THE STABILITY OF CANOLA OIL BLENDED WITH SUNFLOWER OIL OR COTTONSEED OIL

by

SHAUNDA B. DURANCE

A thesis
presented to the University of Manitoba
in partial fulfillment of the
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ABSTRACT

Canola oil was blended with sunflower oil and with cottonseed oil in proportions of 0-100% (in increments of 25%) in order to reduce the linolenic acid (C18:3) content. The oxidative stability of the resulting blends were examined under the following experimental conditions: (1) accelerated storage for 12 days at 65°C; (2) exposure to fluorescent light (250±25 ft.c.) for 4 days at 40°C; and (3) heating to frying temperature (185°C) for 10 minutes. The effect of heating canola oil under nitrogen was also investigated. The progress of lipid oxidation was monitored chemically by peroxide value, hydroperoxide value, TBA value, total volatile carbonyl compounds and furfural. Sensory evaluation of the oils involved odor intensity and acceptability.

A reduction in the C18:3 content of canola oil, by blending it with low linolenate oils, generally increased the stability of canola oil to accelerated storage at 65°C. The effect of blending on the stability of canola oil to fluorescent light exposure at 40°C was not as obvious and, in the case of the cottonseed oil blends, was complicated by the possible development of a "light-struck" flavor.

Cottonseed oil had a more dramatic effect than did the sunflower oil, on retarding the development of odor in canola oil, when the oils were heated to 185°C. The exclusion of oxygen by nitrogen during heating was also demonstrated as having a positive effect on the reduction of the heated odor of canola oil.

Based on the results of this study, 25% canola oil can be successfully blended with 75% sunflower oil or cottonseed oil to produce oils which are close in odor stability to that of the original parent sunflower or cottonseed oil.

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Chapter I

INTRODUCTION

In 1979, the Western Canadian Oilseed Crushers Association adopted the name "canola", to describe an improved type of rapeseed which was low in erucic acid and glucosinolates. Erucic acid, in the edible oil from rapeseed, had been shown to cause accumulation of fat in the heart muscle of rats (Beare-Rogers, 1970), while glucosinolates in rapeseed meal fed to livestock caused growth depression and goiter (Niewiadomski, 1970). The reduction in erucic acid (C22:1) caused a pronounced increase in the oleic acid (C18:1) content, along with lesser increases in linoleic (C18:2) and linolenic (C18:3) acids. Canola is particularly suited to the cooler growing conditions of Western Canada, as well as Northern Europe and China. Varieties grown in the 1980's in Western Canada include Altex, Andor, Regent and Western, all of which are of the Argentine type (Brassica napus), as well as Candle and Tobin of the Polish type (Brassica campestris). The oil of these so-called "double-low" varieties must, by definition, contain a maximum of 5% erucic acid, and the meal a maximum of 3 mg/g isothiocyanates- a measure of the glycosinolate content (Man. Dept. of Agric., 1984).

The production of canola has expanded substantially in recent years, along with its increased commercial importance as a source of edible oil in Canada. Statistics Canada estimated the 1985 Canadian production to be 3,156 tonnes, making canola the third largest crop after wheat and barley. Recently, canola oil was included on the 1984 GRAS (Generally

Regarded As Safe) list by the Food and Drug Administration in the United States (Anon, 1985), making it a potential competitor to soybean oil in that country. From the review of the literature, however, it is apparent that some problems remain in terms of thermal and oxidative stability of soybean and rapeseed oils, as compared to other popular vegetable oils, such as cottonseed, sunflower and peanut oils.

The lower oxidative stability of rapeseed oil and its tendency to undergo flavor reversion have been attributed to the relatively high content of unsaturated fatty acids, especially linolenic acid (Moser et al, 1965; Meijboom and Stroink, 1972). Krishnamurthy (1982) stated that oils containing linolenic acid are less stable than other oils. Of particular concern is the odor stability of high linolenate oils during frying.

Recently, a delegation of food processors from Latin America, sponsored by the Canola Council of Canada, recommended that high linolenate oils, such as canola oil, be blended with cottonseed oil, to reduce their C18:3 content, and thereby increase their oxidative stability. Sunflower oil was included, as an alternate to cottonseed oil, because of its potential importance as an oilseed crop in Manitoba and in the United States. Morrison et al (1973) found Northern sunflower oil to compare favorably during deep-fat frying (180±3°C) to a commercial cottonseed-corn oil mixture used for potato chip frying, in terms of free fatty acids, viscosity and stability to storage using the Active Oxygen Method. Robertson and coworkers (1978) found no difference between stored potato chips fried in either sunflower, cottonseed, or palm oil using chemical and sensory analysis.

1.1 OBJECTIVES

The objectives of this study were:

1. To examine the oxidative stability of canola oil blended with sunflower oil and with cottonseed oil to accelerated storage at 65°C.
2. To examine the oxidative stability of canola oil blended with sunflower oil and with cottonseed oil to exposure to fluorescent light (250±25 ft.c.) at 40°C.
3. To examine the stability of canola oil blended with sunflower oil and with cottonseed oil upon heating to frying temperature (185°C).

Chapter II

LITERATURE REVIEW

2.1 OXIDATION

The rate of lipid oxidation is dependent upon the degree of unsaturation of the fatty acids, as well as temperature, the presence of oxygen, light, antioxidants and prooxidants. The fatty acid composition of some common commercial vegetable oils are presented in Table 1. It is apparent that canola oil and soybean oil are similar in their rather high linolenic acid (C18:3) contents. In contrast, cottonseed, sunflower and peanut oils contain only trace amounts of this fatty acid. Labuza (1971) reported that the rate of oxidation of linolenic acid is 25 times that of oleic acid (C18:1) and twice that of linoleic acid (C18:2). It is believed that linoleic, linolenic and arachidonic acids (C20:4) are important precursors to flavor and odor of foods (Forss, 1972).

TABLE 1

FATTY ACID COMPOSITION OF SOME COMMON COMMERCIAL OILS (%w/w)

FATTY ACID	CANOLA[1] (var. REGENT)	SOYBEAN[2]	COTTONSEED[3]	SUNFLOWER[4]	PEANUT[5]
C16:0	4	11	25	6	13
C18:0	2	2	3	4	3
C18:1	55	23	17	18	42
C18:2	26	54	54	69	34
C18:3	10	8	tr[6]	tr	tr
C20:1	2	tr	1	1	1
C22:1	tr	tr	tr	0	tr

[1] Adapted from Vaisey-Genser and Eskin (1982)
[2] Adapted from Cowan et al (1973)
[3] Adapted from Cherry (1983)
[4] Adapted from Campbell (1983)
[5] Adapted from Ackmann (1977)
[6] trace

2.1.1 Autoxidation

The process of autoxidation consists of three stages; Initiation, Propagation, and Termination (Figure 1). In the initiation step, one hydrogen atom is removed from the methylene group adjacent to the double bond of an olefenic compound to yield a free radical. This process is not yet fully understood. It is known, however, that metals such as iron and copper encourage initiation. It is for this reason that metal chelators such as citric acid, ascorbic acid, phosphoric acid and ethylenediaminotetraacetic acid are added (with antioxidants) to fats and oils (Gunstone, 1984). The free radical formed in the first step combines with oxygen to form a peroxy free radical which may, in turn, abstract hydrogen from another unsaturated molecule to yield a hydroperoxide and a new free radical. This chain reaction or propagation may be followed by termination if the free radicals react with each other to form non-active products. Termination is enhanced by antioxidants. These may be naturally occuring, such as tocopherols, or synthetic as in the case of butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tertiary butylhydroquinone (TBHQ). The hydroperoxides formed during propagation are referred to as "primary oxidation products". These are quite unstable and decompose into "secondary oxidation products", of which carbonyls are the most important.

Flavor reversion is another problem of high linolenate oils often cited in the literature (Smouse, 1979). Flavor reversion was defined by Weiss (1970) as the return of a refined, deodorized fat or oil to its flavor and odor before deodorization. Reversion flavor of soybean oil

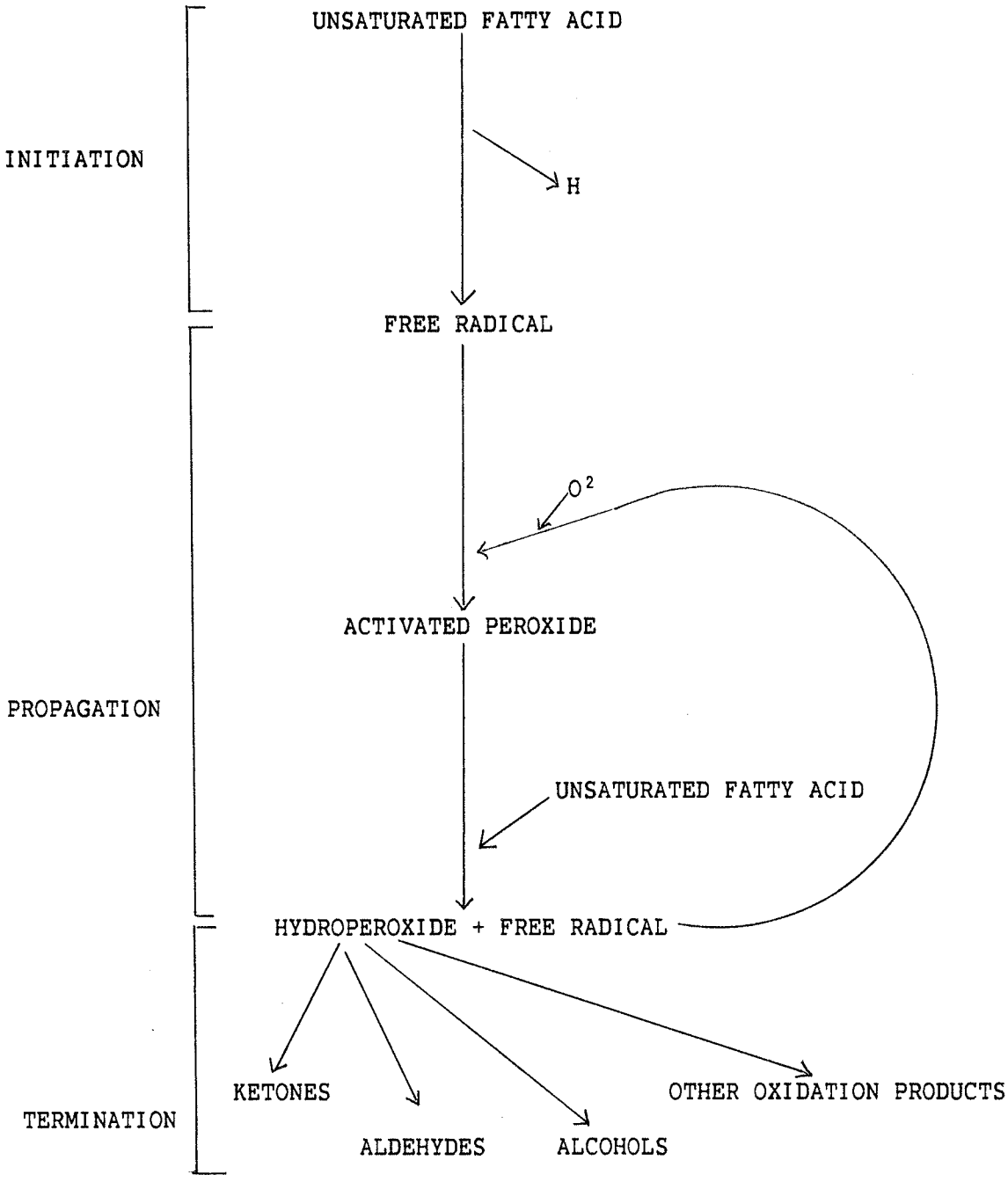

Figure 1: OXIDATION OF AN UNSATURATED FATTY ACID.
(adapted from Badings, 1970)

is typically described as "green-beany", "weedy", "hay-like", and "fishy", while rancidity is often characterized as "painty" (Smouse, 1979). This process requires less oxygen and less time to occur than does rancidity and it is believed that slight oxidation of the fatty acids are the major cause (Sonntag, 1982a).

2.1.1.1 Methods for the Measurement of Autoxidation

A variety of subjective and objective methods exist for the measurement of lipid oxidation. Decomposition of hydroperoxides yield many lower molecular weight compounds which are responsible for the development of the off-flavors and off-odors associated with rancidity. Sensory evaluation of the extent of the accumulation of these secondary oxidation products by a trained panel is an important tool in the study of autoxidation. Most investigators employ some type of scaling technique, either line or category scaling, to evaluate the flavor or odor of oils and fats (Dobbs, 1975; Blumenthal et al, 1976; and Mounts, 1979). Although sensory analysis remains as the final judgement of flavor and odor (Jackson, 1981), it is time consuming and generally lacks reproducibility (Gray, 1978). Chemical methods are, therefore, also used to support sensory measurements, by providing reproducable sensitive and quantitative data.

Peroxide value is a common chemical measurement for the detection of the primary products of lipid oxidation. Numerous analytical procedures are described in the literature (Gray, 1978). The official iodometric AOCS method (Cd 8-53, 1979) is widely used and is based on the measurement of iodine produced from potassium iodide by the peroxides in the

oil (Cocks and van Rede, 1966). The usefulness of the peroxide value is limited to the initial stages of oxidation, since peroxides are very unstable. Fiorti et al (1974) however, reported good correlations between peroxide value and flavor scores of stored soybean oil and for stored corn oil. Eskin and Frenkel (1976) developed a colorimetric method for the determination of hydroperoxides in oil, which involves a specific reaction between a titanium ion and lipid hydroperoxides, resulting in a colored complex, which is read at 415 nm. A high degree of correlation was also obtained by the authors between hydroperoxide value peroxide value, TBA value, and odor intensity value for stored rapeseed oil and for stored soybean oil.

The thiobarbituric acid (TBA) test is a widely used chemical test, that measures the production of malonaldehyde, a secondary oxidation product (Gray, 1978). This colorimetric method is based upon the formation of a pink-colored complex involving two molecules of thiobarbituric acid and one molecule of malonaldehyde (Tarladgis et al, 1962), which can be read at 528 nm. Patton (1974) found this method to be a useful indicator of lipid oxidation. He suggested, however, due to the complex factors leading to color production, the TBA value should be considered in conjunction with other chemical indices and sensory analysis.

Another method which is occassionaly used is the anisidine test. It is based on the reaction between anisidine and unsaturated aldehydes, which yield colored Schiff's bases, the absorption of which can be measured at 350 nm (Henning, 1976).

2.1.1.2 Autoxidation of High Linolenate Oils

Moser and collegues (1965) compared the oxidative stability of rapeseed, mustard and crambe oils with soybean oil. The linolenate contents of these oils were 9%, 7%, 8%, and 8%, respectively. The oils were subjected to accelerated storage at 60°C for 4 days. Flavor intensity, evaluated by a 20 member trained taste panel, and peroxide value were assessed. The results were similar for all the oils and the authors suggested that the linolenic acid was a precursor to the off-flavor development.

Eskin and Frenkel (1977) investigated the autoxidation of canola oil and lightly hydrogenated soybean oil, both containing the antioxidant mixture BHA, BHT, propyl gallate, and citric acid. The oils had C18:3 contents of 12.4% and 3.2%, respectively. The rate of oxidation during storage at 65°C was measured by TBA, peroxide value, and hydroperoxide value, as well as by odor intensity values. It was found that both oils were similar in their rates of peroxide and odor development, while differences existed in relation to TBA and hydroperoxide values. The authors suggested that the accumulation of carbonyls and malonaldehyde, as measured by TBA value, were sufficient for development of off-odor of the soybean oil, as compared to the canola oil.

2.1.2 Photooxidation

Photooxidation and autoxidation proceed by different mechanisms generating similar but not identical products. The former proceeds at a much quicker rate and requires singlet oxygen, which is formed from the

more usual triplet state by the interaction of light and a photosensitizer. Some examples of photosensitizers are chlorophyll, erythrosine, rose bengal and methylene blue (Gunstone, 1984). The singlet oxygen causes a change in configuration, from cis to trans, of an olefinic compound. The antioxidants used for inhibiting autoxidation are reported to be ineffective in photooxidation and, in fact, BHT was found to enhance photoxidation (Logani et al, 1983). Singlet oxygen quenchers such as ß-carotene, however, have been found to be effective (Gunstone, 1984; Kiritsakis and Dugan, 1985).

The products of these two processes of oxidation also differ in that autoxidation of methyl oleate yields 4 hydroperoxides, only two are formed by photooxidation. In the case of methyl linoleate, the reverse is true, while methyl linolenate produces four hydroperoxides by autooxidation and six by photooxidation (Gunstone, 1984).

2.1.2.1 Methods for the Measurement of Photooxidation

Peroxide value has been shown by Sattar et al (1976a) to be highly correlated with average flavor scores of several edible oils and fats subjected to photooxidation. Anisidine value was found by these researchers to be inappropriate for measurement of photooxidation. TBA value, however, appeared to be a useful indicator of the extent of photooxidation of olive oil (Kiritsakis and Dugan, 1985).

2.1.2.2 Photooxidation of High Linolenate Oils

Sattar and coworkers (1976a, 1976b) carried out several studies of the stability of edible oils and fats including low erucic rapeseed oil, soybean oil and corn oil, with linolenate contents of 12.0, 8.4, and 0.8, respectively. All oils were refined, bleached and deodorized but no antioxidants were added. Samples were placed in petrie dishes to maximize surface area, and exposed to 500 foot candle fluorescent light in a low temperature cabinet (25°C). Peroxide values were determined, in addition to flavor evaluation by an eight member panel. The results, presented in Table 2, indicated that the soybean oil had the least flavor stability, corn oil was the most stable, while the stability of the low erucic rapeseed oil was intermediate. The authors noted an increase in peroxide value over the 12 hours (Table 3), which was accompanied by a decrease in average flavor scores. Although peroxide values correlated well with sensory scores, the peroxide value at which each oil was no longer acceptable, differed. For example, soybean oil attained an unacceptable mean flavor score at a peroxide value of 2 meq/kg, while at a peroxide value of 12.9 meq/kg, rapeseed oil was still scored as being acceptable. An important discovery of the Sattar et al, (1976a, 1976b) studies, was that photooxidation terminated when the light was shut off, which is an important consideration when packaging oil.

A recent study by Fan et al (1983) examined the origin of the "light-stuck" flavor of cottonseed oil. This phenomenon was associated with the photochemical oxidation of cottonseed oil and was attributed to the formation of 1-decyne, a photodegradative product of the naturally-

occuring cyclopropenoid fatty acids utilizing chlorophyll as a photosensitizer.

TABLE 2

THE EFFECT OF FLUORESCENT LIGHT (500 ft.c. at 25°C) ON OIL FLAVOR SCORES[1]

OIL	EXPOSURE TIME (hours) 3	6	9	12
RAPESEED	8.9 a[2]	8.9 a	8.0 b	7.9 b
SOYBEAN	6.5 a	5.4 b	5.1 b	4.4 c
CORN	9.4 a	9.1 ab	8.4 bc	8.2 c

[1] Initial flavor scores of unexposed control samples = 10

[2] abc : In each oil, means with the same letters are not significantly different ($p \leq 0.05$).

Scoring system: 9-10 (good); 7-8 (less desirable, but acceptable); 5-6 (objectionable); 3-4 (unpleasant); 1-2 (repulsive)

(Adapted from Sattar et al, 1976a)

TABLE 3

THE EFFECT OF FLUORESCENT LIGHT (500 ft.c. at 25°C) ON PEROXIDE VALUE[1]

OIL	EXPOSURE TIME (hours) 0	3	6	9	12
RAPESEED	1.0[2]	4.9	7.1	10.0	12.9
SOYBEAN	0.3	2.0	3.0	3.9	4.3
CORN	1.0	3.3	4.7	5.3	6.8

[1] meq peroxide/kg fat
[2] Means in each row are significantly different ($p \leq 0.05$)

(Adapted from Sattar et al, 1976a)

2.1.3 Development of Heated Odor in High Linolenate Oils

As previously indicated, temperature is an important factor affecting the rate of lipid oxidation. During deep-fat frying, the oil is heated in the presence of air to elevated temperatures (180-190°C). Under such conditions, oil is very susceptable to oxidation as well as thermal decomposition. Evans et al (1972) demonstrated the relatively low thermal and oxidative stabilities of high linolenate oils. Niewiadomski (1970) was one of the first to report an objectionable smell when rapeseed oil was heated for frying, and theorized that the problem was due to the oxidation of unsaturated fatty acids. McKeag (1977) identified 138 volatile compounds from heated rapeseed oil and was able to classify 43 of them as responsible for "fishy" and "rancid" odors. Soybean oil has also been shown to develop unpleasant "fishy" odors upon heating (Evans et al, 1972). Meijboom and Stroink (1972) identified the "fishy" off-flavor compound in oils containing linolenic acid as 2-trans,4-cis,7-cis,decatrienal.

Mounts (1979) characterized the room odor of several commercial vegetable oils including hydrogenated and unhydrogenated soybean oil. The oil (300 ml) was heated in an open pan to 180°C in a specially-designed laboratory room. Panelists entered through a neutral buffer area into a well ventilated room and stood five feet from the pan. The odor was judged on a scale of 1 (very bad) to 10 (very good). In addition, odor intensity was rated as being weak (1), moderate (2), or strong (3). The frying odor of the unhydrogenated soybean oil was predominantly characterized as "fishy". Mounts (1979) also examined the effect of heating corn oil, cottonseed oil, peanut oil, safflower oil and hydrogenated

soybean oil which had been heated once, then stored for one week in the dark, and then heated once more. Corn oil received the best initial and second heating scores. All oils improved after the second heating, indicating to the authors that the odor did not depend strongly upon the oxidation of oil.

Dobbs (1975) characterized the unpleasant heated odors of rapeseed oil (C18:3=11.0%), as compared to, hydrogenated soybean oil (C18:3=3.2%), sunflower oil (C18:3=0.5%), corn oil (C18:3=0.4%) and safflower oil (C18:3=0.7%). A trained six to nine member panel evaluated rapeseed oil which had been heated at 190°C for 10 minutes and then sniffed at 50°C, as having a significantly stonger odor than sunflower oil, corn oil and safflower oil under these conditions (Figure 2). The soybean oil was assessed as being intermediate in odor intensity. Although the oils were heated for periods of up to 40 minutes, all oils reached a plateau in odor intensity value after 10 minutes of heating. TBA values, measured after 10 minutes of heating, were shown to have a high positive correlation with odor intensity value. In addition, high erucic acid and low erucic acid rapeseed oil were compared for odor intenstiy, in a separate experiment, in terms of odor intensity with the odor of various chemical solutions. High erucic acid rapeseed oil was significantly lower ($p \leq 0.01$) in fishy odor than low erucic acid rapeseed oil. Whether this was due to a slightly lower C18:3 level of the high erucic rapeseed oil, remains to be determined.

In contrast to soybean, rapeseed and canola oils, sunflower oil developed only minor changes in odor upon heating (Dobbs, 1975). Blumenthal et al (1976) reported that both peanut oil and cottonseed oil

had weaker, more pleasant odor scores than hydrogenated soybean oil upon heating to 185±^{0}C for six hours.

