Stability of Edible Oils and Fats to Fluorescent Light Irradiation[1]

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ABSTRACT

Butter, butterfat, and corn, coconut, rapeseed, and soybean oils were exposed to 500 ft-c of fluorescent light at varying time-temperature conditions. Oxidation rates were measured by the peroxide values. Vitamin A and β-carotene content of butterfat were estimated. The effect of wavelength on the relative rates of oxidation was determined. The light transmitting properties of the samples at 15 and 30 C over a spectral range of 380-750 nm were measured. It was observed that there was no increase in oxidation rate when the light was switched off. The stability of the oils as shown by the oxidation rates did not correlate well with the ratios of C18:2 to C18:1 or C18:3 to C18:2 nor with the degree of unsaturation. Increase in temperature alone had minimal effect; however, in the presence of light the rate of oxidation increased considerably with a corresponding decrease in the content of Vitamin A and β-carotene. β-Carotene provided strong protective properties. After the photobleaching of β-carotene in butterfat, there was a rapid increase in peroxide values. With coconut oil, the oxidation rate was greater at 15 C than at 30 C due to greater light absorption at 15 C over the entire spectrum. The rate of oxidation decreased at higher wavelengths, and this effect was more pronounced in the vegetable oils than in butterfat, where the β-carotene was considered to serve as a filter for light of low wavelength.

INTRODUCTION

The action of light has long been known to cause deterioration of oils, fats, and fat-containing products during storage (1). The obvious solution of excluding light is often not recommended for marketing reasons. Under the conditions that normally pertain during oxidation of food fats, the primary products of autoxidation are hydroperoxides. The quantity of hydroperoxides formed during photooxidation has been found to be directly proportional to the total amount of light absorbed (2). Moser et al. (3) have described a light test for the measurement of stability of oils. In this test, oil samples are exposed to fluorescent light at room temperature. This test was used by Moser et al. (4) to test the flavor stability of crambe, mustard seed, rapeseed, and soybean oils. Fioriti et al. (5) recently reported excellent correlations between oxygen absorption, peoxide values, and flavor scores in oxidized fats, whereas the results with the benzidine and thiobarbituric acid methods were not satisfactory. Kinetic work on the oxidation of fatty acids in dim daylight revealed a greater rate of oxidation with higher unsaturation (6). However, Khattab and co-workers (7) found that the stability of oils did not correlate with the degree of unsaturation. Phenolic and other naturally occurring inhibitors are reported to offer weak inhibition to photooxidative processes in oils (8). Lundberg (2) observed that α-tocopherol, which is an effective inhibitor of autoxidation, was virtually ineffective in photochemical oxidation. The role of β-carotene in photochemical reactions is also not conclusive. Some authors have reported that carotene increases the rate of oxidation in fats (9). However, with the evidence now available for the participation of singlet oxygen in sensitized photooxidations, current studies suggest that carotenes are natural inhibitors for singlet oxygen oxidants just as the tocopherols are naturally occurring inhibitors of radical chain autoxidation (10,11).

Most of the work has been carried out either on pure compounds or at elevated temperatures simulating conditions of deep fat frying, and the conclusions so arrived at may not necessarily be applicable to natural products under normal storage conditions. Radtke and co-workers (12) reported that action of light is a major cause for the deterioration of oils and fats and that the photochemical action is dependent on wavelength. Thus, the photochemical effects on the stability of oils and fats and their inhibition remains a subject of importance. This is particularly true for vegetable oils sold in clear glass bottles as well as for butter, an excellent source of vitamin A and β-carotene, which is frequently sold in transparent or translucent wrapping materials.

The objective of this study was to determine the relative stabilities of several oils and fats to fluorescent light and the dependence of photochemical effects on light absorption and wavelength.

EXPERIMENTAL PROCEDURES

Materials

Rapeseed, soybean, and coconut oils were obtained from Monarch Fine Foods Co. Ltd. (Rexdale, Ontario) and corn oil from St. Lawrence Starch Co. Ltd. (Toronto, Ontario). All of the oils were refined, bleached, and deodorized and were obtained at the factory immediately from the deodorizer, before addition of antioxidants or metal scavengers. Soybean and rapeseed oils are always degummed with a phosphoric acid treatment. Butter samples were obtained from Stacey Brothers Ltd. (Mitchell, Ontario), taken directly from the packaging lines, and transported to Guelph in light-impervious containers. Milk fat was prepared from butter by melting and repeated washing with warm water to remove nonlipid materials, followed by drying under vacuum and filtration.

