film and solid β-carotene are stable in the absence of oxygen. Products resulting from destruction by radiation appear to be shorter compounds with shorter chromophoric groups (7).

Stereomutation is another phenomenon occurring during the thermal and photochemical treatment of carotenoids (2). It is very slow at room temperature, but practically all carotenoids are completely stereomutated within 10–30 min of heating at 180°C to form mixtures of geometrical isomers. All carotenoids undergo *cis-trans* isomerization on irradiation by light with the wavelength corresponding to the main absorption bond (400–500 nm), as was the sunlight in the present case. All *cis* bonds can be transformed into the *trans* form by prolonged exposure to sunlight. There is no report of stereomutation during IR irradiation.

Bleaching achieved by irradiation is comparable to that achieved by heating. The general quality of the resulting oils was better if they were bleached by irradiation than by heating, as the amount of polar fraction resulting from irradiation was minimal relative to that found in heat-treated oil. IR bleaching is economically more viable than solar irradiation techniques and heat bleaching, as it can be performed easily, with no oil loss, and less energy consumption than with heating at 180°C.

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[Received March 3, 2003; accepted January 22, 2004]

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