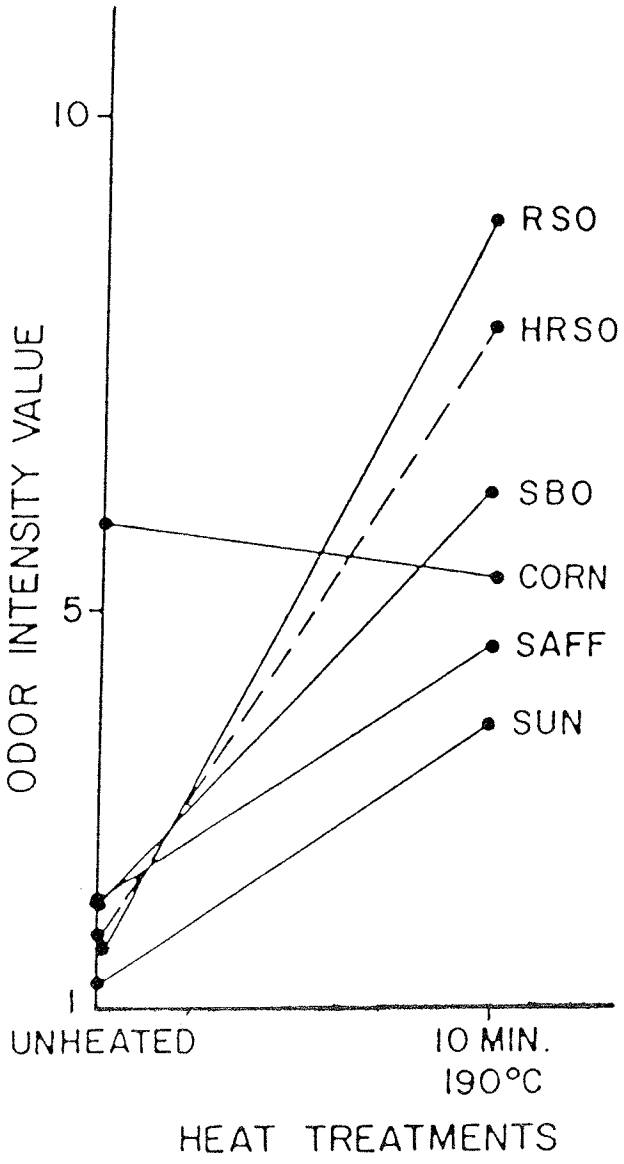

Figure 2: COMPARISON OF ODOR CHANGES AFTER HEATING VARIOUS OILS TO 190°C FOR 10 MINUTES

(Dobbs, 1975)

2.2 POTENTIAL METHODS FOR IMPROVEMENT OF OIL STABILITY

Several approaches have been taken to improve the oxidative stability of high linolenate oils to lipid oxidation. These include selective hydrogenation, addition of antioxidants, exclusion of oxygen, blending with low linolenate oils and plant breeding.

2.2.1 Selective Hydrogenation

The process of hydrogenation involves the addition of hydrogen at the site of the double bond under conditions of high temperature and pressure in the presence of a nickel catalyst. The selectivity of the procedure is improved through incorporation of a copper catalyst, such that, the greater the degree of unsaturation of the fatty acids, the greater the tendency to add on hydrogen. Thus, linolenic acid, with three double bonds, is preferentially hydrogenated leaving linoleic acid essentially unchanged (Cowan et al, 1970). This reduction in C18:3 may have been responsible for the improvement in flavor stability of copper-hydrogenated soybean oil from that of unhydrogenated soybean oil upon storage at 60^{0}C for 8 days; after exposure to fluorescent light for 4 hours; and in room odor after heating to frying temperatures (Cowan et al, 1970, 1973).

The use of a copper catalyst was found to be effective for the hydrogenation of rapeseed oil, as well as soybean oil by Johannson and Lundin (1979). Dobbs (1975) reported that hydrogenation of rapeseed oil tended to limit the development of heated odor and sharply reduce the development of malonaldehyde, as measured by TBA value.

2.2.2 Antioxidants

The role of antioxidants, as a factor affecting the rate of oxidation, has been previously cited (Section 2.1). Most of the commonly used antioxidants, including BHA, BHT, propyl gallate, and TBHQ, are phenolic compounds. These act to prevent autoxidation by donating a hydrogen atom to free radicals. The antioxidant free radical is then further degraded to form quinones, thereby, teminating the chain reaction (deMan, 1980).

The lack of protection exhibited by phenolic antioxidants in lipid photooxidation has also been discussed (Section 2.1.2). Logani et al (1983) suggested that BHT enhanced photooxidation by acting as a photosensitizer through rapid production of quinones. BHA and tocopherol were found to neither inhibit nor enhance the photooxidation of unsaturated fatty acids, possibly due to the relatively slow rates of photooxidation of these antioxidants.

In a study of accelerated oxidation of low and high erucic rapeseed oil, Erkilla et al (1977) stated that BHA decomposed thermally between 110 and 140°C. This statement was later disputed, in a letter to the editor by White (1978), who argued that the loss of BHA from silicone and rapeseed oil was due to the volatility of BHA at the aforementioned temperatures. The effectiveness of BHA and BHT were compared during static heating of palm olein at 180°C for 4 hours a day over two days and during intermittent frying of french fries in palm olein at hourly intervals at the same temperature and over the same period of time (Augustine and Berry, 1983). The researchers found BHA to be effective

in retarding oxidation , in terms of anisidine value and the ratio of C18:2 to C16:0, during static heating. Neither BHA nor BHT proved effective in limiting oxidation during intermittent frying. The loss of antioxidants from the heated oil was attributed to volatization of the antioxidant through evaporation, as well as, thermal decomposition, scavenging reactions and steam distillation (during frying).

2.2.3 Exclusion of Oxygen

Since oxygen is a primary factor in the rate of oxidation, it follows that the process may be limited by its exclusion. Evans et al (1973) found that cottonseed oil or hydrogenated or unhydrogenated soybean oil packaged under nitrogen did not show much, if any, reduction in oxidative stability after 26 weeks of storage at 38°C.

Peers and Swoboda (1982) examined the effect of using argon to exclude oxygen during simulated frying of sunflower oil at 180°C for up to 22.5 hours. Under such conditions, oxidative deterioration, as measured by octanoate increase, was retarded.

2.2.4 Blending with Low Linolenate Oils

Cowan et al (1971) blended 25% and 60% hydrogenated soybean oil with 75% and 40% peanut oil, respectively. Flavor and AOM peroxide value of the blends were evaluated after storage for eight days at 60°C; and after heating to 170°C. Neither blend was significantly different from the peanut oil, in either flavor score or peroxide value, after accelerated storage. After heating to 170°C, the blend containing 25% soybean

oil was not significantly different than the peanut oil, whereas, the 60% soy blend was significantly lower in flavor score and in peroxide value than the peanut oil.

Evans et al (1972) blended soybean oil with cottonseed oil in proportions of 0-100%, in increments of 25%. After heating to 192°C for 20 minutes, the number of "fishy" room odor responses declined as the proportion of cottonseed oil increased. The authors attributed this effect to a lowering of the linolenate content of the mixture.

2.2.5 Plant Breeding

Plant breeding of rapeseed has recently resulted in the development of a cultivar with a linolenate content in the oil of less than 3%. This cultivar is currently being examined for agronomic viability (Steffanson, unpub. data).

2.3 SUMMARY

In summary, it appears that the relatively high C18:3 contents of soybean and rapeseed oils may be reponsible for their poor stabilities to heat and to light, as compared to low linolenate oils. A similar relationship can be hypothesized for canola oil stability. Although hydrogenation may be a feasible method for the reduction of C18:3 and improvement of oxidative stability, it is a fairly expensive procedure. Antioxidants are useful in retarding oxidation, however, consideration must be given to the suitability of the antioxidant(s) to the particular oil and its possible use. The use of gases, such as nitrogen and argon,

to exclude oxygen is a consideration for oil product packaging, but it is not likely a feasible method of protection once the seal has been broken.

A relatively simple procedure involves the blending of canola oil with low linolenate oils to reduce the resultant C18:3 content. This may be especially appropriate for countries, such as those in Latin America, where oil must be imported to extend indigenous oils, such as cottonseed oil.

Chapter III

EXPERIMENTAL METHODS AND MATERIALS

3.1 EXPERIMENTAL DESIGN

Canola oil was blended with sunflower oil or cottonseed oil to yield 9 oils and oil blends as illustrated in the Table 4.

TABLE 4

COMPOSITION OF OIL BLENDS

	PERCENTAGE OF OILS IN BLENDS				
CANOLA OIL	100%	75%	50%	25%	0%
SUNFLOWER OIL	0%	25%	50%	75%	100%
OR					
COTTONSEED OIL	0%	25%	50%	75%	100%

Fatty acid composition, free fatty acid content and iodine value were determined for each blend. These oils/oil blends were then subjected to:

1. Accelerated Storage at 65°C in the dark for 12 days (Modified Schaal Oven Test)

2. Fluorescent Light Exposure (250±25 ft.c.) at 40°C for 4 days.

3. Heating to Frying Temperature (185°C) for 10 minutes.

The effects of the above experiments were evaluated by sensory assessment of odor intensity and acceptability, as well as by chemical measurements of oxidation.

3.2 MATERIALS

Canola oil and sunflower oil samples were provided by CSP Ltd. (Saskatoon) in June,1984. Both oils were bleached and deodorized, and contained 0.04% of the antioxidant mixture G-50C (Griffiths, Toronto, Ont.). This mixture consisted of 10.7% butylated hydroxytoluene, 4.7% butylated hydroxyanisole, 4.0% propyl gallate 4.0% citric acid, and 76.6% carrier oil. Refined cottonseed oil was provided by Canbra Foods (Lethbridge) and then sent to POS Pilot Plant Corporation (Saskatoon) where it was deodorized and 0.04% G-50C was added. This oil was recieved in August, 1984. All of the oil samples were immediately stored at 4°C in a walk-in refrigerator, and held for a maximum of 6 months. Chemicals used were all reagent grade except for toluene, which was spectrophotometric grade.

3.3 SAMPLE PREPARATION

Prior to each experiment, sufficient quantities of each oil blend were prepared. The blending procedure involved accurate measurement of the appropriate oils into a pyrex beaker. The oils were then mechanically stirred on a Corning Hot Plate-Stirrer (PC-351) at 4°C for 10 minutes.

3.4 INITIAL ANALYSIS

3.4.1 Free Fatty Acid Analysis

Free fatty acid content of the parent oils were determined in duplicate by a method adapted from Lowry and Tinsley (1976) by Jeffrey (1982), using spectrophotometric grade toluene and cupric acetate (5% w/v aqueous; pH 6.0). The centrifuge used was an International centrifuge (model CS). Absorbance was read on a Pye Unicam spectrophotometer (SP6-300) and compared to a standard oleic acid curve.

Free Fatty Acid Procedure:

1. Weigh accurately 100-200 mg oil into a 7 ml screw cap tube. Add 5.0 ml toluene; mix on a vortex.
2. Add 1.0 ml cupric acetate reagent; mix on a vortex for 2 min.
3. Centrifuge 15 min. at 3000 RPM.
4. Read absorbance of upper phase at 715 nm against a toluene blank. Color is stable for 30 minutes.

A reagent blank and one standard was run with each set of samples.

Standard : oleic acid 0.3 mg/ml

Stock Standard: 50 mg oleic acid/100 ml toluene

Calculation:

$$\%\text{Free Fatty Acid} = \frac{\text{Abs. sample} - \text{Abs. blank}}{\text{Abs. standard} - \text{Abs. blank}} \times 0.03 \times \frac{5 \text{ ml.}}{\text{wt. sample(mg)}}$$

3.4.2 Peroxide Value

Peroxide value of the parent oils were analyzed in duplicate according to the method developed by Cocks and van Rede (1966).

Reagents:

saturated potassium iodide solution - add 28 g KI to 20 ml water. Stir magnetically for 30 minutes. Some solid must remain. Prepare fresh daily.

1% starch solution -dissolve 0.5 g starch in 50 ml water. Bring to a boil and maintain for 3 min. Prepare fresh daily.

0.002 N sodium thiosulphate solution - dissolve 0.2482 g $Na_2S_2O_3.5H_2O$ in 400 ml water; adjust to 500 ml.

Procedure:

1. Accurately weigh 1.0 g oil into a 250 ml ground glass stoppered Erlenmeyer flask. Add 25 ml glacial acetic acid:chloroform (2:1) to each sample and a blank. Stopper flasks and swirl to dissolve fat.
2. Add 1.0 ml fresh saturated potassium iodide solution, swirl and allow to stand in the dark for exactly one minute.
3. Mix on a vortex for 1 minute if the solution is not homogeneous. Add 35 ml water and 1 ml fresh saturated 1% starch solution.
4. Titrate, keeping flask contents in motion against 0.002 N sodium thiosulfate solution until a clear end-point is reached.

Calculation:

$$\frac{1000 \times (V_1 - V_2) \times N \text{ of } Na_2S_2O_3}{\text{wt. of oil (g)}} = \text{Peroxide Value (meq peroxide/kg fat)}$$

where : V_1 = volume of sample titration (ml)
V_2 = volume of blank titration (ml)

Note:
The value of the blank titration must be less than 2 ml 0.002N $Na_2S_2O_3$.

3.4.3 Iodine Value

Iodine values were deterimined in duplicate for all oils and oil blends according to the AOCS official method (Cd 1-25) (1979) using Wij's iodine solution (Fisher Scientific Co.).

Reagents:

10% Potassium iodide - dissolve 100g KI in 900 ml H_2O; adjust volume to 1L

Standardized sodium thiosulfate solution -

Solution 1 - dissolve 26 g $Na_2S_2O_2.5H_2O$ in 400 ml water

Solution 2 - dissolve 3.8 g borax (Na borate, tetra $Na_2B_4O_7.10\ H_2O$) in 400 ml. water.

Combine Solutions 1 and 2; adjust volume to 1L. Allow to stand in the dark 24 hours. Filter before standardizing.

To standardize $Na_2S_2O_2$:

1) prepare an accurate solution of 0.1 N $K_2Cr_2O_7$

2) prepare a fresh 1% starch solution (0.5 g starch in 50 ml water, bring to a boil and maintain for 3 minutes, cool)

Titration: (done in duplicate)

50 ml water, 20 ml of 10% KI, 10.0 ml of 0.1 N $K_2Cr_2O_7$, and 10 ml of 2 N HCl are placed in a 250 ml glass stoppered flask, shaken, and allowed to stand in the dark 10 minutes. The mixture is then titrated with the sodium thiosulfate solution. When the yellow iodine color has almost disappeared, add 1 ml of starch solution and continue titrating until the deep blue color has changed to background sea green (chromic ions).

Calculation:

$$\text{N of } Na_2S_2O_3 = \frac{\text{g } K_2Cr_2O_7 \times 1000}{\text{ml.}Na_2O_3 \times 49.032}$$

Procedure:

1. Accurately weigh 0.50 g of oil into a 250 ml ground glass stoppered Erlenmeyer flask. Working under a fume hood, add approximately 15 ml carbon tetrachloride to each sample and a blank. Swirl to mix.
2. Add 20.0 ml Wij's iodine solution. Mix.
3. Allow the samples to stand in the dark for 30 minutes.
4. Add 20.0 ml 10% KI and approximately 50 ml water.
5. Titrate against the standardized sodium thiosulphate solution until the yellow color almost disappears. Stopper the flask and shake vigorously. Continue titrating until the sample is colorless.

Calculation:

$$\text{Iodine Value} = \frac{12.69 \times N \times (V_2 - V_1)}{\text{wt. of oil (g)}}$$

where: N = normality of sodium thiosulphate solution
V_2= volume of blank titration (ml)
V_1= volume of sample titration (ml)

3.4.4 Fatty Acid Analysis

Fatty acid composition of the 9 oils and oil blends were performed in duplicate by the method of Metcalfe et al (1966) using the boron trifluoride methylation procedure.

Boron Trifluoride Methylation Procedure:

1. Weigh approximately 150 mg oil into a 20 ml screw top tube
2. Add 2.0 ml 0.5N methanolic NaOH . Seal and place in an 80°C Temp-Blok module heater (#2090) for 5-10 minutes, until fat goes into solution.
3. Cool; add 2.5 ml BF_3-methanol . Reflux 2 minutes.
4. Cool; add 2.0 ml saturated NaCl solution and 1.0 ml hexane.
5. Shake well and allow to separate.
6. Transfer hexane layer to a small vial containing a pinch of anhydrous sodium sulfate.
7. Inject approximately 0.3 ul into GLC.

The fatty acid pattern was determined using a Varian gas liquid chromatogragh (GLC) (series 1700) and Hewlett-Packard recording integrator

(model 3380-S). The initial column temperature of 190°C was programmed to increase 2°C/min. to an upper limit of 220°C. The 8'x1/8" stainless steel column contained 3% SP-2310 and 2% SP-2300 on 100/120 Chromosorb WAW. Helium pressure was set at 60 psi; air at 20 psi and hydrogen at 18 psi.

3.5 EXPERIMENT 1 : ACCELERATED STORAGE AT 65°C

To test the oxidative stability of the oils/oil blends, accelerated storage was carried out for a 12 day period at 65°C. Samples (60 ml) were stored in the dark in a Precision Thelco oven (model 28) in open 80 ml red pyrex glasses. At 0, 2, 4, 6, 8, 10, and 12, day intervals, 240 ml aliquots of each oil were removed. The oil was transfered to glass vials, flushed with nitrogen, and frozen at -20°C for up to 2 months until quality evaluations could be carried out. The canola oil/ sunflower oil blends were stored separately, but under identical conditions, from the canola oil/cottonseed oil blends due to space constraints. A 100% canola oil sample was included in both storage sets. Unfortunately, an unavoidable power outage lasting 6 hours occured on day 11 of the cottonseed oil storage.

In addition to sensory evaluation of total odor intensity and acceptability, oxidation was monitored by peroxide value, thiobarbituric acid value, hydroperoxide value, total carbonyl compounds, and furfural concentration. One replication of storage was conducted. Measurements of all chemical tests were done in duplicate except for total volatile carbonyl compounds and furfural.

3.5.1 Chemical Analyses

3.5.1.1 Peroxide Value

Refer to Subsection 3.4.2.

3.5.1.2 Hydroperoxide Value

Hydroperoxide values were determined in duplicate for all oils and oil blends according to the method developed by Eskin and Frenkel (1976) An International Centrifuge (model CS) was used.

Reagents:

Titanium tetrachloride ($TiCl_4$)-(20% w/w $TiCl_4$ in concentrated HCl)-

- 25 ml $TiCl_4$ + 148 ml HCl
- Place 20-30 ml HCl in bottle. Add $TiCl_4$ slowly by pipet. Gradually add remaining HCl.

Procedure:

1. Weigh 0.05 g oil in a 20 ml screw cap tube. Add 10 ml acetone to each sample and a blank.
2. Add 0.5 ml $TiCl_4$ solution; vortex and let stand 5 minutes.
3. Add 2.0 ml conc. NH_4OH. Centrifuge 3 minutes at 3/4 speed.
4. Pour off supernatant. Add 10 ml 6N H_2SO_4. Mix.
5. Filter through Watman #3 paper.
6. Read absorbance on a Pye-Unicam SP6-300 spectrophotometer at 415 nm against blank.

Calculation:

$$\text{Hydroperoxide Value} = \frac{\text{absorabance at 415 nm}}{\text{wt. of oil (g)}}$$

3.5.1.3 Thiobarbituric Acid Value

Determination of thiobarbituric acid (TBA) values was carried out in duplicate for all oils and oil blends, according to the method of Tarladgis et al (1962) modified by Dobbs (1975).

Reagents:

0.02 M TBA - Dissolve 0.238 g of 2-thiobarbituric acid in a small amount of water and warm to dissolve completely. Dilute to 100 ml making the final adjustment when the solution is at room temperature. Prepare fresh daily.

1. Accurately weigh 0.50 g of oil into a 15 ml screw cap tube
2. Add 5.0 ml hexane to each tube and a blank. Cap tubes and vortex for 15 seconds.
3. Accurately add 5.0 ml of 0.02 M TBA solution to each tube. Cap tightly and shake well.
4. Place tubes in a dark cupboard and leave overnight.
5. Aspirate off all of the top hexane layer. Pipet remaining solution into cuvettes.
6. Read absorbance against blank at 528 nm on a Pye-Unicam SP6-300 spectrophotometer.

Calculation:

$$\text{TBA Value} = \frac{\text{absorabance at 528 nm}}{\text{wt. of oil (g)}}$$

3.5.1.4 Analyses of Total Volatile Carbonyl Compounds and Furfural

All oil samples were analyzed for total carbonyls and furfural according to the method of Przybylski (in press) and were performed through the courtesy of R. Przybylski of the Department of Plant Science, University of Manitoba. Duplicates were not performed.

Procedure:

1. Pipet 25 ml oil into glass tube.
2. Pipet 5 ml $NH_2OH.H$ into trap and attach trap to glass tube.
3. Connect glass tubes to waterbath (85°C) and to nitrogen tank (80ml/min.).
4. Run for 2 hours. Drain traps into a 10 ml graduated cylinder, using compressed air to force solution out. Wash trap with distilled water, diluting reaction solution to 7 ml.
5. Read absorbance of furfural at 274 nm and carbonyls at 212 nm on Beckman (model 25) spetrophotometer.

Calculation:

Standard curves were prepared for carbonyl and furfural concentration using hexanal and furfural, respectively, from which the following equations were derived.

a) Hexanal:

$\mu g/100\ \mu l$ carbonyls = 5.2368 x abs. at 212 nm + 0.30324

b) Furfurals:

for absorbance > 2:

µg/100 µl furfural = 0.2165 x abs. at 274 nm

for absorbance < 2:

µg/100 µl furfural = 1.5562 x abs. at 274 nm - 1.9843

This method has a 80-85% recovery rate in 2 hrs. with the remaining 15-20% coming out after about 6-8 hrs. The above equations take this fact into account.

3.5.2 Sensory Evaluation

Odor evaluation was carried out by a ten member (9 female,1 male) trained panel. Panelists were selected from eighteen volunteers from the department of Foods and Nutrition on the basis of their ability to discriminate differences in odor intensity between stored samples of canola, sunflower and cottonseed oils. The screening procedure consisted of six triangle tests. Ten panelists with scores of 5/6 correct or better were selected.

Successful panelists continued in a series of 5 training sessions in which a 15 cm semi-structured line scale (Figure 3) was used to evaluate odor intensity of canola, sunflower and cottonseed oils stored for various periods of time at 65^{0}C. Panelists were instructed to place a vertical stroke on the line scale to indicate their perceived odor intensity of the oil. A numerical odor intensity value (OIV) was obtained by measurement of the length (cm.) between the bland end-point

and the panelist's mark. Examples of the bland and strong end-points of the scale were provided. These were 0 day 100% sunflower oil and 100% canola oil stored 12 days at 65°C, respectively, which had been selected during preliminary testing with a small experienced panel. Panelists were also required to state whether or not each sample was acceptable, using a forced-choice procedure.

Discussion periods following each sniffing session during training considered the use of the ballot, the strong and bland end-points, as well as individual and panel performance and consistency. "Acceptability" was defined by the panel as "willingness to use the product". Actual panels began when it was determined by Analysis of Variance (ANOVA) procedure that no significant ($p < 0.05$) Judge x Replication interaction existed.

Odor evaluation took place in a standard sensory testing room with samples presented under red light. Fifty-milliliter samples of oil were presented in 80 ml red pyrex glasses covered loosely with aluminum foil lids, and coded with three digit random numbers. The oils were sniffed at 50°C, the recommended temperature for oil odor evaluation (Jackson, 1981). To maintain a constant temperature, the glasses were placed in waterbaths filled with distilled water, on small Corning hot-plates (PC-35) (Figure 4).

All panel sessions were held in the morning from 9:00 to 11:00 a.m. A preliminary investigation of the effect of holding the oils for 3 hours at 50°C showed no change in peroxide value. Panelists were required to sniff two sets of samples, which were placed in separate

booths. The panelists were given a juice break between sets, to minimize odor fatigue. In this way, two oils or oil blends could be tested each day. Each set was comprised of samples of one oil or oil blend for all storage periods (7 samples) plus the bland reference. The strong reference was available to sniff for those panelists who wished to re-familiarize themselves with it, but it was thought by the panel to be too strong to sniff routinely without becoming fatigued. The presentation of each set was randomized for each panelist but all panelists sniffed the oils in the first booth and then in the second. Sensory evaluation of each oil/oil blend was duplicated and the order of each replication was randomized.