Methods

The fatty acid composition of the oils and fats was determined by gas-liquid chromatography after transesterification with sodium methoxide as reported by Shehata et al. (13). The resulting methyl esters were analyzed with a Hewlett-Packard gas chromatograph. Conditions: 15% diethyleneglycol succinate on Chromosorb WAW (80-100 mesh), column length 3 m; detector temperature 250 C; injector temperature 220 C; and column temperature 190 C.

Samples (5 ml) of each oil or fat were placed in disposable petri dishes (53 x 12 mm inside diameter, 22.20 cm^2 surface area) and exposed to light of 500 ft-c at different time-temperature conditions in a low temperature cabinet. Lighting consisted of 40 Watt cool-white fluorescent tubes, and the samples were placed at the proper distance from the light source to obtain the desired intensity, which was measured by means of a General

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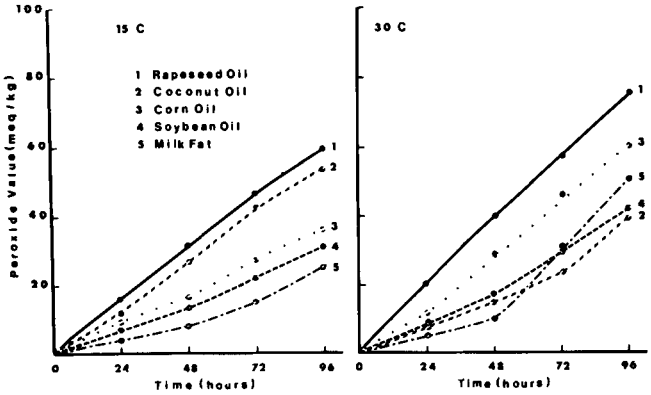

FIG. 1. Effect of 500 ft-c fluorescent light on oxidation rates of oils and fats at 15 and 30 C.

Electric type 213 light meter. Control samples were kept for corresponding time-temperature conditions in the dark.

Light transmittance characteristics of the samples at different temperatures were determined with an ISCO model SR spectroradiometer using a cool-white fluorescent tube as the light source in a walk-in type incubator. Transmission was measured at 25 nm intervals over the wavelength range of 380-750 nm.

Oxidation rate of the samples was followed by measuring peroxide values (POV) according to AOCS Official Method Cd 8-53 (14). Vitamin analyses of the milk fat were made using methods described by Wilkinson and Conochie (15). After saponification, extraction of the samples was carried out by using a mixture of diethyl ether and petroleum ether (bp$<$40 C; 1:3). The optical density of the mixture was measured at 451 nm for β-carotene. An aliquot of the same ether mixture was placed in a colorimeter tube and the ether removed under a stream of nitrogen. The residue was dissolved in chloroform, and the color developed with Carr-Price reagent was measured at 620 nm for vitamin A content. Vitamin A values were obtained after making the necessary corrections for the presence of β-carotene.

In preliminary work to study the influence of wavelength on the oxidation rate, two long wavelength transmitting color filters (2 in. x 2 in.) exhibiting a sharp cutoff at 480 and 560 nm of the pass region were used. The filters were obtained from Bausch and Lomb, Canada, Analytical Systems Division (Toronto, Ontario). The coatings used in these filters transmit exactly defined wavelength intervals of the visible spectrum, rejecting the remainder by virtue of their high wavelength-selective reflectance. Detailed work on the effect of wavelength on the oxidation rate of these oils and fats will be the subject of later publications.

RESULTS AND DISCUSSION

The relative rates of photooxidation of the oils and fats at 15 and 30 C are shown in Figure 1. Analysis of variance of the change in peroxide values as affected by light, exposure time, and temperature indicated that each of these variables had a significant effect on peroxidation (Table I). Table II shows the rate of peroxidation after 160 hr at 25 C as well as the ratios of 18:2 to 18:1 and 18:3 to 18:2. It would be expected that samples with high unsaturation should exhibit correspondingly high rates of oxidation (16). However, comparison of these ratios with the peroxide values of the oils at 25 C after 95 hr as well as with the kinetic data of Figure 1 revealed that the rate of oxidation does not depend entirely on the degree of unsaturation nor on the ratios of 18:3 to 18:2 and 18:2 to 18:1.