NAME: _____

DATE: _____

You have been given a bland reference, labelled 'B'. Sniff the reference, and then sniff the coded samples, in order. Place a vertical stroke on the line scale to indicate their odor intensity. Also indicate whether or not you find the sample acceptable, (ie. 'would you use it?'). Please wait between the samples.

SAMPLE
CODE

_____ bland ——————————————— strong

ACCEPTABLE? YES _____ NO _____

_____ bland ——————————————— strong

ACCEPTABLE? YES _____ NO _____

_____ bland ——————————————— strong

ACCEPTABLE? YES _____ NO _____

_____ bland ——————————————— strong

ACCEPTABLE? YES _____ NO _____

_____ bland ——————————————— strong

ACCEPTABLE? YES _____ NO _____

_____ bland ——————————————— strong

ACCEPTABLE? YES _____ NO _____

_____ bland ——————————————— strong

ACCEPTABLE? YES _____ NO _____

Figure 3: BALLOT FOR ODOR EVALUATION.

NOTICE/AVIS

PAGE(S) 40 IS/~~ARE~~ EST/~~SONT~~ colour photo

PLEASE WRITE TO THE AUTHOR FOR INFORMATION, OR CONSULT THE ARCHIVAL COPY HELD IN THE DEPARTMENT OF ARCHIVES AND SPECIAL COLLECTIONS, ELIZABETH DAFOE LIBRARY, UNIVERSITY OF MANITOBA, WINNIPEG, MANITOBA, CANADA, R3T 2N2.

VEUILLEZ ECRIRE A L'AUTEUR POUR LES RENSEIGNEMENTS OU VEUILLEZ CONSULTER L'EXEMPLAIRE DONT POSSEDE LE DEPARTEMENT DES ARCHIVES ET DES COLLECTIONS SPECIALES, BIBLIOTHEQUE ELIZABETH DAFOE, UNIVERSITE DU MANITOBA, WINNIPEG, MANITOBA, CANADA, R3T 2N2.

Figure 4: PRESENTATION OF ONE SET OF SAMPLES FOR ODOR EVALUATION.

3.6 EXPERIMENT 2 : FLUORESCENT LIGHT EXPOSURE AT 40°C

Fifty milliliter aliquots of each oil/oil blend were placed in disposable petrie dishes (8.6 cm x 1.2 cm) and exposed to fluorescent light (250±25 ft.c.) for up to 4 days at 40°C, in a specially designed light cabinet. The light intensity, as measured with a Holophane Photometer (model DPMT-1CC SER), was found to vary throughout the cabinet making it necessary to establish regions of low (225-237 ft.c.); medium-low (238-250 ft.c.); medium-high (251-262 ft.c.); and high (263-275 ft.c.) intensity. Two replications of storage were performed. Table 5 illustrates how the samples were placed with respect to light intensity and days of storage. Within each region, samples were randomized.

At 0, 1, 2, 3, and 4 day intervals, 150 ml samples were transfered to glass vials, flushed with nitrogen for 15 seconds and frozen at -20°C for up to 2 months until quality assessment could be conducted. Rate of oxidation was determined by measurement of peroxide value, thiobarbituric acid value, hydroperoxide value, volatile total carbonyl compounds, and furfural. Sensory evaluation of total odor intensity and acceptability was also performed.

TABLE 5

ARRANGEMENT OF OIL SAMPLES WITH RESPECT TO LIGHT INTENSITY AND DAYS OF STORAGE.

	LIGHT INTENSITY (250 ± 25 ft.c.)			
REPLICATION	225-237 ft.c.	238-250 ft.c.	251-262 ft.c.	263-275 ft.c.
1	1 DAY	2 DAYS	3 DAYS	4 DAYS
2	4 DAYS	3 DAYS	2 DAYS	1 DAY

3.6.1 Chemical Analyses

3.6.1.1 Peroxide Value

Refer to section 3.4.2

3.6.1.2 Hydroperoxide Value

Refer to section 3.5.1.2

3.6.1.3 Thiobarbituric Acid Value

Refer to section 3.5.1.3

3.6.1.4 Analyses of Total Volatile Carbonyl Compounds and Furfural

Refer to section 3.5.1.4

3.6.2 Sensory Evaluation

Refer to section 3.5.2. Five samples plus the bland reference were evaluated per set. The strong endpoint was originally going to be canola oil stored for 4 days in the light. During preliminary training, however, it was discovered that the 4 day cottonseed oil sample was much stronger than the strong reference. Based on panel discussion, a strong reference (canola oil stored for 4 days under fluorescent light at 40^{0}C) was placed on the line at 10.6 cm.

3.7 EXPERIMENT 3 : HEATING TO FRYING TEMPERATURE

One hundred and fifty milliliter samples of each of the oils and oil blends were heated separately in open 250 ml pyrex beakers on a Corning Hot Plate-Stirrer (model PC-351) to 185°C±5°C, the commonly recommended temperature for deep fat frying. This temperature was maintained for exactly 10 minutes using a magnetic stirrer to ensure constant temperature throughout the oil. In addition, a 100% Canola oil sample was heated under nitrogen . After heating, the beakers were covered with a watch glass and allowed to cool. Upon cooling, the oil was transfered to glass vials, flushed with nitrogen for 15 seconds, capped and stored at -20°C for up to 2 weeks until chemical and sensory evaluation could be carried out.

3.7.1 Chemical Analyses

3.7.1.1 Peroxide Value

Refer to section 3.4.2

3.7.1.2 Hydroperoxide Value

Refer to section 3.5.1.2

3.7.1.3 Thiobarbituric Acid Value

Refer to section 3.5.1.3

3.7.1.4 Anaylses of Total Carbonyls Volatile Compounds and Furfural

Refer to section 3.5.1.4

3.7.2 Sensory Evaluation

Refer to section 3.5.2. The task involved evaluating the odor of all heated oils and oil blends in addition to unheated samples of the three parent oils and a bland reference. A reference for the strong endpoint (canola oil heated for 10 minutes at 185°C) was used for training and was also made available during odor testing. The group was divided into two sets with 7 oil samples, plus the bland reference, in each set.

3.8 STATISTICAL METHODS

The 1982 edition of the Statistical Analysis System (SAS) was used to analyze the data from Experiments 1, 2, and 3.

3.8.1 Experiment 1 and 2

The strength of the relationships between the methods used to evaluate rate of oxidation were assessed by determination of correlation coefficients for the chemical tests and sensory evaluation. Since high positive r values were obtained for all chemical tests, regression analysis was performed using the data from one method only. The method selected was the TBA test, since it measured secondary oxidation products, which are reported to be responsible for the development of off-odor (Gunstone, 1984). Bartlett's Test (Neter and Wasserman, 1974) was used to test the equality of variance for the blends (Appendix A) before

the equality of slopes could be assessed using a t-test (Appendix B). Correlation coefficients were also determined for each panelists' odor intensity values, over the two replications of sensory evaluation, to assess individual consistency. Analysis of Variance (ANOVA) was performed to identify the sources of variation in odor intensity for the sunflower and the cottonseed oil blends. Significant differences among blends were determined by Tukey's Studentized Range Test. A Chi square test (Fleiss, 1981) was used to compare the final proportions of blend acceptability (Appendix C).

3.8.2 Experiment 3

The chemical tests could not be subjected to statistical analysis due to the fact that duplications were not performed. The analysis of sensory data is as per Experiments 1 and 2.

Chapter IV

RESULTS

After ensuring that the oils were of good quality and determination of their fatty acid compositions, canola oil blended with sunflower oil and with cottonseed oil were examined for oxidative stability to (1) accelerated storage at 65°C for 12 days; (2) fluorescent light exposure at 40°C for 4 days; and (3) heating to frying temperature (185°C) for 10 minutes. Peroxide value, hydroperoxide value, and TBA value were determined for the first two experiments. Total volatile carbonyl compounds and furfural accumulation were measured for all three experiments. Sensory evaluation, of odor intensity and acceptability, was conducted for all three experiments, as well.

4.1 INITIAL ANALYSIS

4.1.1 Initial Oil Quality

Examination of the parent oils (Table 6) showed them to be of good quality as exibited by the absence of free fatty acids and low peroxide values (< 1.0) (Henning, 1976).

4.1.2 Iodine Value

Iodine values of the oils and oil blends are presented in Table 7. Those of the parent oils are within reported ranges (Sonntag, 1982b). The greater degree of saturation of the cottonseed oil blends is reflected by their lower iodine values.

4.1.3 Fatty Acid Analysis

The fatty acid composition of the oils and oil blends used in this study is presented in Table 7. Canola oil had the highest linolenic acid (C18:3) content (6.4%), which decreased following blending with cottonseed or with sunflower oil. This decrease in linolenic acid was accompanied by an increase in palmitic (C16:0), stearic (C18:0), oleic (C18:1) and linoleic (C18:2) acids. Increasing levels of sunflower oil in the blends was also accompanied by an increase in behenic acid (C22:0).

Cottonseed oil had a much higher content of saturated (C16:0 +) fatty acids, (23.3%) as compared to sunflower oil (13.5%) or canola oil (8.0%).

TABLE 6

INITIAL OIL QUALITY

OIL	FREE FATTY ACID VALUE[1] (as oleic)	PEROXIDE VALUE[1] (meq/kg)
SUNFLOWER OIL	0.00%	0.5
CANOLA OIL	0.00%	1.0
COTTONSEED OIL	0.00%	0.4

[1] Values presented are means of duplicate readings.

TABLE 7

FATTY ACID COMPOSITION OF CANOLA/SUNFLOWER AND CANOLA/COTTONSEED OIL BLENDS

OIL BLEND	IODINE VALUE[1]	% METHYL ESTERS[1]								
		16:0	18:0	18:1	18:2	18:3	20:0	20:1	22:0	22:1
100% SUNFLOWER OIL	98.81	7.4	4.6	19.1	66.4	0.4	0.6	0.5	0.9	----
75% SUNFLOWER 25% CANOLA OIL	98.81	6.6	3.9	27.9	56.8	1.9	0.7	0.7	0.7	0.2
50% SUNFLOWER 50% CANOLA OIL	99.07	5.7	3.2	39.9	43.5	4.1	0.8	1.3	0.4	0.5
25% SUNFLOWER 75% CANOLA OIL	99.20	5.4	2.8	46.3	36.3	5.2	0.9	1.5	0.3	0.5
100% CANOLA OIL	98.81	4.5	2.2	55.6	26.3	6.4	1.0	1.8	0.3	0.5
25% COTTONSEED 75% CANOLA OIL	89.70	8.5	2.3	47.2	32.0	5.7	0.9	1.5	0.3	0.5
50% COTTONSEED 50% CANOLA OIL	89.70	12.0	2.3	40.0	38.0	4.2	0.7	1.0	0.3	0.4
75% COTTONSEED 25% CANOLA OIL	89.70	15.8	2.6	32.3	41.9	3.4	0.7	0.9	0.2	0.5
100% COTTONSEED OIL	89.70	19.8	2.7	24.4	47.4	1.9	0.6	0.6	0.2	0.6

[1] Values presented are means of duplicate readings.

4.2 EXPERIMENT 1 : ACCELERATED STORAGE AT 65°C

4.2.1 Chemical Analyses

4.2.1.1 Peroxide Value

All oils and oil blends increased in peroxide value during twelve days storage at 65°C as illustrated in Figures 5 and 6. The rate of peroxide development of the cottonseed blends did not appear to be affected by the six hour power outage between days 10 and 12, as evident from the similar values attained for each of the 100% canola oil samples. Of the three parent oils, sunflower oil accumulated the greatest level of peroxides by the 12th day of storage, more than double that of canola oil. Cottonseed oil, by comparison, had a final peroxide value less than half that of canola oil.

Generally, as the proportion of sunflower oil to canola oil increased, an increase in the final peroxide value was observed, with the blend containing 25% sunflower oil being similar to the 100% canola oil. In contrast to sunflower oil, the addition of cottonseed oil to canola oil served to retard the rate of peroxide development over the twelve day storage period.

4.2.1.2 Hydroperoxide Value

Figures 7 and 8 illustrate the development of hydroperoxides in the oils and oil blends over the storage period. The power failure appeared to have affected the rate of hydroperoxide formation by the cottonseed oil blends as illustrated by the lower final value attained by the canola oil stored with that set, as compared to the one stored with the

sunflower oil set. In addition, all oils and blends in Figure 8 experienced a decline in hydroperoxide value between days 10 and 12.

After 10 days storage, sunflower oil had the greatest accumulation of hydroperoxides, of the three parent oils, followed by cottonseed oil. Canola oil had the lowest hydroperoxide value. By blending increasing amounts of canola oil with sunflower oil, the rate of hydroperoxide development was depressed. This trend was not apparent for the corresponding cottonseed oil blends. At ten days, the hydroperoxide values for the 25% and the 75% cottonseed oil blends lie between that for 100% canola oil and 100% cottonseed oil. The 50% cottonseed/canola oil blend had a higher mean hydroperoxide value that that of the 100% cottonseed oil.

4.2.1.3 Thiobarbituric Acid Value

The development of secondary oxidation products, as measured by thiobarbituric acid (TBA) value, did not appear to be affected by the aforementioned power outage. All oils and oil blends increased in TBA value over the twelve day period as shown in Figures 9 and 10. Of the three parent oils, sunflower oil exhibited the greatest increase especially after day 8. Canola oil had a final TBA value approximately double that of cottonseed oil.

The final TBA value generally increased as the amount of sunflower oil in the blends was increased. Both the 75% canola oil blend and the 50% canola oil blend, however, had TBA values below that of 100% canola oil. In contrast to the sunflower oil, the addition of increasing

amounts of cottonseed oil to canola oil improved the oxidative stability of canola oil as monitored by TBA value.

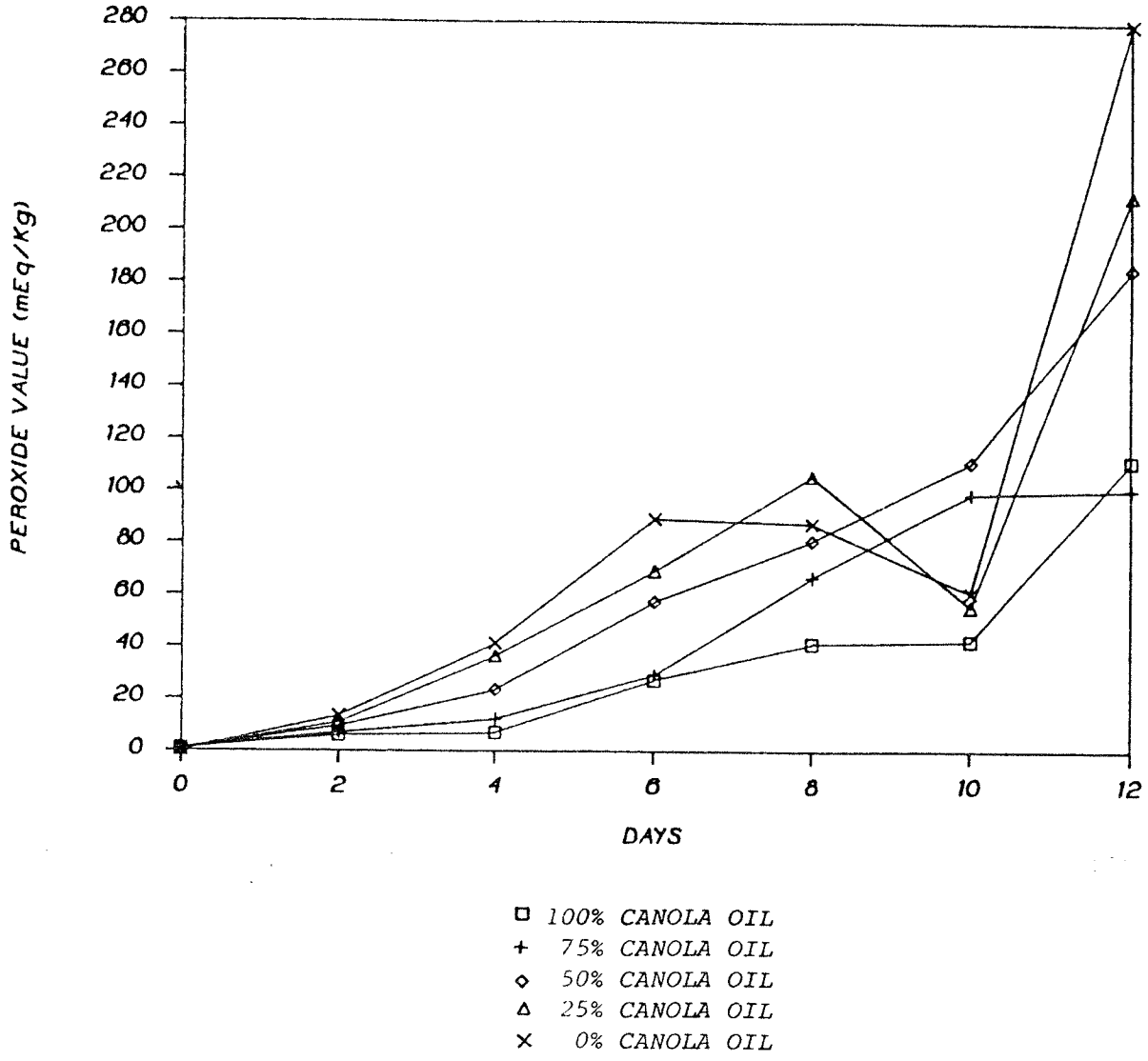

Figure 5: CHANGES IN PEROXIDE VALUE OF CANOLA/SUNFLOWER OIL BLENDS DURING STORAGE AT 65°C.

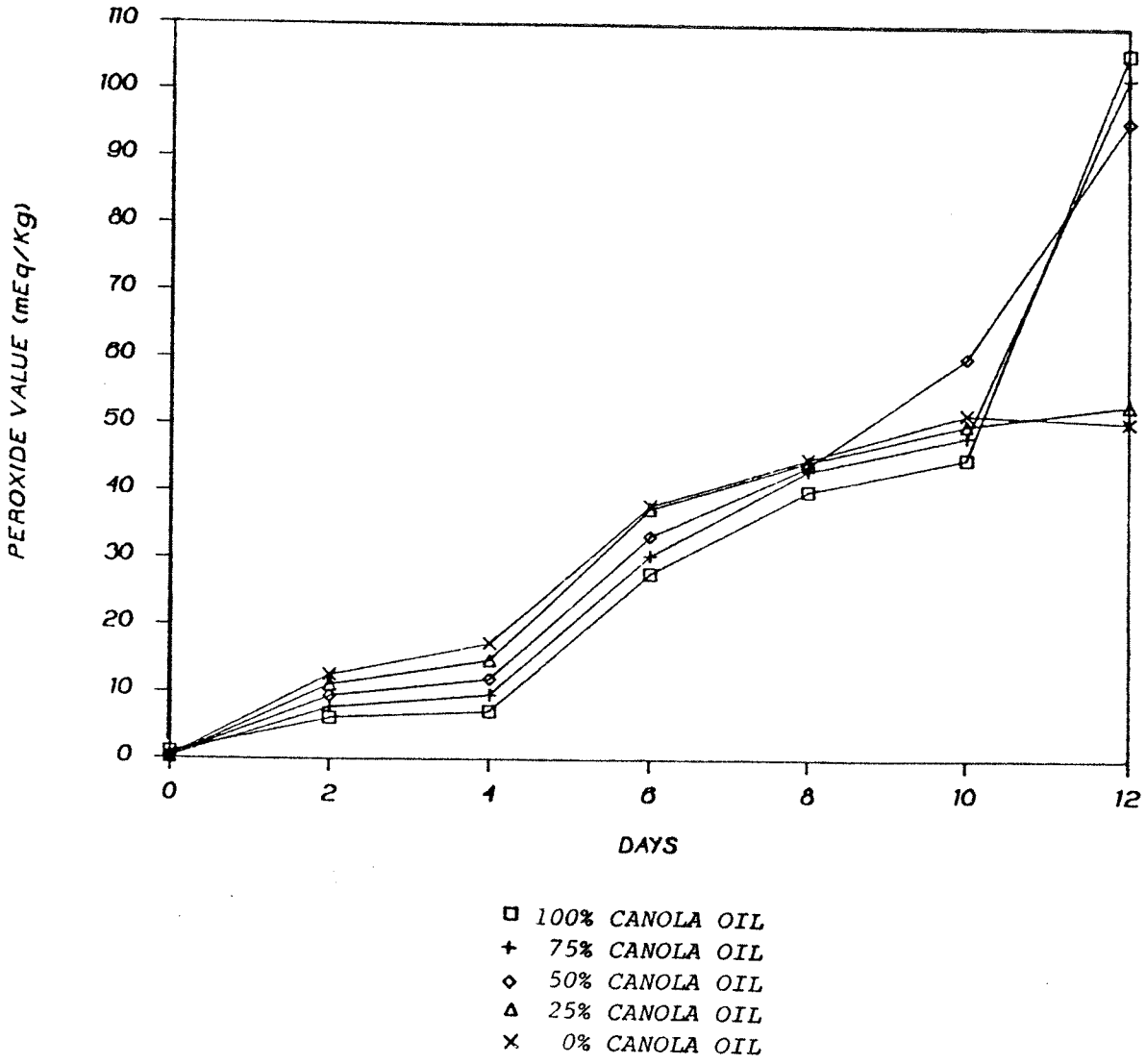

Figure 6: CHANGES IN PEROXIDE VALUE OF CANOLA/COTTONSEED OIL BLENDS DURING STORAGE AT 65°C.

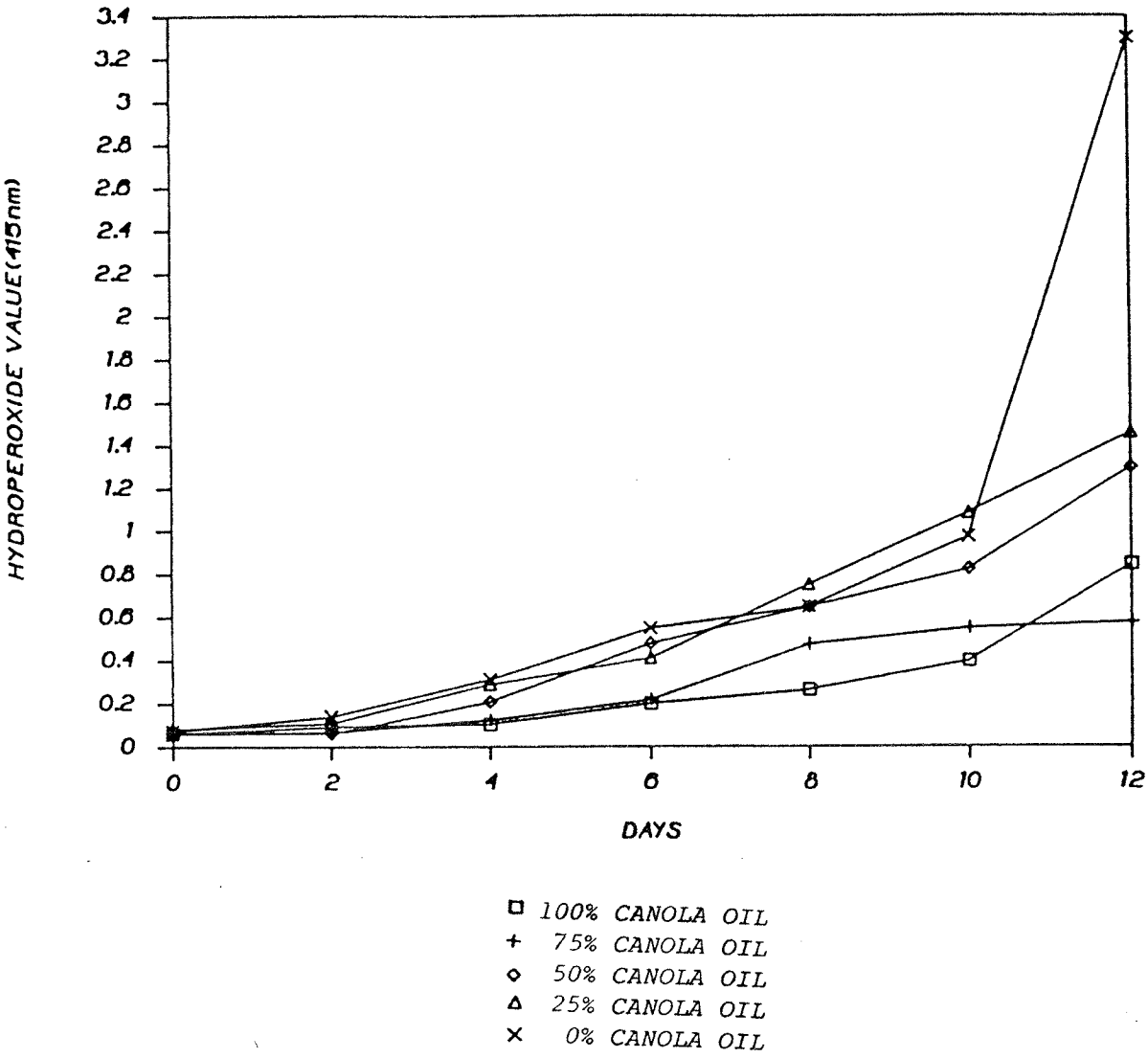

Figure 7: CHANGES IN HYDROPEROXIDE VALUE OF CANOLA/SUNFLOWER OIL BLENDS DURING STORAGE AT 65°C.

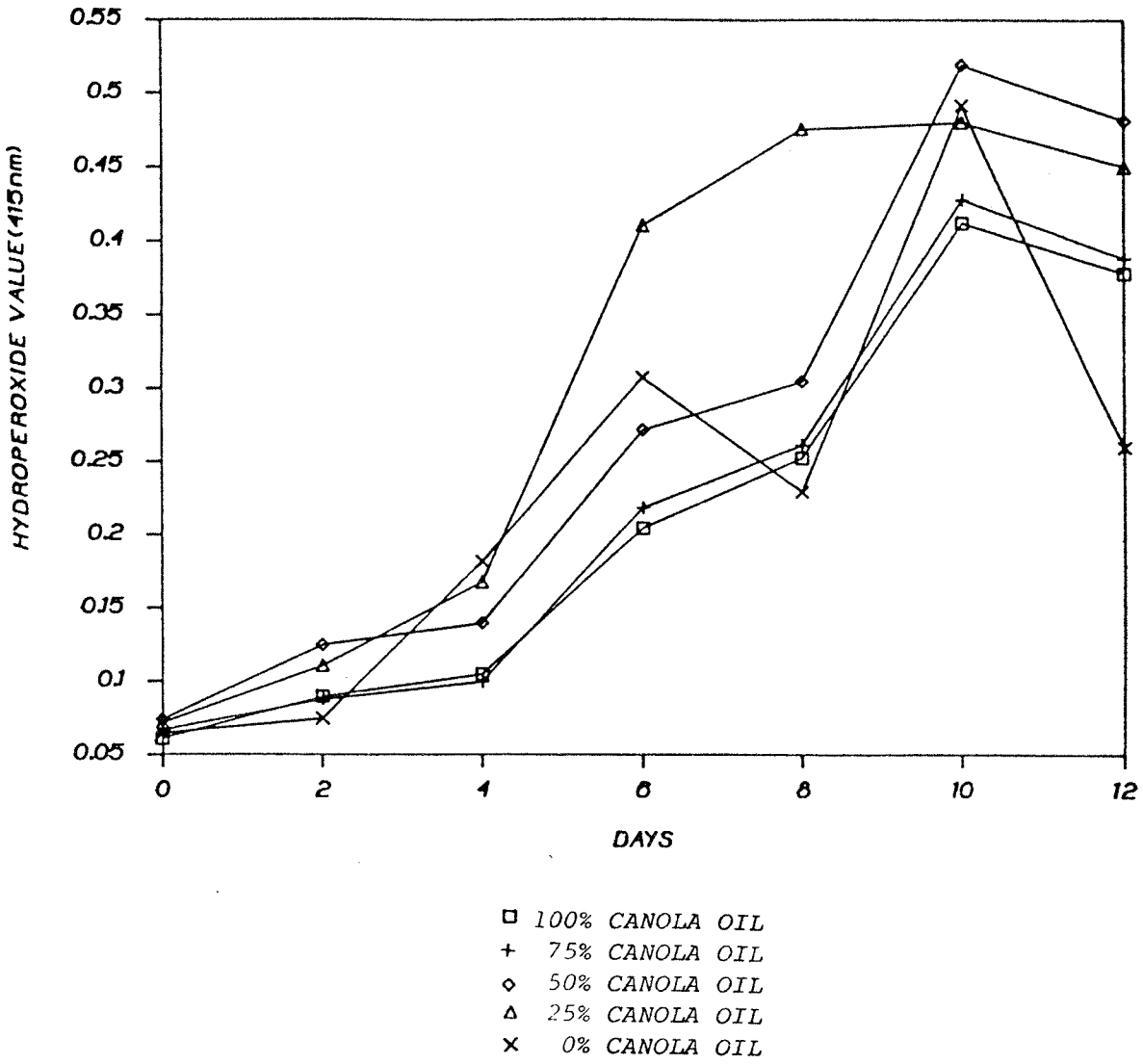

Figure 8: CHANGES IN HYDROPEROXIDE VALUE OF CANOLA/COTTONSEED OIL BLENDS DURING STORAGE AT 65°C.

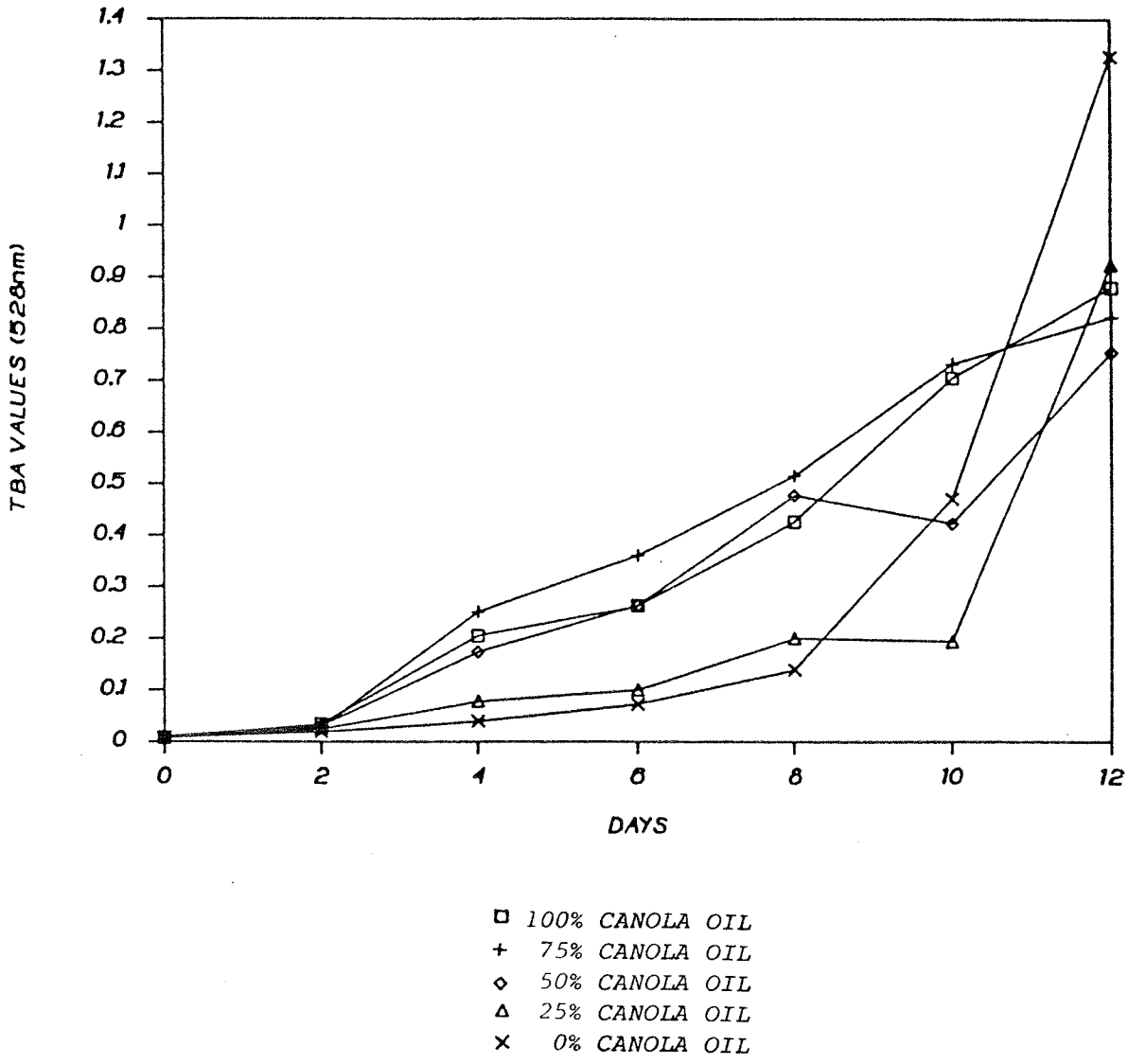

Figure 9: CHANGES IN TBA VALUE OF CANOLA/SUNFLOWER OIL BLENDS DURING STORAGE AT 65°C.

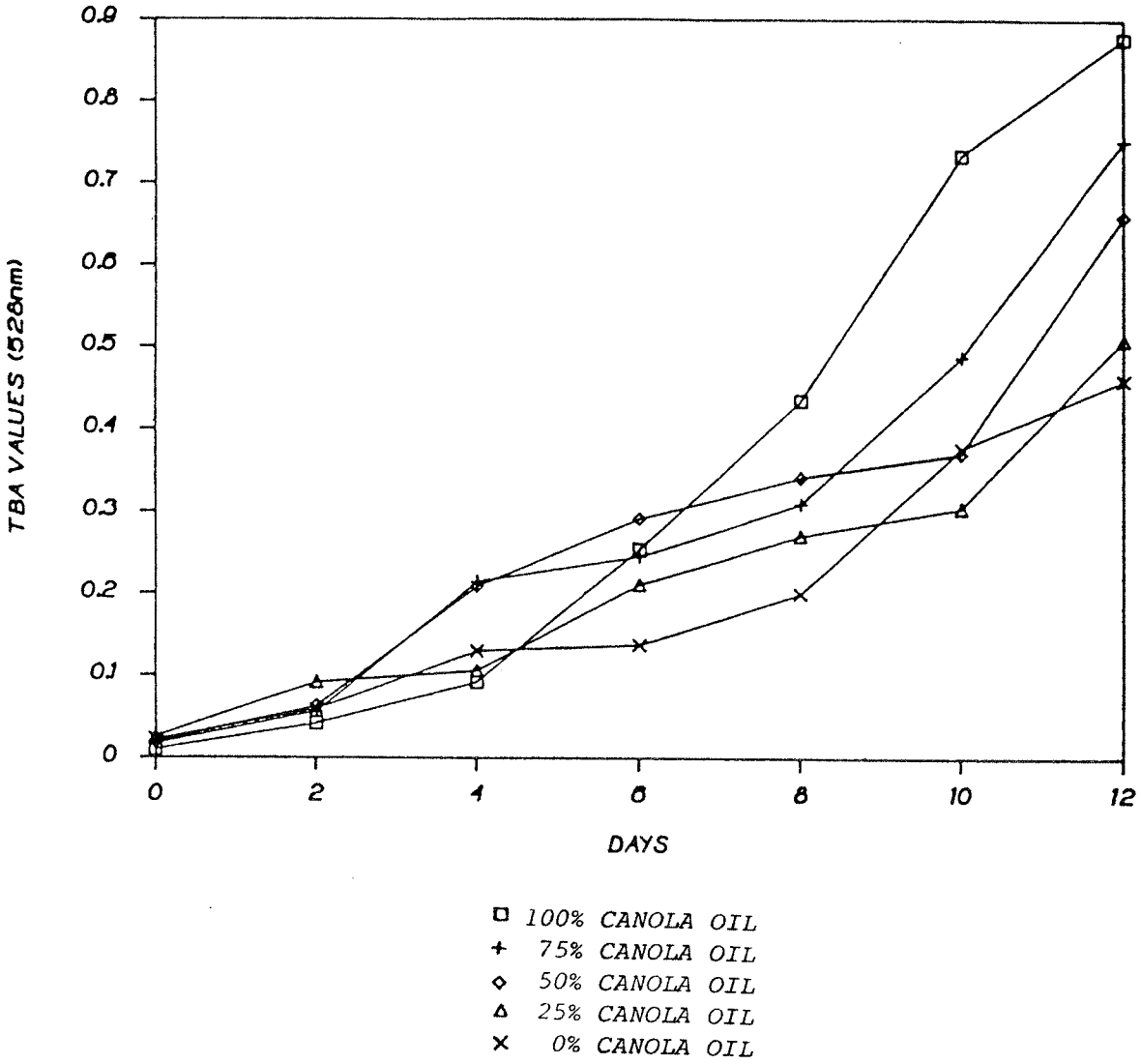

Figure 10: CHANGES IN TBA VALUE OF CANOLA/COTTONSEED OIL BLENDS DURING STORAGE AT 65°C.

4.2.1.4 Total Volatile Carbonyl Compounds

Figures 11 and 12 show that an increase in concentration of total volatile carbonyl compounds occured over time for all oils and oil blends. It should be noted that each value represents a single reading as no duplicates were run. The 100% canola oil had the largest final accumulation of carbonyls, followed by 100% sunflower oil, and then cottonseed oil. With the addition of sunflower oil, the final carbonyl concentration was reduced as the amount of canola oil was decreased. A similar, but more pronounced effect was seen with the addition of cottonseed oil.

4.2.1.5 Furfural

An increase in the concentration of furfural is evident for all oils and oil blends after 12 days of storage at 65°C, as illustrated in Figures 13 and 14. The canola oil had the highest final concentration of the three parent oils, followed by sunflower oil and then by cottonseed oil. A decrease in furfural concentration occured as the level of sunflower oil decreased from 75% to 25%. The addition of cottonseed oil served to reduce the final concentration of furfural.

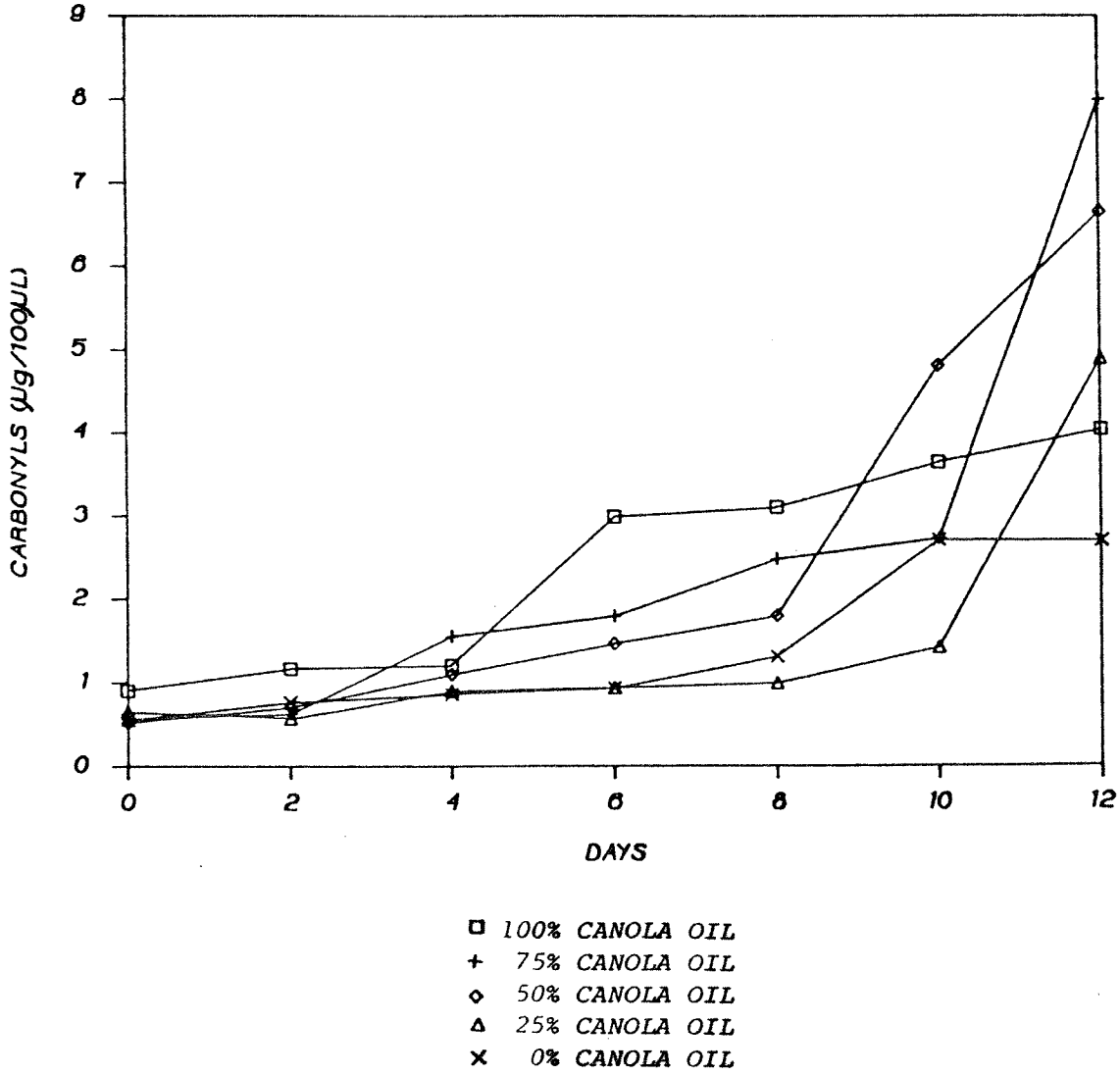

Figure 11: CHANGES IN TOTAL CARBONYL COMPOUNDS OF CANOLA/SUNFLOWER OIL BLENDS DURING STORAGE AT 65°C.

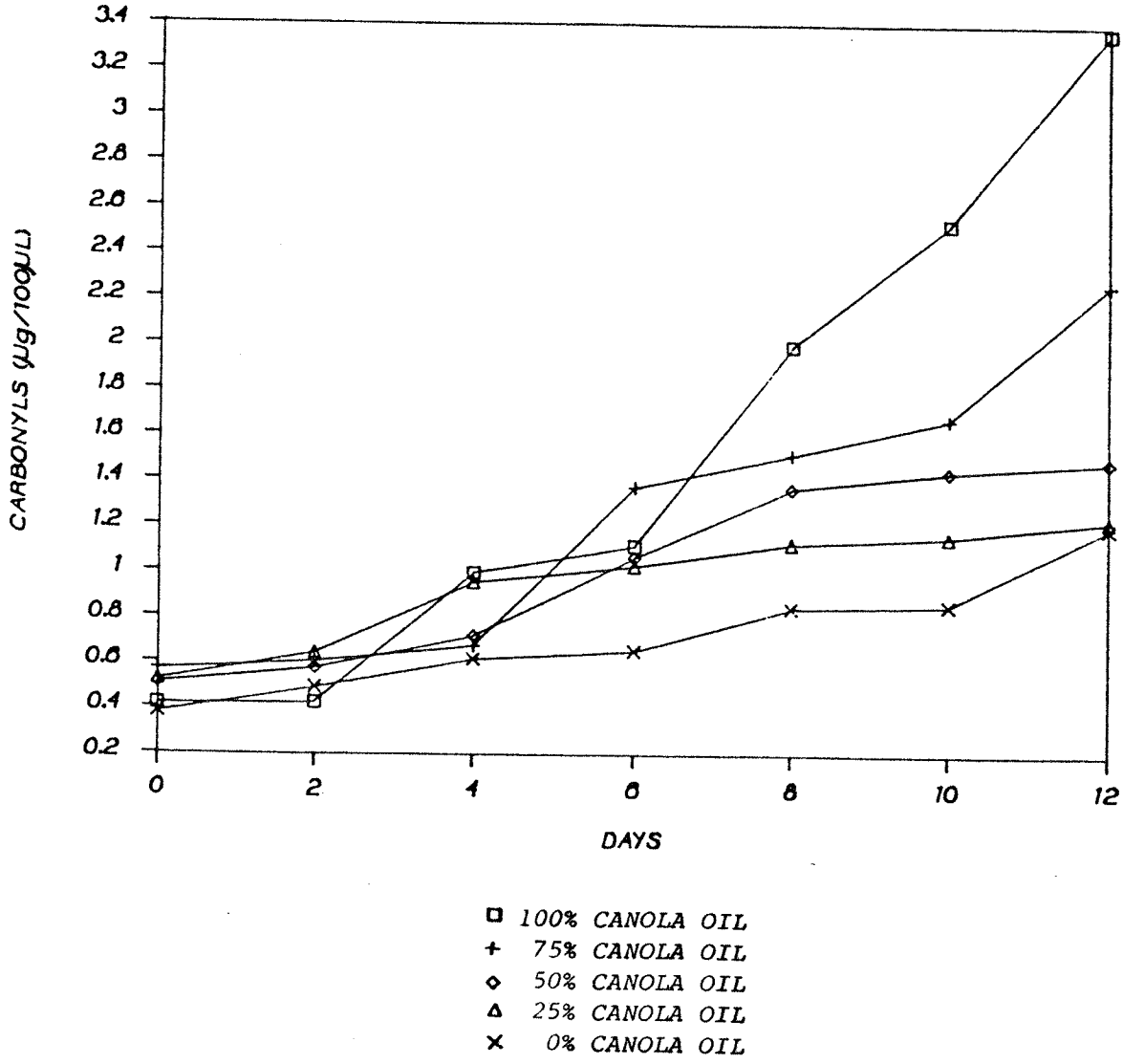

Figure 12: CHANGES IN TOTAL CARBONYL COMPOUNDS OF CANOLA/COTTONSEED OIL BLENDS DURING STORAGE AT 65°C.