Statistical analysis of the data when transformed into oxidation rate per hour (POV/hr) during each storage interval as affected by fluorescent light for all oils and fats is presented in Table I. After analysis of variance, the means were separated by the Duncan multiple range test. The results indicate that there was a significant ($P<0.05$) difference in the oxidation rates of the different oils and fats. Comparison of these oxidation rates with unsaturation ratios as well as with degree of unsaturation showed that photochemical oxidation does not depend on any of these factors. It is suggested that, owing to the presence of sensitizers, antioxidants, and other natural inhibitors, the degree of unsaturation of oils and fats may not be responsible for the readings with which they are oxidized. The

TABLE I

Effect of Fluorescent Light of 500 ft-c Intensity on Oxidation Rate (POV/hr) of Oils and Fats after Different Exposure Times[a]

	Temperature 15 C Exposure time (hr)				Temperature 30 C Exposure time (hr)			
Oils or fats	0-24	24-48	48-72	72-96	0-24	24-48	48-72	72-96
Rapeseed	0.637	0.670[b]	0.641[c]	0.509[c]	0.885	0.782[c]	0.687	0.719[c]
Corn	0.370	0.291[c]	0.504	0.265[b]	0.447	0.695[c]	0.800	0.561[b]
Soybean	0.266	0.277[c]	0.429	0.305[b]	0.296[c]	9.394	0.506	0.584[b]
Coconut	0.466	0.635[b]	0.692[c]	0.403	0.199[c]	0.283[b]	0.365	0.721[c]
Milk fat	0.185	0.148	0.311	0.495[c]	0.194[c]	0.189[b]	0.809[c]	1.325

[a]POV = peroxide value (meq/kg).

[b,c]For each interval, values sharing common letters are not statistically different ($P < 0.05$).

TABLE II

Peroxide Values of Oils and Fats at 25 C Exposed for 160 hr to Fluorescent Light of 500 ft-c Intensity and Ratios of Unsaturation

Oil or fat	Peroxide value (meq/kg)	Fatty acid ratios		
		Unsaturated/saturated	18:2/18:1	18:3/18:2
Rapeseed	113.7	11.59	0.43	0.545
Corn	93.1	4.65	2.33	0.014
Soybean	71.0	5.25	2.10	0.164
Coconut	68.6	0.12	0.35	--
Milk fat	135.7	0.45	0.05	0.320

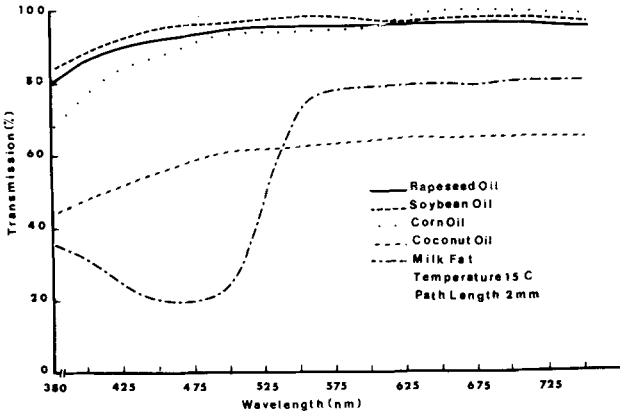

FIG. 2. Light transmission of pure oils and fats at 15 C.