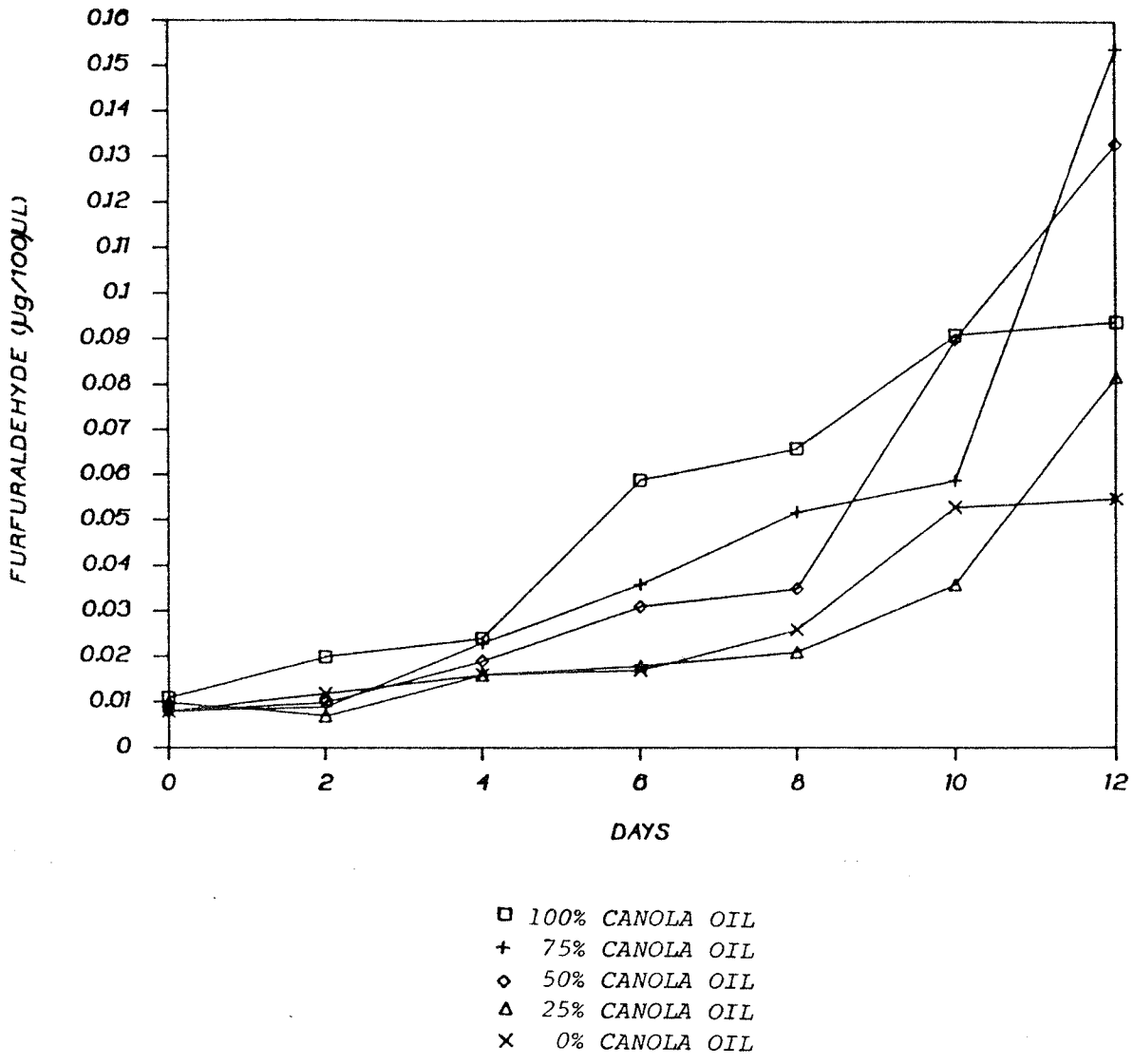

Figure 13: CHANGES IN FURFURAL CONCENTRATION OF CANOLA/SUNFLOWER OIL BLENDS DURING STORAGE AT 65°C.

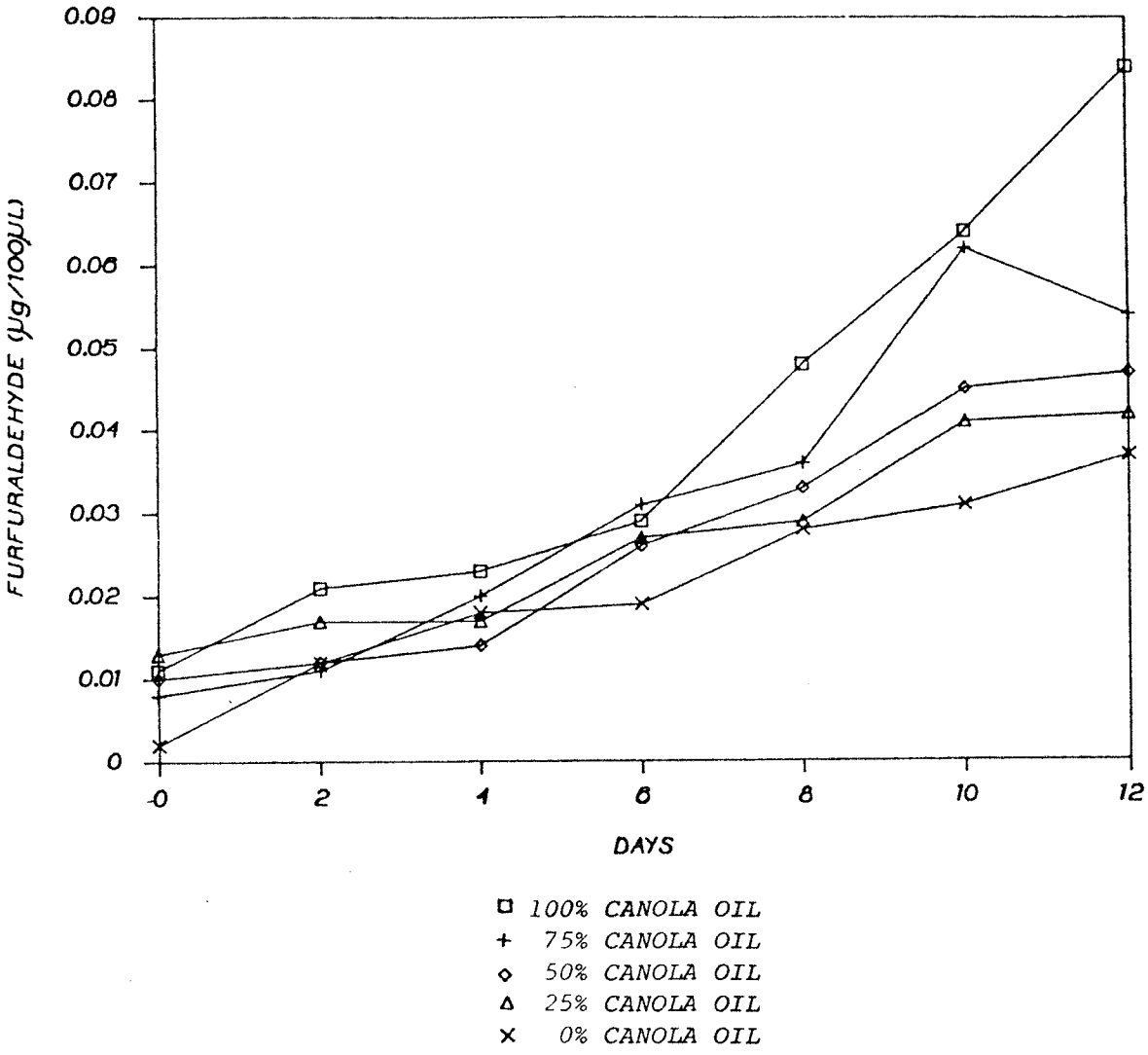

Figure 14: CHANGES IN FURFURAL CONCENTRATION OF CANOLA/COTTONSEED OIL BLENDS DURING STORAGE AT 65°C.

4.2.2 Correlation of Chemical Methods

The mean correlation coefficients for the chemical measurements of the canola/sunflower oil blends and canola/cottonseed oil blends, over the 12 days storage period at 65°C, are presented in Tables 8 and 9, respectively. A high degree of correlation was evident for all measurements, with $r \geq 0.83$., indicating that changes in each chemical indices appear to follow the same direction.

TABLE 8

MEAN CORRELATION COEFFICIENTS FOR CHEMICAL MEASUREMENTS OF RANCIDITY OF CANOLA/COTTONSEED OIL BLENDS DURING ACCELERATED STORAGE AT 65°C.

	PV	HV	TBA	[C]	[F]
PEROXIDE VALUE (PV)	1.00	0.96	0.95	0.84	0.86
HYDROPEROXIDE (HV) VALUE	0.96	1.00	0.95	0.83	0.87
THIOBARBITURIC (TBA) VALUE	0.95	0.95	1.00	0.89	0.91
TOTAL CARBONYL ([C]) COMPOUNDS	0.84	0.87	0.91	1.00	0.99
FURFURAL ([F]) CONCENTRATION	0.86	0.87	0.91	0.99	1.00

TABLE 9

MEAN CORRELATION COFFICIENTS FOR CHEMICAL MEASUREMENTS OF RANCIDITY OF CANOLA/COTTONSEED OIL BLENDS DURING ACCELERATED STORAGE AT 65°C.

	PV	HV	TBA	[C]	[F]
PEROXIDE VALUE (PV)	1.00	0.89	0.93	0.93	0.93
HYDROPEROXIDE (HV) VALUE	0.89	1.00	0.86	0.87	0.91
THIOBARBITURIC (TBA) VALUE	0.93	0.86	1.00	0.93	0.94
TOTAL CARBONYL ([C]) COMPOUNDS	0.93	0.87	0.93	1.00	0.94
FURFURAL ([F]) CONCENTRATION	0.93	0.91	0.94	0.94	1.00

4.2.3 Regression Analysis

Regression analysis performed on the TBA values, which developed over over 12 days storage at 65°C, showed that most of the blends fit a linear model (Table 10). A quadratic model, however, provided a much better fit for the 75% and 100% sunflower oils. A calculation of Bartlett's Test for Homogeniety of Variances (Appendix A) did not result in rejection of the null hypothesis with $p = 0.10$. The mean square error terms for all oils were then pooled and the slopes of the blends fitting a linear model were compared in their natural order of decreasing canola oil.

100% canola oil oxidized at a significantly greater rate ($p \leq 0.05$), as measured by TBA value, than the 50% sunflower oil blend (Table 11). There was no significant difference ($\alpha = 0.05$) between 100% canola oil and 25% sunflower oil. Canola oil showed significantly more rapid production of malonaldehyde ($p \leq 0.05$) than did the blend containing 25% cottonseed oil (Table 15). No significant difference occurred between the 25% and 50% cottonseed oil blends or between the 75% cottonseed oil blend and 100% cottonseed oil ($\alpha = 0.05$) The 50% cottonseed oil blend, however, oxidized at a significantly faster rate ($p = 0.036$) than did the 75% cottonseed oil blend.

TABLE 10

COEFFICIENTS OF DETERMINATION (r^2) for REGRESSION ANALYSIS OF TBA VALUES FOR CANOLA/SUNFLOWER AND CANOLA/COTTONSEED OIL BLENDS DURING ACCELERATED STORAGE AT 65°C.

	BLEND	MODEL LINEAR (r^2)		MODEL QUADRADIC (r^2)
SUNFLOWER OIL BLENDS	100% CANOLA OIL	0.95		0.99
	75% CANOLA : 25% SUNFLOWER OIL	0.98		0.98
	50% CANOLA : 50% SUNFLOWER OIL	0.92		0.94
	25% CANOLA : 75% SUNFLOWER OIL	0.60	------->	0.83
	100% SUNFLOWER OIL	0.62	------->	0.91
COTTONSEED OIL BLENDS	100% CANOLA OIL	0.93		0.99
	75% CANOLA : 25% COTTONSEED OIL	0.92		0.97
	50% CANOLA : 50% COTTONSEED OIL	0.92		0.94
	25% CANOLA : 75% COTTONSEED OIL	0.93		0.96
	100% COTTONSEED OIL	0.92		0.97

TABLE 11

A COMPARISON OF REGRESSION SLOPES OF TBA VALUES FOR CANOLA/SUNFLOWER AND CANOLA/COTTONSEED OIL BLENDS DURING ACCELERATED STORAGE AT 65°C.

BLEND	MEAN SQUARE ERROR (MSE)	SLOPE	VALUE OF t STATISTIC[1]	p VALUE
A. 100% CANOLA : 0% SUNFLOWER OIL	0.005664	0.074350		
			} 0.178	0.43
B. 75% CANOLA : 25% SUNFLOWER OIL	0.001949524	0.073643		
			} 2.283	0.012
C. 50% CANOLA : 50% SUNFLOWER OIL	0.005554565	0.059446		
F. 100% CANOLA : 0% COTTONSEED OIL	0.008274637	0.077339		
			} 3.334	0.0006
G. 75% CANOLA : 25% COTTONSEED OIL	0.005322762	0.056607		
			} 1.413	0.08
H. 50% CANOLA : 50% COTTONSEED OIL	0.003650381	0.047821		
			} 1.815	0.036
I. 25% CANOLA : 75% COTTONSEED OIL	0.001966548	0.036536		
			} 0.066	0.47
J. 0% CANOLA : 100% COTTONSEED OIL	0.002267994	0.036125		

Thus, A B C and F G H I J with $p \leq 0.05$

[1]See Appendix B for t Statistic for Comparison of Slopes

4.2.4 Sensory Evaluation

4.2.4.1 Judge Consistency

Correlation coefficients for individual judges performance over the two replications are presented in Table 12. All judges were included in further data analysis based on the observation that all were within the range r = 0.59 ± 0.16.

TABLE 12

CONSISTENCY OF JUDGES' MEASUREMENTS OF ODOR INTENSITY FOR EXPERIMENT 1

JUDGE	r (REP 1 VS REP 2)
1	0.55
2	0.75
3	0.61
4	0.65
5	0.60
6	0.67
7	0.43
8	0.44
9	0.43
10	0.53

4.2.4.2 Total Odor Intensity Value

Mean total odor intensity value (OIV) was plotted against number of days storage as shown in Figures 15 and 16. A larger value for OIV indicates greater mean odor intensity.

The canola oil attained the strongest final OIV of the parent oils, followed by sunflower oil and then cottonseed oil. As the proportion of canola oil to sunflower oil was decreased, a general decrease in the mean total OIV was observed, although, the 50% sunflower oil:50% canola oil blend had the lowest final OIV of this set. As the proportion of cottonseed oil to canola oil increased, an improvement in the final odor intensity was observed. It is interesting to note that initial odor intensity values increased with increasing amounts of cottonseed oil.

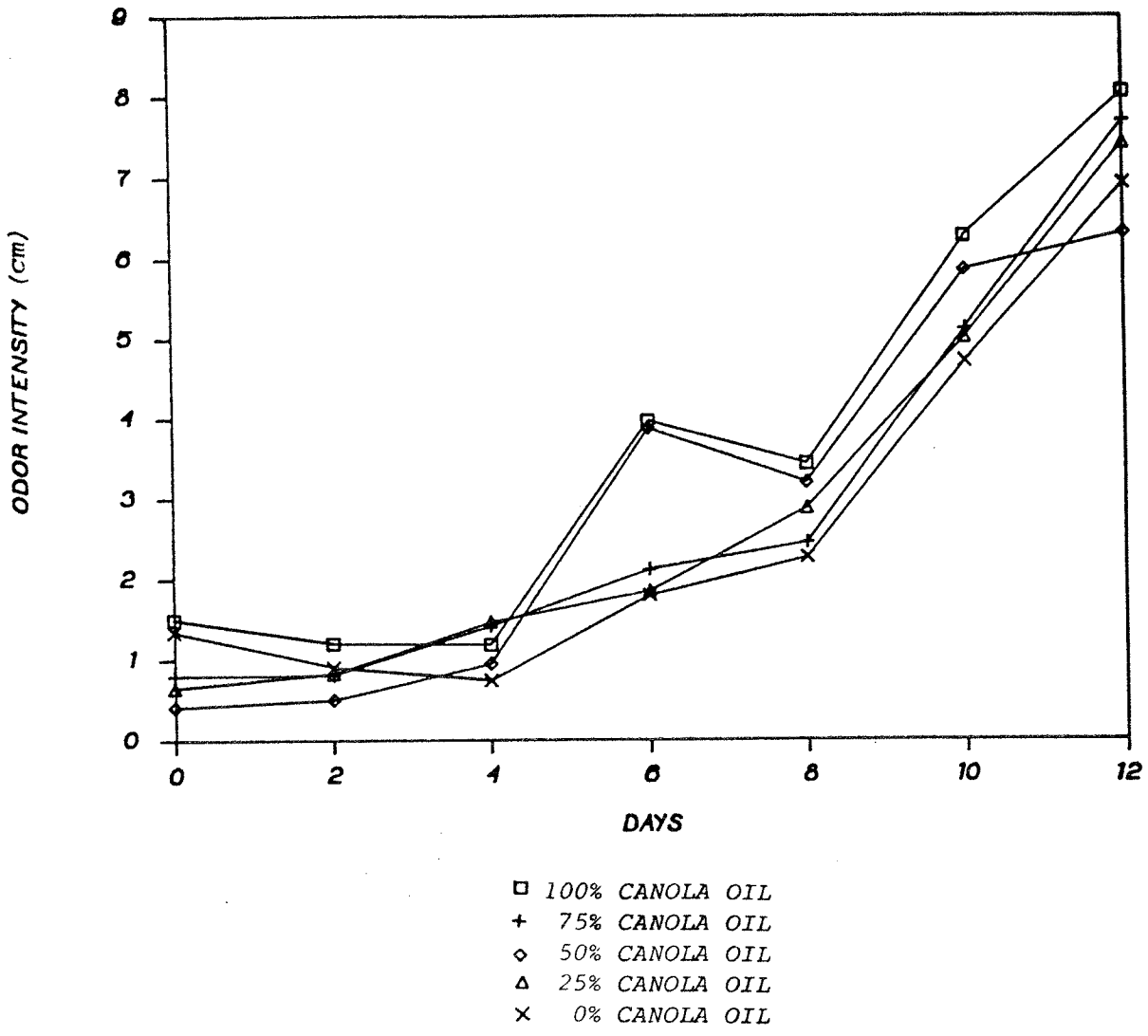

Figure 15: CHANGES IN ODOR INTENSITY VALUE OF CANOLA/SUNFLOWER OIL BLENDS DURING STORAGE AT 65°C.

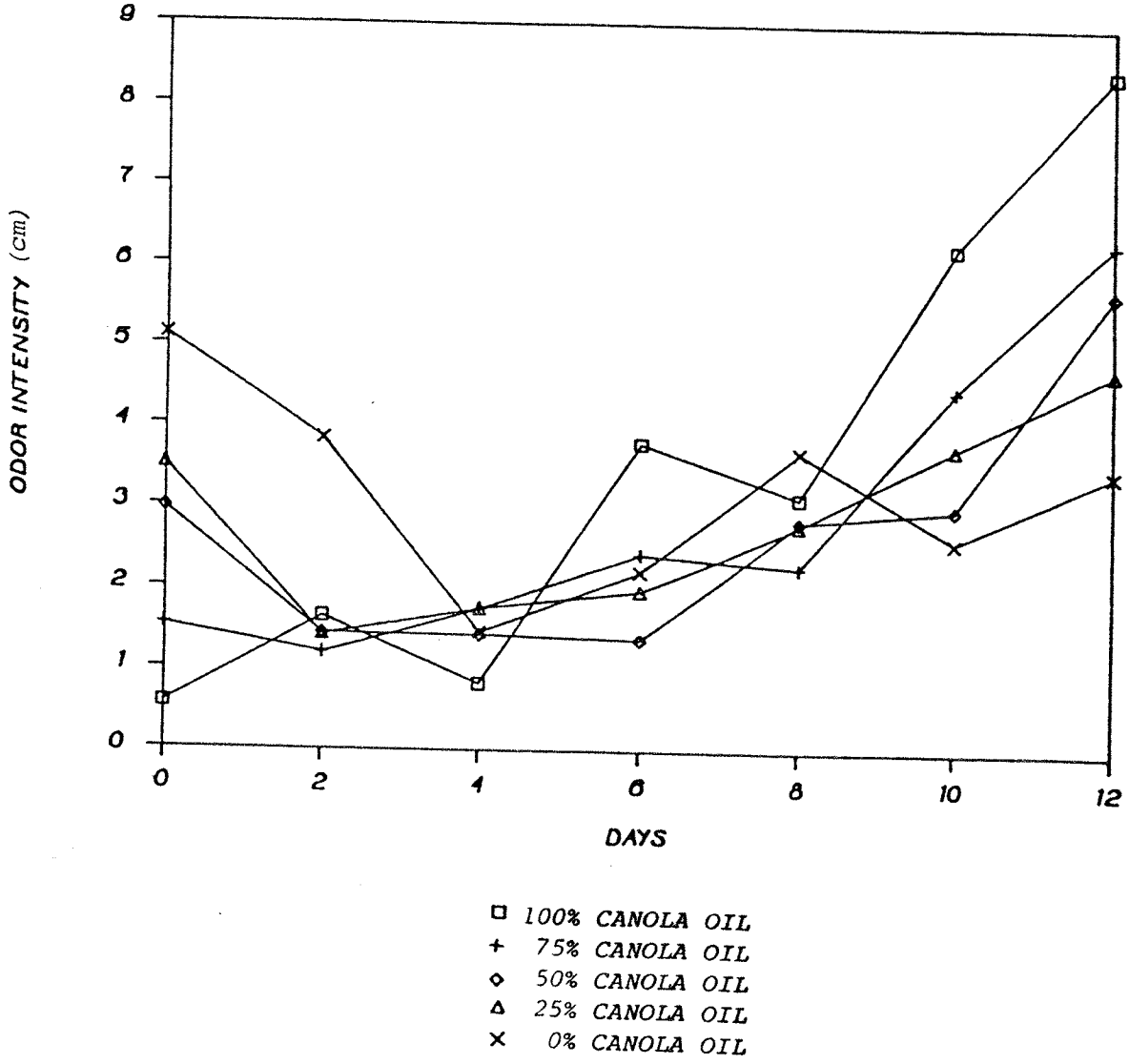

Figure 16: CHANGES IN ODOR INTENSITY VALUE OF CANOLA/COTTONSEED OIL BLENDS DURING STORAGE AT 65°C.

4.2.5 Correlation of Chemical and Sensory Analyses

The correlation coefficients between sensory measurement and chemical measurements of oxidation are presented in Table 13. The chemical parameters correlated much better with odor development of sunflower oil than with cottonseed oil. TBA value and furfural concentration correlate the best with OIV for both sunflower and cottonseed oil blends.

TABLE 13

MEAN CORRELATION COEFFICIENTS FOR CHEMICAL AND SENSORY ANALYSES OF CANOLA OIL BLENDS STORED AT 65°C FOR 12 DAYS.

CHEMICAL METHOD	SUNFLOWER OIL BLENDS OIV	COTTONSEED OIL BLENDS OIV
PV	0.90	0.55
HV	0.94	0.47
TBA	0.96	0.62
[C]	0.92	0.52
[F]	0.95	0.56

4.2.6 Analysis of Variance

Tables 14 and 15 list the results for the Analyses of Variance (ANOVA) performed on odor intensity values (OIV) for the sunflower oil blends and for the cottonseed oil blends, respectively. The major sources of variation for the sunflower set were Day, Judge, and Blend. Although the F values for many of the interactions were significant, the F values themselves were small compared to the individual sources of variation. With such large degrees of freedom, the null hypothesis of no interactions was easier to reject (Conover, 1971).

In the case of the cottonseed oil blends, the major sources of variation were Day, Judge, Day*Blend and Blend. Based upon the observation that the 0 day cottonseed oil was judged by a number of panelists to have a strong initial odor, the 0 day values were deleted from a second ANOVA (Table 16) calculated to determine the effect of this phenomenon. It is apparent that by ignoring the initial odor intensity, the Blend effect is increased while the Day*Blend interaction is reduced.

4.2.7 Multiple Comparison

The sunflower oil blends were compared with respect to odor development throughout the storage test using Tukey's Studentized Range Test. The cottonseed oil blends could only be compared on the basis of their final odor intensity due to the presence of a significant Day*Blend interaction ($p = 0.0001$), in conjunction with a relatively high F value. Table 17 contains the results of the blend comparisons.

The 100% canola developed significantly more odor ($p \leq 0.05$) than the 25%, 75%, or 100% sunflower oil upon storage. No significant difference ($\alpha = 0.05$) occurred upon blending equal amounts of sunflower oil and canola oil. Cottonseed oil significantly improved ($p \leq 0.05$) the odor intensity of canola oil after 12 days storage. Blending with 25% cottonseed oil was sufficient to cause a significant slowing of the development of off-odor ($p \leq 0.05$).

TABLE 14

ANALYSIS OF VARIANCE OF ODOR INTENSITY VALUES FOR SUNFLOWER OIL BLENDS DURING ACCELERATED STORAGE AT 65°C.

SOURCE OF VARIATION	DF	F VALUE	PR > F
DAY	6	14.51	0.0001
JUDGE	9	25.24	0.0001
BLEND	4	4.59	0.0013
DAY*BLEND	24	1.34	0.1332
JUDGE*BLEND	36	2.61	0.0001
DAY*JUDGE	54	2.14	0.0001
DAY*JUDGE*BLEND	216	0.19	0.7687

TABLE 15

ANALYSIS OF VARIANCE OF ODOR INTENSITY VALUES FOR COTTONSEED OIL BLENDS DURING ACCELERATED STORAGE AT 65°C.

SOURCE OF VARIATION	DF	F VALUE	PR > F
DAY	6	44.96	0.0001
JUDGE	9	29.33	0.0001
BLEND	4	3.42	0.0092
DAY*BLEND	24	7.33	0.0001
JUDGE*BLEND.	36	1.64	0.0142
DAY*JUDGE	54	2.92	0.0001
DAY*JUDGE*BLEND	216	1.52	0.0003

TABLE 16

ANALYSIS OF VARIANCE OF ODOR INTENSITY VALUES FOR COTTONSEED OIL BLENDS DURING ACCELERATED STORAGE AT 65°C (0 DAY VALUES DELETED).

SOURCE OF VARIATION	DF	F VALUE	PR > F
DAY	5	49.51	0.0001
JUDGE	9	16.09	0.0001
BLEND	4	7.30	0.0001
DAY*BLEND	20	4.82	0.0001
JUDGE*BLEND.	36	1.35	0.0937
DAY*BLEND	45	1.54	0.0194
DAY*JUDGE*BLEND	180	1.30	0.0219

TABLE 17

THE EFFECT OF BLEND ON ODOR INTENSITY AFTER 12 DAYS STORAGE AT 65°C.

BLENDS[1]	PROPORTION OF CANOLA OIL IN BLEND				
	100%	75%	50%	25%	0%
SUNFLOWER OIL	3.66 a[2]	2.92 b	3.02 ab	2.88 b	2.67 b
COTTONSEED OIL	8.43 a	6.31 b	5.68 b	4.72 bc	3.46 c

[1] For sunflower oil blends, means were compared over all Days. For cottonseed oil blends, means at Day 12 only compared due to significant Day*Blend interaction.

[2] abc : Means in the same row with the same letter are not significantly different ($p \leq 0.05$)

4.2.7.1 Acceptability

The effect of storage time on % acceptability of the sunflower and cottonseed oil blends is illustrated in Figures 17 and 18. While the cottonseed oil became 100% acceptable to the panel after 4 days storage at 65°C, and remained so through to 12 days, the sunflower oil and the canola oil both became unacceptable to 55% and 55-60% of the panel, respectively.

The blends of sunflower oil and canola oil were all more acceptable than the 100% sunflower oil or the 100% canola oil. The 100% sunflower oil and the blend containing 75% sunflower oil remained 100% acceptable to 6 days. The cottonseed oil blends all had low initial acceptability levels which improved upon storage. These blends followed a trend such that % acceptability increased as the proportion of cottonseed oil increased.

The final proportions of acceptability for each blend were compared via contingency tables (See Appendix C.) Based on the sample size, there was insufficient evidence to reject the null hypothesis that the sunflower blends were equally acceptable after 12 days. In contrast, the cottonseed oil blends were significantly different ($p \leq 0.001$) and followed a linear model where acceptability varied with percentage of cottonseed oil.

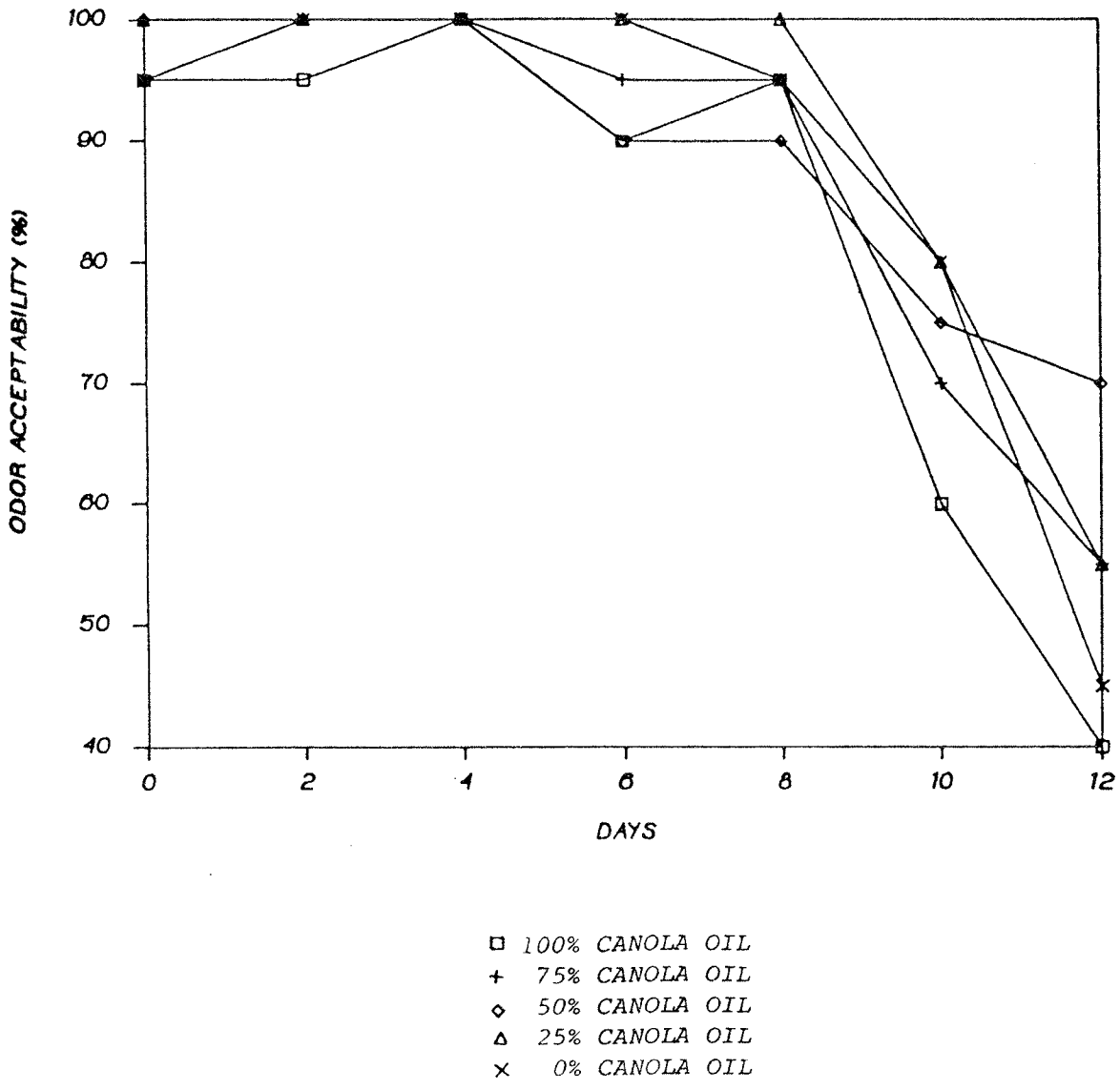

Figure 17: CHANGES IN % ACCEPTABILITY OF CANOLA/SUNFLOWER OIL BLENDS DURING STORAGE AT 65°C.

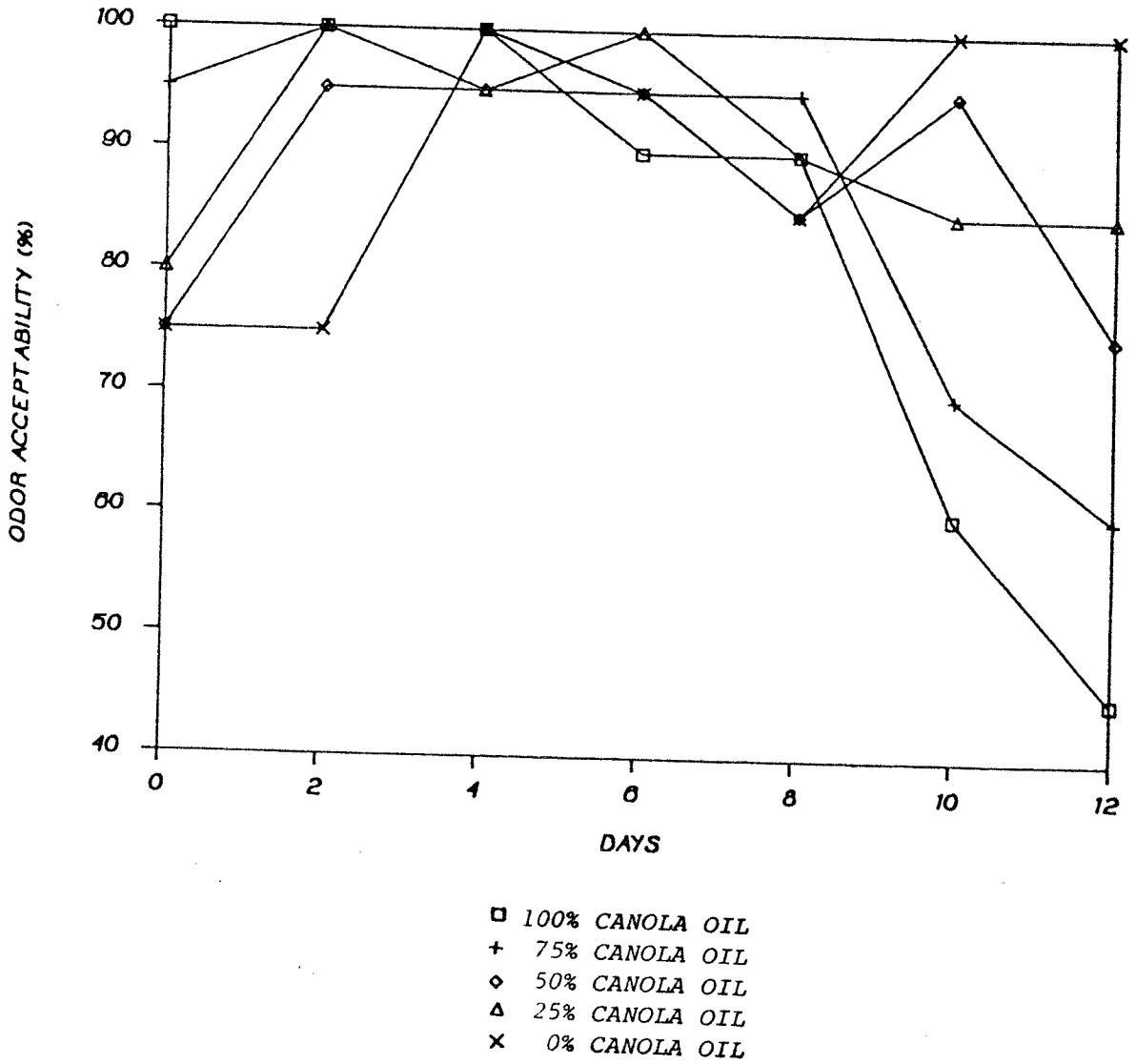

Figure 18: CHANGES IN % ACCEPTABILITY OF CANOLA/COTTONSEED OIL BLENDS DURING STORAGE AT 65°C.

4.3 EXPERIMENT 2 : FLUORESCENT LIGHT EXPOSURE AT 40°C

4.3.1 Chemical Analyses

Differences in all chemical values for the two storage replications reflected differences in light intensity. For replication 1, oil samples were stored in areas of increasing light intensity as the number of days increased, whereas for replication 2, samples were arranged in areas of decreasing light intensity as the length of storage increased. The mean values for all measurements for replication 1 were lower for days 1 and 2 but higher for days 3 and 4 as compared to the mean values for the second storage replication. Subsequent discussion will be based on the mean over the two replications except for total carbonyl and furfural values which were measured only for the first replication.

4.3.1.1 Peroxide Value

All oils and oil blends increased in mean peroxide value over the four day storage period (Figures 19 and 20). Sunflower oil had the highest final peroxide value of the parent oils, over twice as high as canola oil and about four times as much as that of cottonseed oil. The final mean peroxide value increased as canola oil was blended with sunflower oil. In contrast, as the proportion of cottonseed oil to canola oil increased, the final peroxide values were depressed.

4.3.1.2 Hydroperoxide Value

Hydroperoxide value increased for all oils and oil blends upon fluorescent light exposure as illustrated in Figures 21 and 22. The

development of hydroperoxides was greatest for sunflower oil, with the final value being more than twice that of canola oil. The cottonseed oil attained the lowest value of the three parent oils. The effect of blending sunflower oil with canola oil was an increase in the rate of hydroperoxide development as the proportion of sunflower oil increased. In contrast, the addition of cottonseed oil depressed the rate of hydroperoxide formation, in order of increasing cottonseed oil.

4.3.1.3 TBA Value

An increase in TBA value was seen for all oils and oil blends upon fluorescent light storage (Figures 23 and 24). Canola oil attained the highest TBA value of the parent oils, followed by cottonseed oil and then sunflower oil. The final TBA value of sunflower oil was less than half that of the canola oil. A decrease in the rate of oxidation as measured by TBA value was seen as the effect of increased levels of sunflower oil. The blends of 50% canola oil:50% cottonseed oil and 25% canola oil:75% cottonseed oil developed higher TBA values after 4 days than the 100% canola oil, while the 75% canola oil:25% cottonseed oil attained a final TBA value just slightly less than the 100% canola oil.

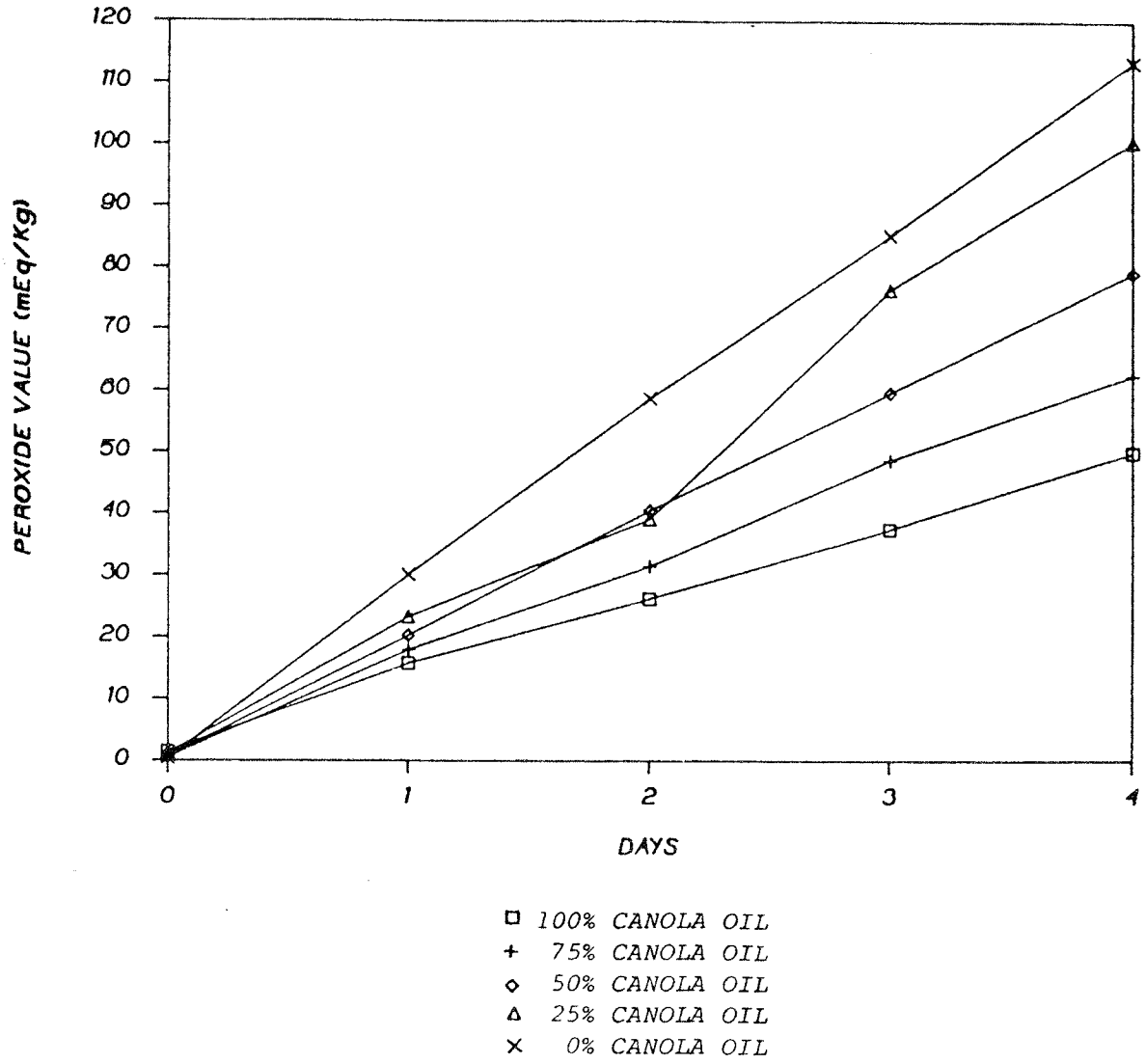

Figure 19: CHANGES IN PEROXIDE VALUE OF CANOLA/SUNFLOWER OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

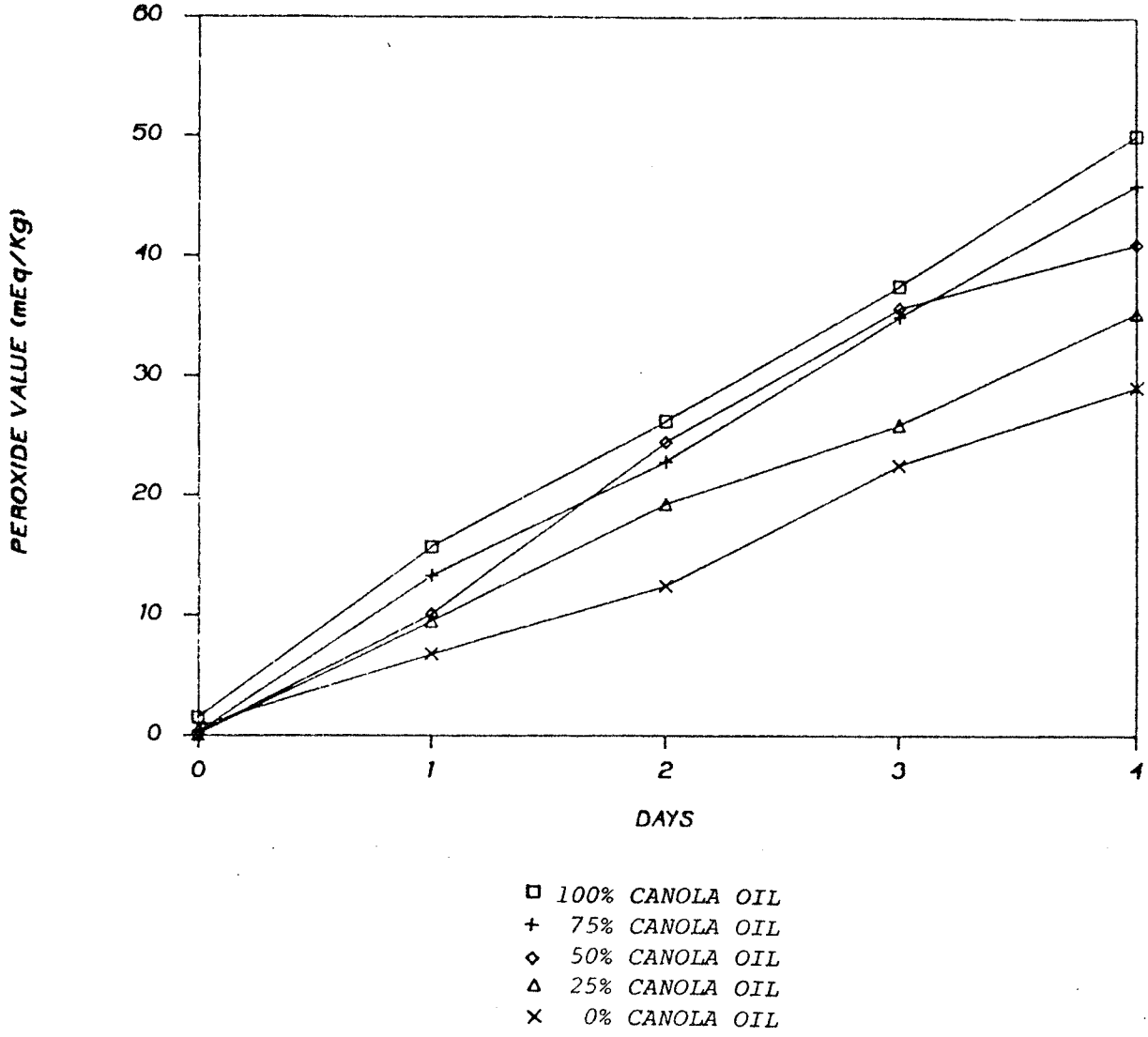

Figure 20: CHANGES IN PEROXIDE VALUE OF CANOLA/COTTONSEED OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

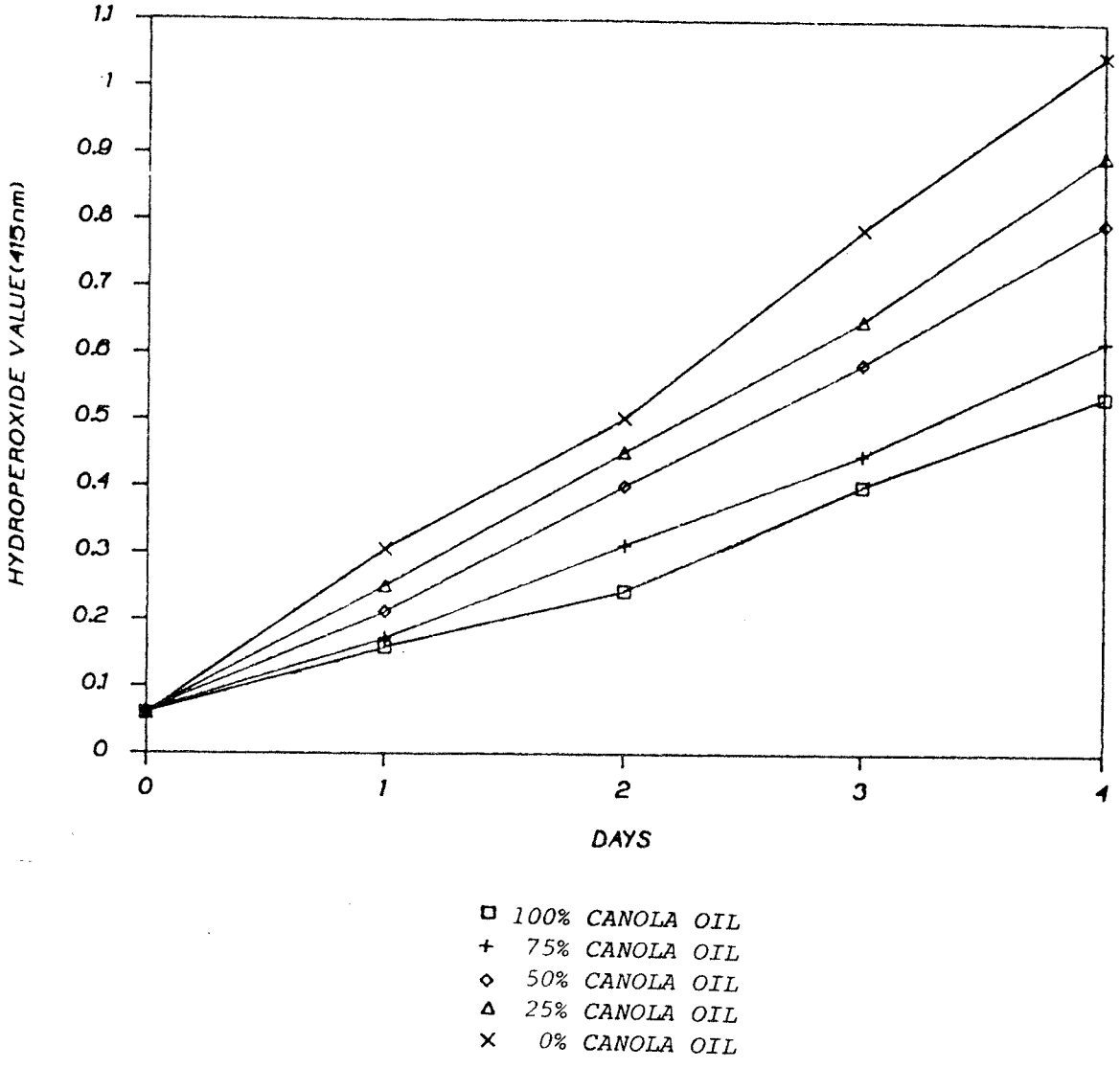

Figure 21: CHANGES IN HYDROPEROXIDE VALUE OF CANOLA/SUNFLOWER OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