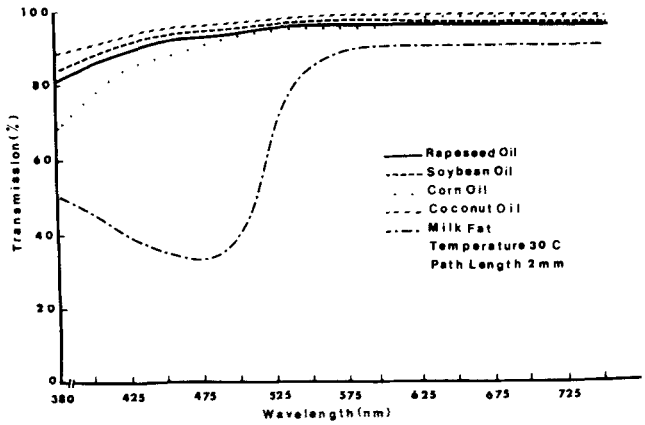

FIG. 3. Light transmission of pure oils and fats at 30 C.

data show that milk fat, which is composed mainly of saturated fatty acids, oxidized significantly ($P<0.05$) more than any other oil or fat at later stages of exposure to fluorescent light at 30 C. This was probably due to the photobleaching of β-carotene, which may act as a strong inhibitor in the earlier stages. Similarly, coconut oil exhibited greater oxidation than might have been expected from the degree of unsaturation. Gunstone and Hilditch (6) have reported the relative rates of autoxidation of oleate, linoleate, and linolenate at 20 C, in dim daylight, to be in the ratio of 1:12:25. This has been ascribed to the lower activation energy of the more unsaturated esters (14). There appear to be good reasons to assume that spontaneous autoxidation and photooxidation proceed by different mechanisms, as has been suggested by Lundberg (2).

The influence of exposure times to fluorescent light followed by dark periods on the oxidation of milk fat and rapeseed oil at 20 C was studied. It was noted that as the light was switched off, there was no further increase in peroxide values, suggesting that the reactions taking place during photooxidation of natural systems, at least at low temperatures, may not be of autocatalytic nature. It is expected that photooxidation of the other vegetable oils used in this study proceeds in a similar manner.

It was observed that on exposure to light, the oxidation rate for coconut oil at 15 C was faster than that at 30 C. This was believed due mainly to the variation in solid-liquid ratios between these temperatures, which changed the spectral transmission over the wavelength range of 380-750 nm (Figs. 2 and 3). Light absorption by coconut oil was greater at 15 C than 30 C, which resulted in greater oxidation at 15 C. The same phenomenon was not exhibited by milk fat, though the light absorption was greater at 15 C than 30 C. The slow rate of photobleaching of carotene in milk fat at lower temperatures probably was a decisive factor. The spectral transmission of other oils did not change at these temperatures. The rate of peroxidation of milk fat dring the last 24 hr period at 30 C was calculated to be greater than that of any other oil due to the almost complete photobleaching of carotene. The reason for the slow oxidation of soybean oil, which has an appreciable content of 18:3 and 18:2 as compared to several other oils used in this study, is not clear. Lundberg (2) reported that the hydroperoxides of linolenate autoxidation are generally unstable. This explanation is not sufficient, since rapeseed oil also had considerable quantities of 18:3. Koo and Kim (17), while studying the effects of several kinds of light, observed that sunlight exerts the strongest prooxidant activity, followed by ultraviolet, fluorescent, and incandescent lights. Clements et al. (18) reported that, owing to the presence of natural antioxidants, the degree of unsaturation may not alone be responsible for the readiness with which the oils and fats are oxidized by light. The photochemical reactions of pure fatty acids may not necessarily simulate the mechanisms taking place in natural systems. It appears, therefore, that stability of oils and fats packaged in clear glass or transparent materials cannot be predicted from the data obtained on model systems.

A study of the antioxidative properties of some carotenoids and vitamin A has shown that both β-carotene and vitamin A were inhibitors of spontaneous fat and oil oxidation (19). It has now been established that singlet oxygen is the primary source of the original hydroperoxides produced during autoxidation or photooxidation (20). It also has been suggested that quenching of singlet oxygen by

TABLE III

Effect of Fluorescent Light (500 ft-c) on β-Carotene, Vitamin A, and Peroxide Value of Milk Fat

Exposure time (hr)	Temperature (C)	β-Carotene (μg/g)	Vitamin A (μg/g)	Peroxide value (meq/kg)
0	15	3.93	6.83	0.18
	30	3.93	6.83	0.18
24	25	3.40	4.27	4.42
	30	3.07	3.75	4.90
48	15	3.07	2.56	7.97
	30	2.21	0.85	9.52
72	15	2.05	1.54	14.82
	30	0.34	0.17	29.80
96	15	1.36	1.19	22.44
	30	0.17	—	51.12
120	15	0.68	0.85	37.62
	30	0.10	—	71.72