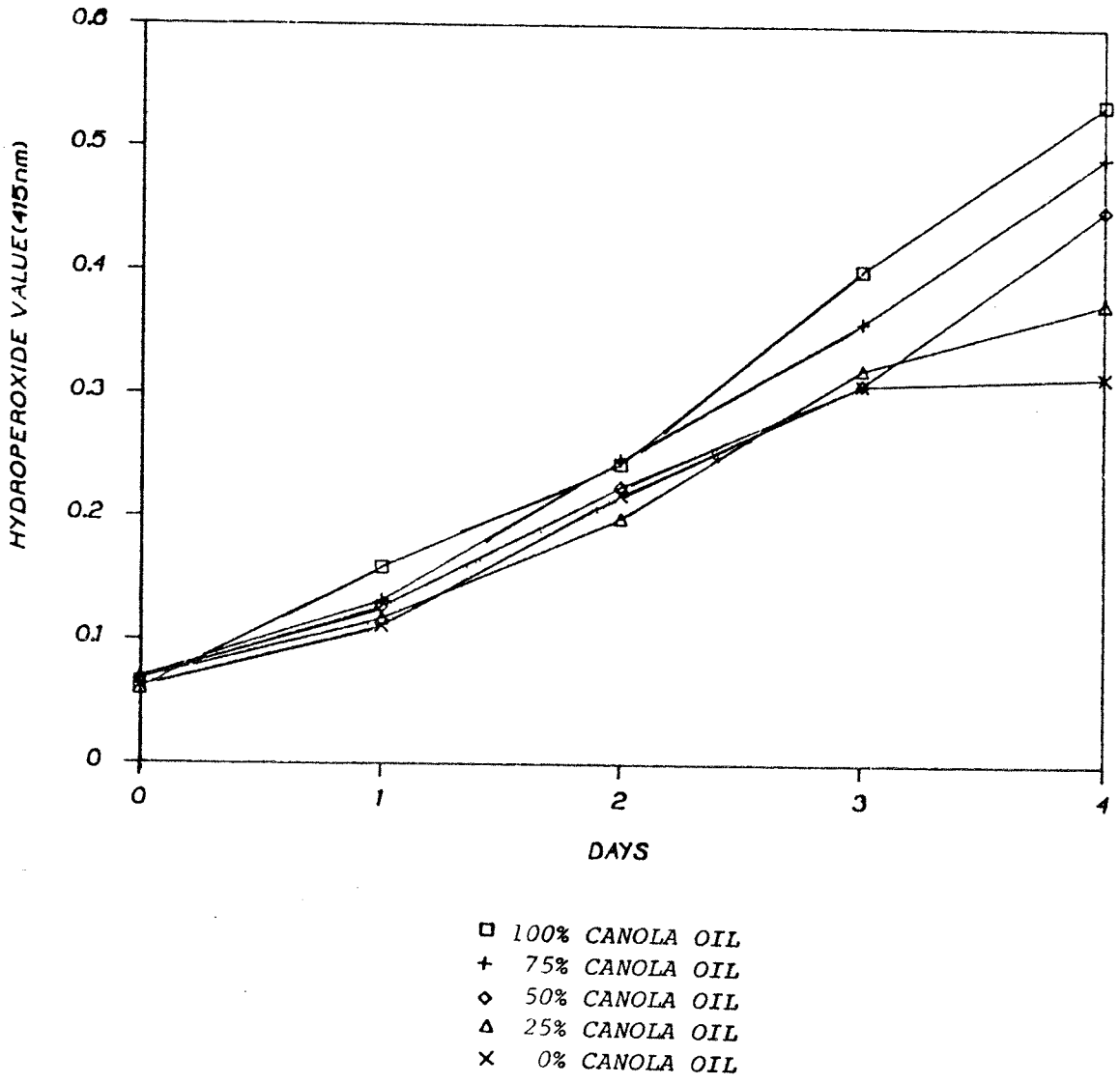

Figure 22: CHANGES IN HYDROPEROXIDE VALUE OF CANOLA/COTTONSEED OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

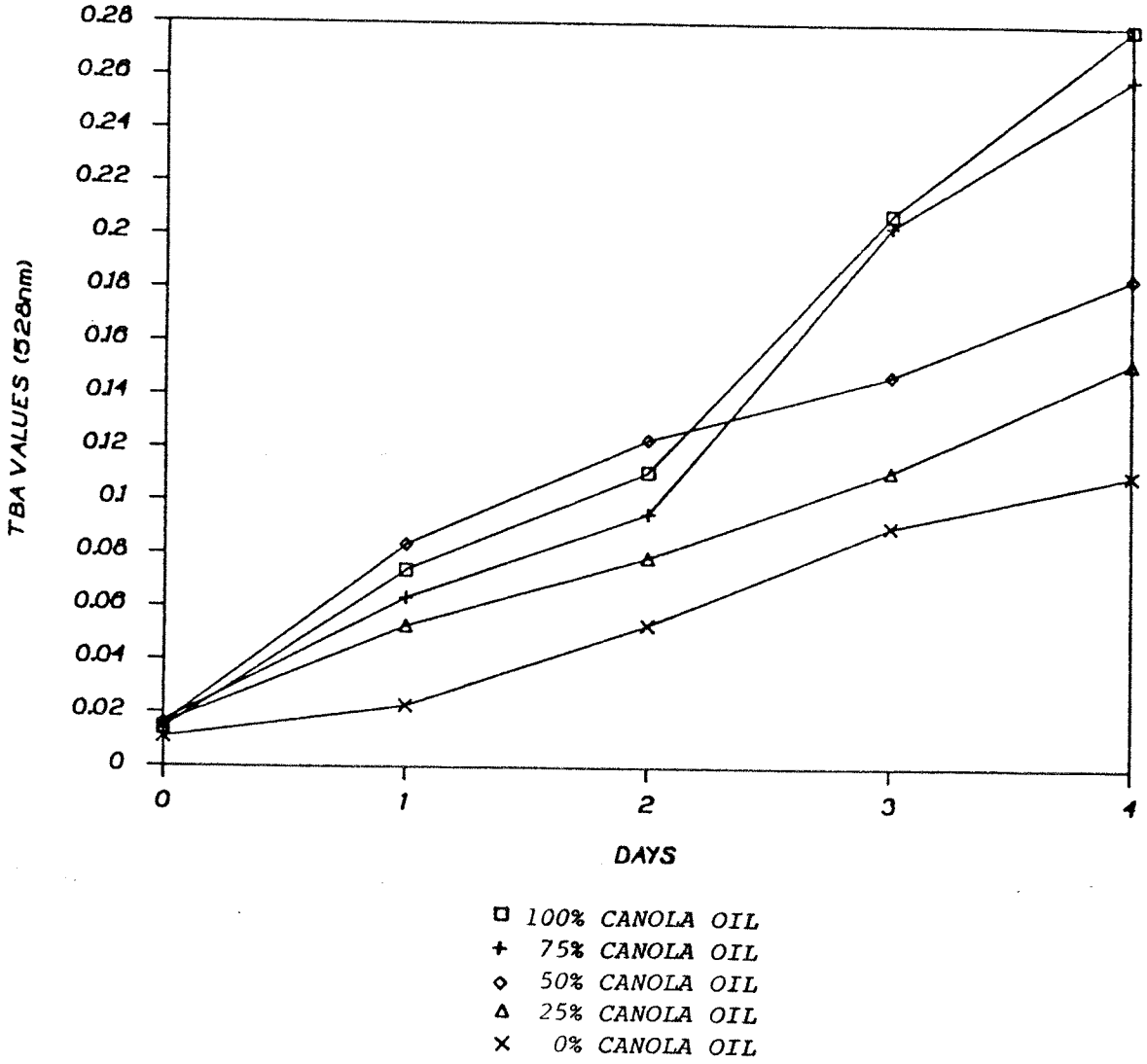

Figure 23: CHANGES IN TBA VALUE OF CANOLA/SUNFLOWER OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

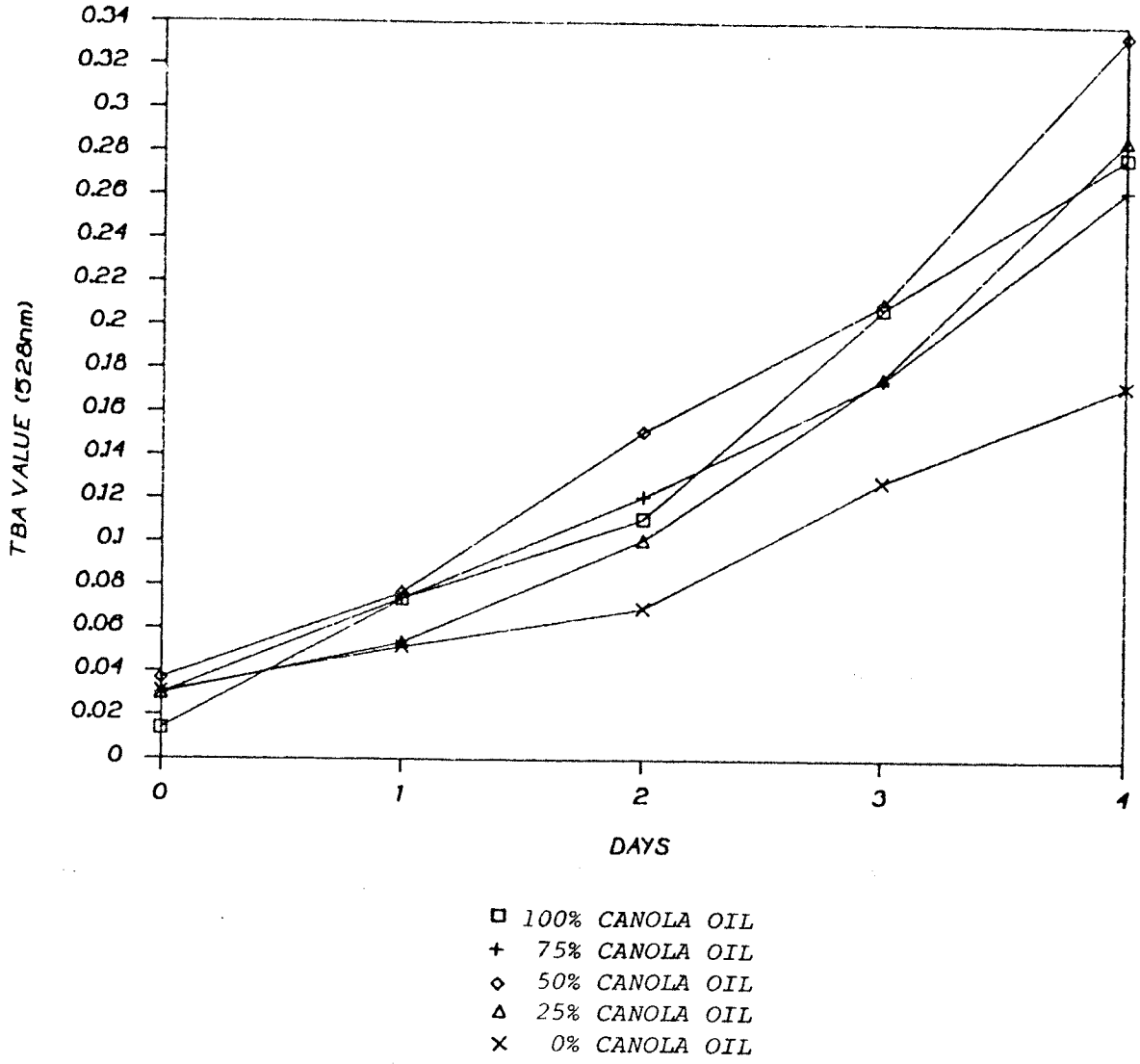

Figure 24: CHANGES IN TBA VALUE OF CANOLA/COTTONSEED OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

4.3.1.4 Total Volatile Carbonyl Compounds

All oils and oil blends increased in concentration of total volatile carbonyl compounds over the four day storage period, as illustrated in Figures 25 and 26. The final carbonyl concentration was greatest for the canola oil followed by sunflower oil and then by cottonseed oil. Sunflower oil developed less than one half the concentration of carbonyl compounds of the canola oil, while cottonseed oil had a final concentration of carbonyls which was greater than one third that of the canola oil. The final carbonyl concentrations generally decreased with increased levels of sunflower oil, with the exception of the reversed order for the 75% and 100% sunflower oil samples. In the case of the cottonseed oil blends, an increase in the level of cottonseed oil resulted in a decrease in final carbonyl concentration.

4.3.1.5 Furfural

All oils and oil blends increased in furfural concentration upon fluorescent light exposure for 4 days (Figures 27 and 28). Of the three parent oils, cottonseed oil accumulated the least furfural, approximately one half that of sunflower oil and about one fifth that of canola oil. The effect of blending canola oil with sunflower oil, was a general decrease in final furfural concentration over the 4 day storage period. The blend of 75% sunflower oil:25% canola oil accumulated the least furfural of this set. Final furfural concentration decreased with increased cottonseed oil concentration, except in the case of 25%

cottonseed oil and 50% cottonseed oil where the furfural values reversed.

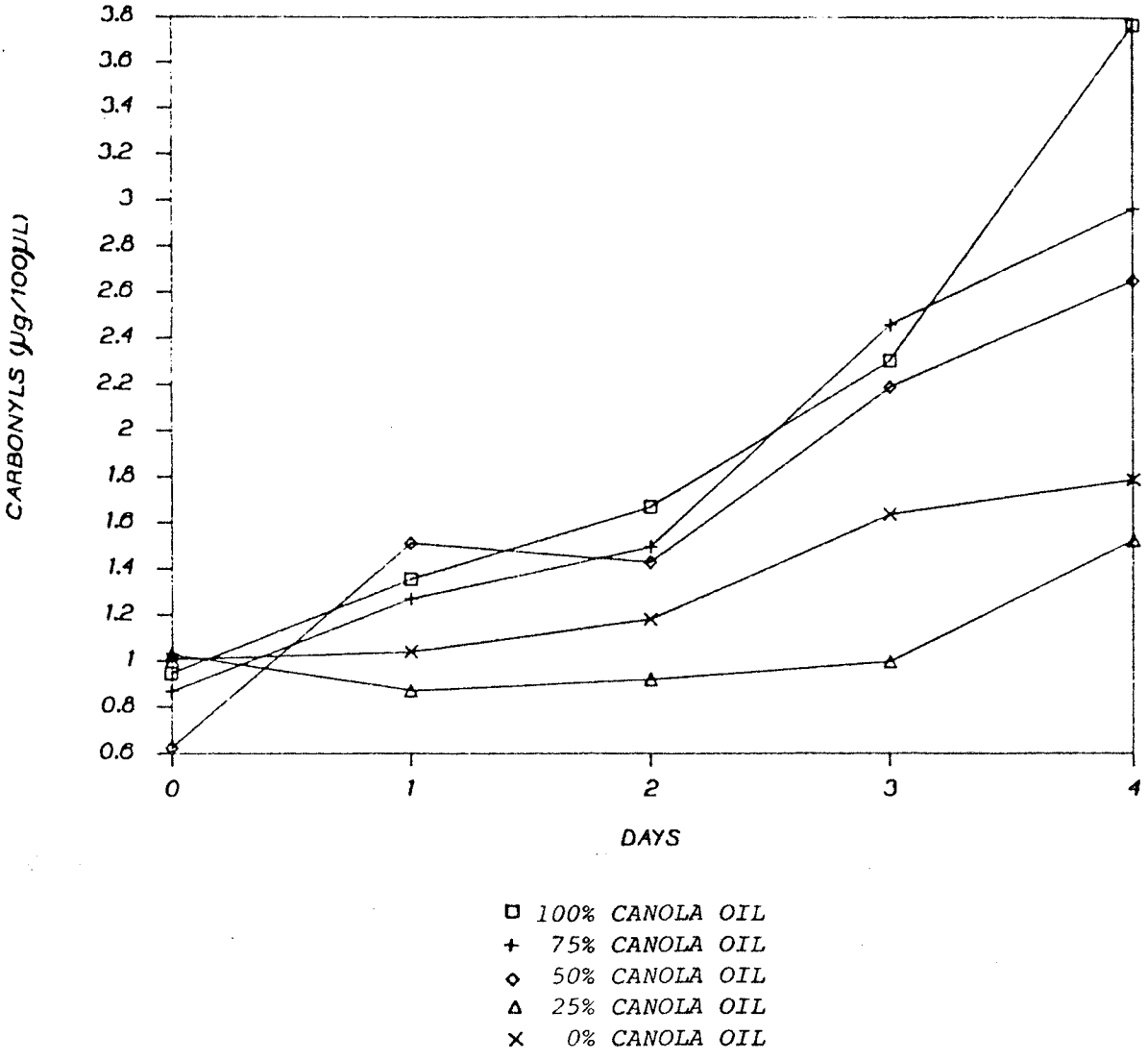

Figure 25: CHANGES IN TOTAL CARBONYL COMPOUNDS OF CANOLA/SUNFLOWER OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

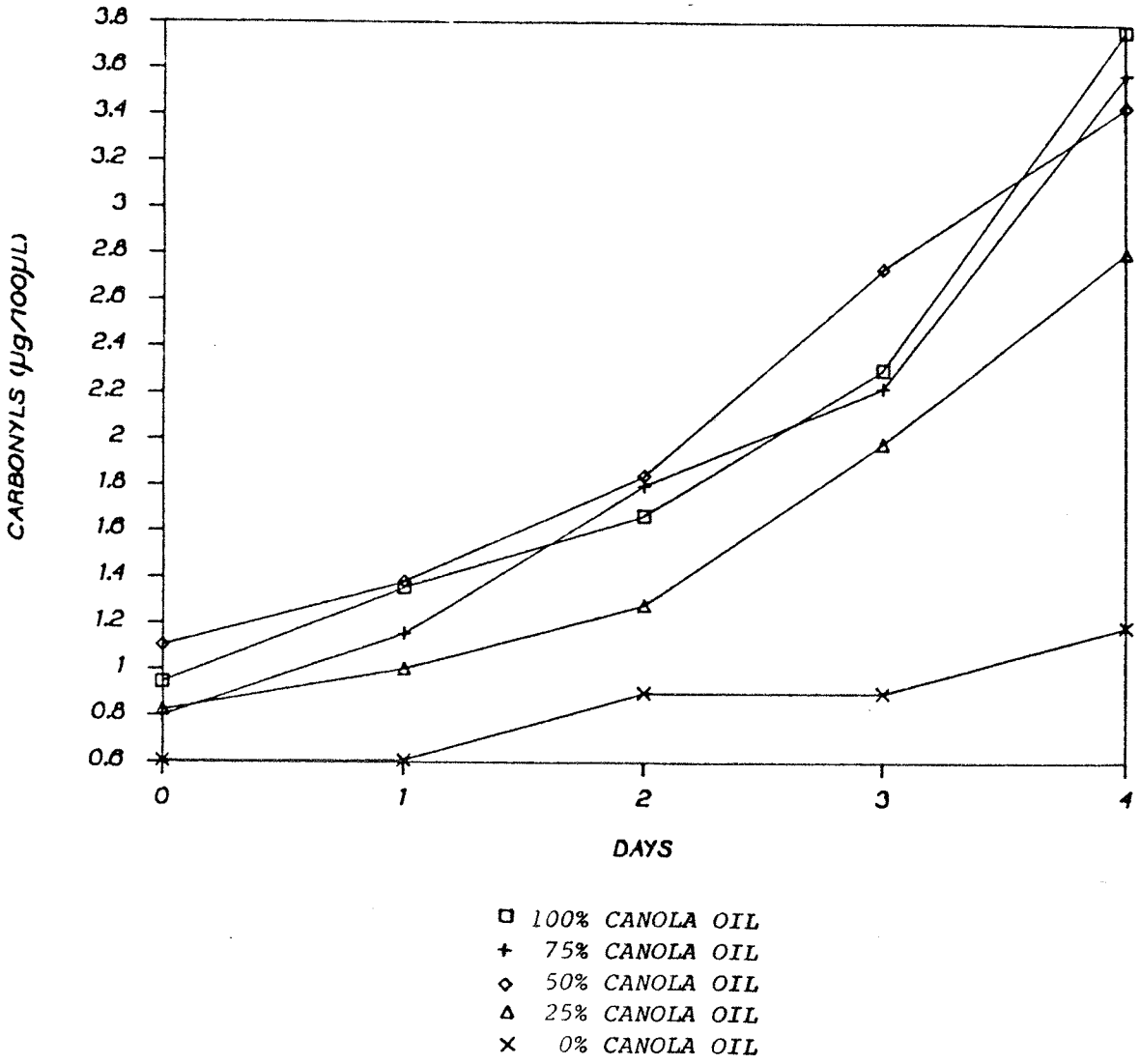

Figure 26: CHANGES IN TOTAL CARBONYL COMPOUNDS OF CANOLA/COTTONSEED OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

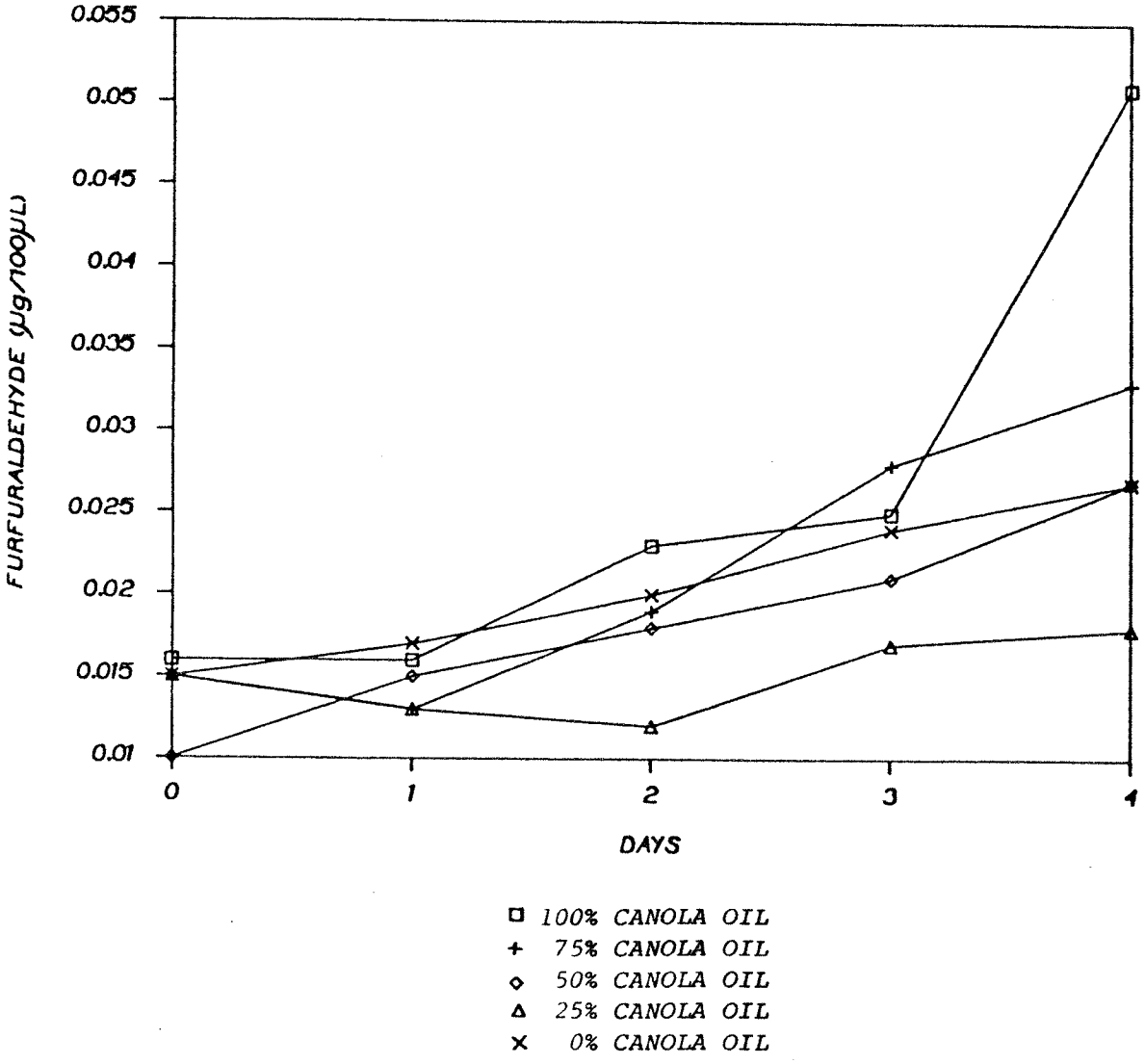

Figure 27: CHANGES IN FURFURAL CONCENTRATION OF CANOLA/SUNFLOWER OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