TABLE IV

Regression Equations and Coefficients of Correlation Between Peroxide Values and β-Carotene Content of Milk Fat

Temperature (C)	Type of equation	Equation	r^2	r(Coefficients of correlation)
15 C	Linear	$y = 40.24306 - 10.6286x$	.9485	.9739
	Quadratic	$y = 49.87365 - 21.78588x + 2.41908x^2$	.9843	.9921
30 C	Linear	$y = 52.83499 - 15.2448x$	.7846	.8858
	Quadratic	$y = 58.51867 - 34.35421x + 5.13188x^2$	.8509	.9224

TABLE V

Peroxide Values of Oils and Fats at 20 C Exposed for 20 hr to Fluorescent Light of 500 ft-c Intensity[a]

Long wavelength Transmitting filter Code number	Wavelength range (nm)	Oils or fat					
		Rapeseed	Corn	Soybean	Coconut	Milk fat	SE of means
Exposed	350-750	17.70	9.35	6.03	10.12	3.67	0.316
90 - 2 - 480	480-750	9.60	4.95	2.60	4.40	2.59[b]	
90 - 2 - 560	560-750	6.80	3.30	1.56	1.96	2.19[b]	
Dark	---	1.00	1.70	0.38	0.12	0.20	

[a]Pathlength = 2.25 mm; surface area 22.2 cm^2.

[b]For each, oil values sharing common letter are not statistically different ($P < 0.05$).

β-carotene is an important mechanism against photodynamic damage (10,11). El-Tinay and Chichester (21) reported that the rate of free radical initiated autoxidation of β-carotene is considerably enhanced in the presence of stearic acid, thus demonstrating the importance of saturated fatty acids in natural systems.

After exposure to light, milk fat was analyzed for β-carotene, vitamin A, and peroxide values at 15 and 30 C (Table III). It was found that, as the β-carotene and vitamin A contents decreased, there was a corresponding increase in the peroxide values. Obviously, the rate of loss of β-carotene and vitamin A was faster at 30 C than at 15 C, along with an increase in peroxide values. A linear relationship was found between the loss in β-carotene and time, and the reaction rate increased with increasing temperature. Since β-carotene is widely considered as an oxidation inhibitor, the data regarding β-carotene and peroxide values of milk fat were subjected to regression analysis using equations of both linear and quadratic types. The coefficients of correlation and the fitted equations for both temperatures given in Table IV indicate that the quadratic regression of peroxide values (Y) on β-carotene content (X) gave the best fit. This shows a high correlation, indicating that β-carotene serves as a strong natural inhibitor of photooxidation. This inhibition is interpreted as being simply due to light absorption, i.e., it functions as a built-in filter. It is perhaps significant from the point of view of flavor deterioration, since the tocopherols are usually largely retained during the bleaching step whereas the β-carotene is not. Therefore, the oils that have been neutralized, bleached, and deodorized are known to become rancid quicker than crude oils and even unbleached refined oils. β-Carotene has been reported at 0.002% concentration to be an inhibitor of photooxidative deterioration of corn and cottonseed oils (8).

Preliminary results showing the effect of two color filters with defined wavelength pass bands are shown in Table V. The effect of these filter wavelengths on the oxidation rate of corn oil during a period of 96 hr exposure

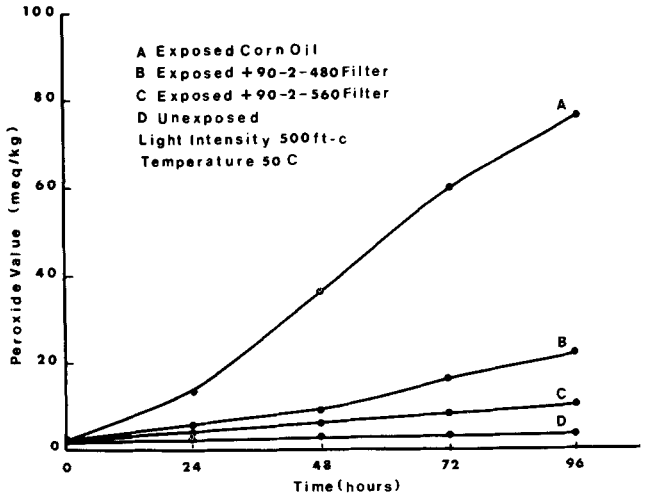

FIG. 4. Effect of long wavelength transmitting filters on oxidation of corn oil.

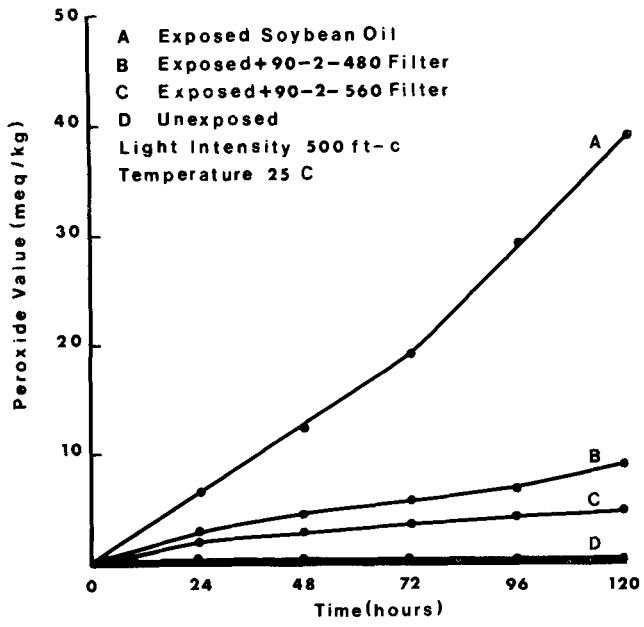

FIG. 5. Effect of long wavelength transmitting filters on oxidation of soybean oil.

at 50 C, soybean oil at 25 C, and fresh butter at 5-6 C is presented in Figures 4, 5, and 6, respectively. It is evident that the rate of oxidation decreased with increase in wavelength. The effect of temperature on oxidation with corn oil seems to be minimal, whereas in the presence of light oxidation increased greatly. At lower temperature, the filters did not exhibit marked protection of butter, possibly due to the presence of β-carotene. However, over an extended period of time with the decrease in β-carotene, the oxidation rate was influenced by the filter wavelengths. Paul et al. (22) have reported similar effects on different colored lights on the oxidation of soybean, sunflower, and peanut oils. It appears, therefore, that relatively simple and inexpensive changes in packaging materials may bring about a greatly reduced light transmittance which can ensure flavor quality and retention of light-sensitive vitamins. A detailed study on the influence of several wavelength pass bands of the visible spectrum on the oxidation rate of these oils and fats as well as β-carotene and vitamin A content of milk fat will be the subject of a later publication.

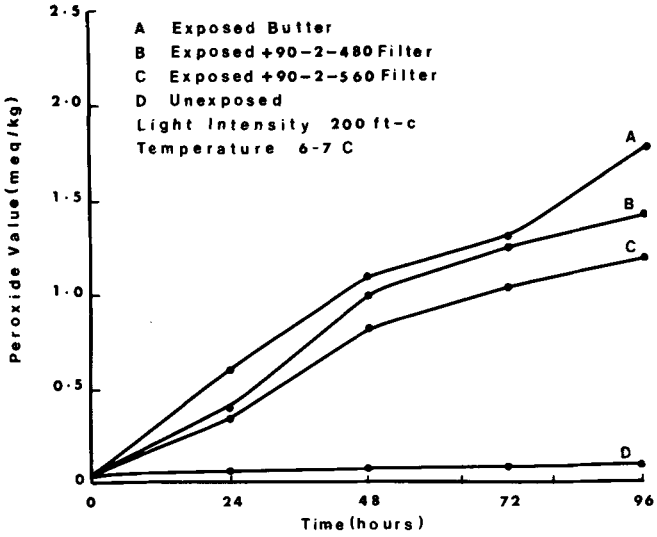

FIG. 6. Effect of long wavelength transmitting filters on oxidation of butter.

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