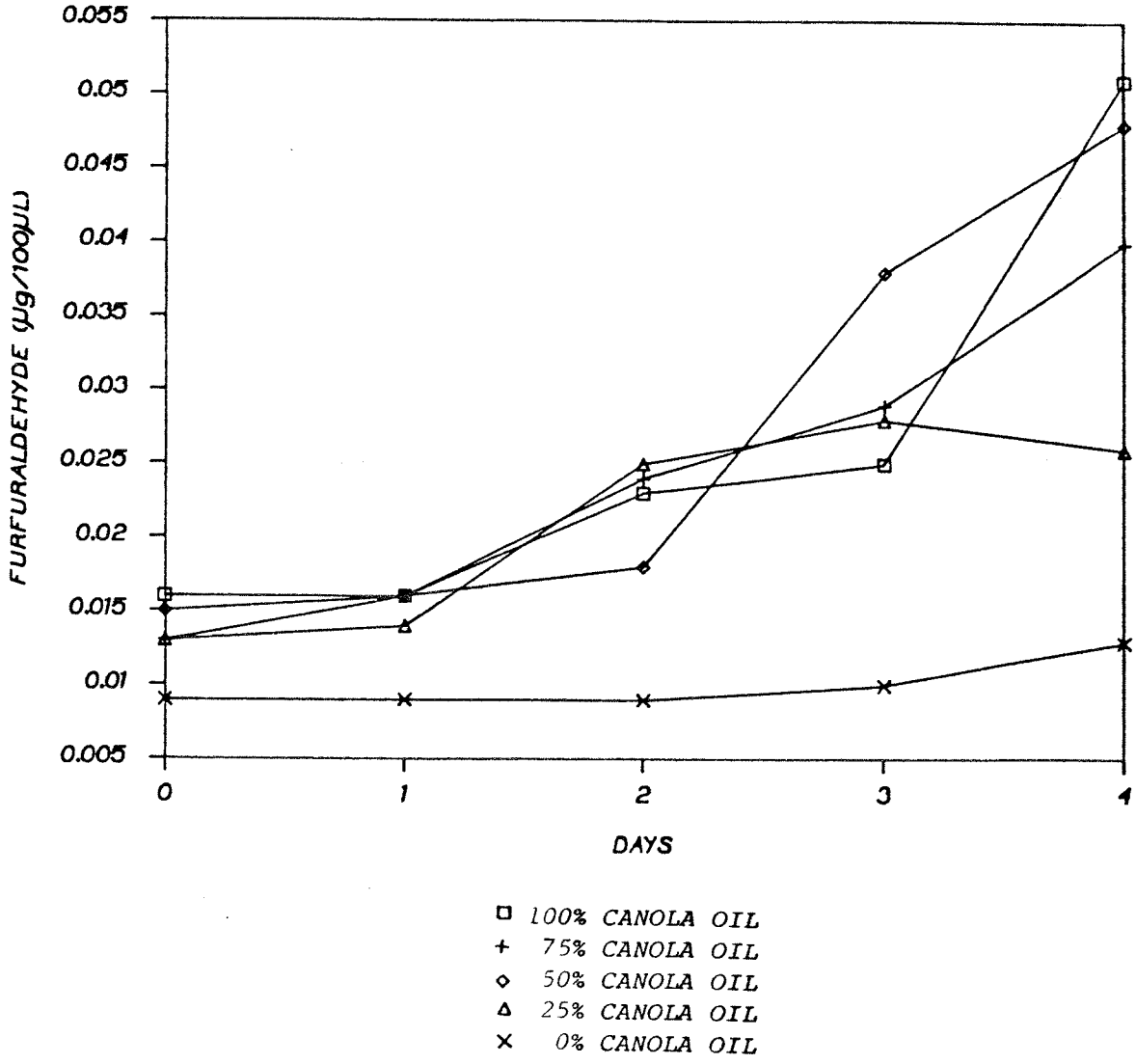

Figure 28: CHANGES IN FURFURAL CONCENTRATION OF CANOLA/COTTONSEED OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

4.3.2 Correlation of Chemical Methods of Analyses

The mean correlation coefficients for the chemical methods of analysis were calculated separately for the sunflower oil blends and cottonseed oil blends and are presented in Tables 18 and 19. All correlation coefficients were high ($r > 0.89$) indicating a strong relationship between all chemical indices of photoxidation.

TABLE 18

MEAN CORRELATION COEFFICIENTS FOR CHEMICAL MEASUREMENTS OF PHOTOOXIDATION OF CANOLA / SUNFLOWER OIL BLENDS.

	PV	HV	TBA	[C]	[F]
PEROXIDE VALUE (PV)	1.00	0.99	0.98	0.91	0.90
HYDROPEROXIDE (HV) VALUE	0.99	1.00	0.99	0.92	0.89
THIOBARBITURIC (TBA) VALUE	0.98	0.95	1.00	0.92	0.89
TOTAL CARBONYL ([C]) COMPOUNDS	0.91	0.92	0.92	1.00	0.93
FURFURAL ([F]) CONCENTRATION	0.90	0.90	0.89	0.93	1.00

TABLE 19

MEAN CORRELATION COFFICIENTS FOR CHEMICAL MEASUREMENTS OF PHOTOOXIDATION OF CANOLA / COTTONSEED OIL BLENDS.

	PV	HV	TBA	[C]	[F]
PEROXIDE VALUE (PV)	1.00	0.98	0.98	0.95	0.89
HYDROPEROXIDE (HV) VALUE	0.98	1.00	0.98	0.96	0.89
THIOBARBITURIC (TBA) VALUE	0.98	0.98	1.00	0.97	0.90
TOTAL CARBONYL ([C]) COMPOUNDS	0.95	0.96	0.97	1.00	0.92
FURFURAL ([F]) CONCENTRATION	0.89	0.89	0.90	0.92	1.00

4.3.3 Regression Analysis

Regression analysis performed on the TBA values showed all blends fit a linear model well (Table 20). Calculation of Bartlett's Test for Homogeneity of Variances (See Appendix A) for all nine blends resulted in rejection of the null hypothesis that all variances are equal. However, it was observed that the 75% and 100% sunflower oil blends had much lower Mean Square Error (MSE) terms than did the rest of the blends. When these blends were omitted, the null hypothesis was not rejected with $p = 0.2166$. The MSE terms for the remaining seven blends were pooled and the slopes compared in their natural order of decreasing canola oil. The slopes of the 75% and the 100% sunflower oil blends were compared to each other and, as well, the 50% and the 75% sunflower oil blends were compared using Satterthwaite's Approximation for comparing slopes with unequal variances (Satterthwaite, 1946). The results of the comparisons are presented in Table 21.

The canola oil was not significantly different ($p \leq 0.05$) from 75% canola oil blended with 25% sunflower oil. The blend of 50% canola:50% sunflower oil appeared to develop secondary oxidation products at a significantly slower rate ($p = 0.0001$) than the blend with 75% canola oil. but significantly more rapidly ($p = 0.02$) than the blend containing 75% sunflower oil. There was no significant difference ($p \leq 0.05$) between the 75% and 100% sunflower oils.

In the cottonseed oil group, no significant difference ($p \leq 0.05$) is evident between either the 100% canola oil and the 25% cottonseed oil blend, or between the 50% and 75% cottonseed oil blends. The 50%

cottonseed oil increased in TBA value significantly more rapidly ($p = 0.004$) than the 25% cottonseed oil. In addition, the 100% cottonseed oil developed significantly less ($p = 0.001$) malonaldehyde than did the 75% cottonseed oil blend.

TABLE 20

COEFFICIENTS OF DETERMINATION (r^2) for REGRESSION ANALYSIS OF TBA DEVELOPMENT OVER TIME OF FLUORESCENT LIGHT EXPOSURE.

	BLEND	LINEAR MODEL (r^2)
SUNFLOWER OIL BLENDS	100% CANOLA OIL	.98
	75% CANOLA : 25% SUNFLOWER OIL	.96
	50% CANOLA : 50% SUNFLOWER OIL	.96
	25% CANOLA : 75% SUNFLOWER OIL	.99
	100% SUNFLOWER OIL	.97
COTTONSEED OIL BLENDS	75% CANOLA : 25% COTTONSEED OIL	.97
	50% CANOLA : 50% COTTONSEED OIL	.96
	25% CANOLA : 75% COTTONSEED OIL	.93
	100% COTTONSEED OIL	.95

TABLE 21

A COMPARISON OF REGRESSION SLOPES OF TBA VALUES OVER TIME OF FLUORESCENT LIGHT EXPOSURE.

BLEND	MEAN SQUARE ERROR (MSE)	SLOPE	VALUE OF t STATISTIC[1]	p VALUE
A. 100% CANOLA : 0% SUNFLOWER OIL	0.0001819562	0.066450		
			} 0.655	0.258
B. 75% CANOLA : 25% SUNFLOWER OIL	0.0003784438	0.062650		
			} 3.863	0.0001
C. 50% CANOLA : 50% SUNFLOWER OIL	0.0001522938	0.040250		
			} 2.351[2]	0.02
D. 25% CANOLA : 75% SUNFLOWER OIL	0.0000176125	0.033400		
			} 0.923	0.185
E. 0% CANOLA : 100% SUNFLOWER OIL	0.0000462625	0.026800		
A. 100% CANOLA : 0% COTTONSEED OIL	0.0001809562	0.066450		
			} 1.638	0.054
G. 75% CANOLA : 25% COTTONSEED OIL	0.0001874438	0.056850		
			}-2.768	0.004
H. 50% CANOLA : 50% COTTONSEED OIL	0.0005040125	0.073000		
			} 1.604	0.057
I. 25% CANOLA : 75% COTTONSEED OIL	0.0007193875	0.063700		
			} 4.734	0.001
J. 0% CANOLA : 100% COTTONSEED OIL	0.0001809562	0.036250		

Thus, A B C D E and A G H I J with $p \leq 0.05$

[1] See Appendix B for t Statistic for Comparison of Slopes
[2] Using Sattertwaites Approximation for Unequal Variances

4.3.4 Sensory Evaluation

4.3.4.1 Judge Consistency

Pearsons correlation coefficients for individual judges performance over the two replications are presented in Table 22. Judge 7 was eliminated from further analysis because her correlation coeficient of r = 0.22 was well below that for the other judges.

TABLE 22

CONSISTENCY OF JUDGES' MEASUREMENTS OF ODOR INTENSITY FOR EXPERIMENT 2

JUDGE	r (REP 1 VS REP 2)	
1	0.50	
2	0.47	
3	0.62	
4	0.77	
5	0.70	
6	0.78	
7	0.22	*
8	0.74	
9	0.57	

4.3.4.2 Total Odor Intensity Value

All oils and oil blends increased in total odor intensity value (OIV) during the 4 day period of fluorescent light exposure (Figures 29 and 30). Cottonseed oil developed the highest final odor intensity of the three parent oils, while sunflower oil showed the least development of off-odor. A decrease in odor intensity appears to parallel an increase in the proportion of sunflower oil to canola oil with the exception of 25% sunflower oil. The latter had a higher final OIV than did the 100% canola oil. The 50% sunflower oil and 75% sunflower oil blends had similar mean OIV's after 4 days.

The 100% sunflower oil developed the least odor intensity of all the oil samples studied. The cottonseed oil blends generally developed more odor after storage in fluorescent light than did the sunflower oil blends. An increase in OIV accompanied an increase in the proportion of cottonseed oil.

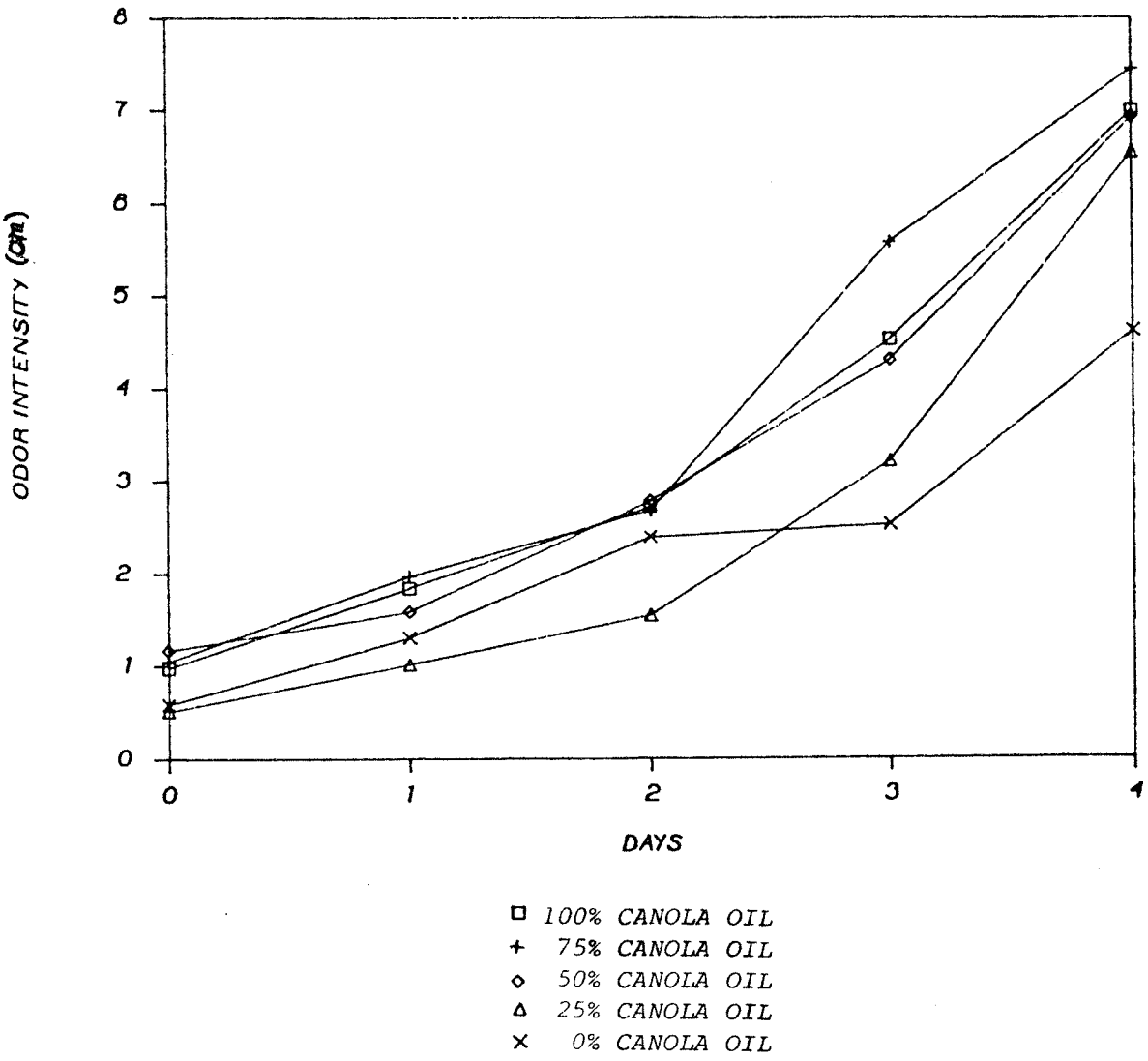

Figure 29: CHANGES IN ODOR INTENSITY VALUE OF CANOLA/SUNFLOWER OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

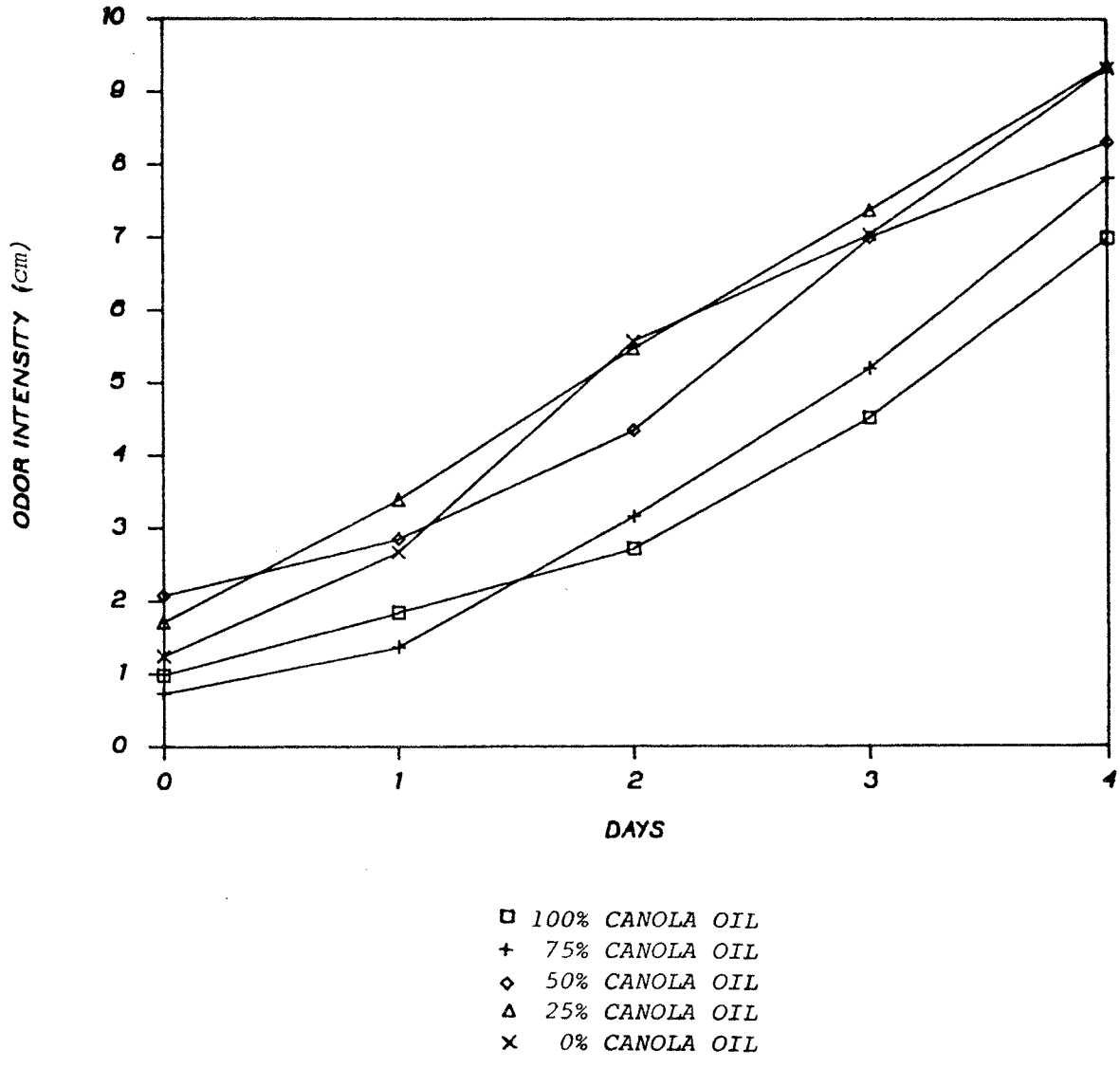

Figure 30: CHANGES IN ODOR INTENSITY VALUE OF CANOLA/COTTONSEED OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250 ±25 FT.C.) AT 40°C.

4.3.5 Correlation Between Sensory and Chemical Measurements of Photooxidation

The correlation coefficients between the sensory measurements and chemical measurements are presented in Table 23. All r values are very high ($r > 0.90$). Of the chemical methods, the TBA values correlated the best with OIV's. All chemical measurements except furfural concentration were better correlated with cottonseed oil odor development than with sunflower oil odor.

TABLE 23

MEAN CORRELATION COEFFICIENTS FOR CHEMICAL AND SENSORY ANALYSES OF CANOLA OIL BLENDS EXPOSED TO FLUORESCENT LIGHT.

CHEMICAL METHOD	SUNFLOWER OIL BLENDS OIV	COTTONSEED OIL BLENDS OIV
PV	0.90	0.98
HV	0.94	0.98
TBA	0.95	0.99
[C]	0.94	0.98
[F]	0.95	0.92

4.3.6 Analysis of Variance

The results from the separate Analyses of Variance (ANOVA) performed on odor intensity values (OIV) for the sunflower oil blends and for cottonseed oil blends, are presented in Tables 24 and 25. The main sources of variation for both sets were Day, Judge, and Blend.

4.3.7 Multiple Comparison

The sunflower oil blends and cottonseed oil blends were compared for odor development during fluorescent light exposure. The results obtained from Tukey's Studentized Range Test to compare the effect of blend, are summarized in Table 26. There was no significant difference ($p \leq 0.05$) between either the 75% canola oil and the 100% canola oil or between the 75% sunflower oil and the 100% sunflower oil. Both the 100% canola oil and the 50% canola:sunflower oil blend developed significantly more odor following fluorescent light exposure than did 100% sunflower oil. The 75% canola oil had a significantly higher mean OIV than either the 75% or 100% sunflower oil samples. The 100% cottonseed oil, the 75% cottonseed oil blend and the 50% cottonseed oil blend developed significantly more ($p \leq 0.05$) odor upon fluorescent light exposure than the 75% canola oil blend or the 100% canola oil.

TABLE 24

ANALYSIS OF VARIANCE OF ODOR INTENSITY VALUES FOR THE SUNFLOWER OIL BLENDS DURING STORAGE AT 40°C UNDER FLUORESCENT LIGHT.

SOURCE OF VARIATION	DF	F VALUE	PR > F
DAY	4	101.99	0.0001
JUDGE	7	10.68	0.0001
BLEND	4	7.58	0.0001
DAY*BLEND	16	1.23	0.2489
JUDGE*BLEND	28	2.65	0.0001
DAY*JUDGE	28	1.60	0.0358
DAY*JUDGE*BLEND	112	0.73	0.9669

TABLE 25

ANALYSIS OF VARIANCE OF ODOR INTENSITY VALUES FOR THE COTTONSEED OIL BLENDS DURING STORAGE AT 40°C UNDER FLUORESCENT LIGHT.

SOURCE OF VARIATION	DF	F VALUE	PR > F
DAY	4	146.41	0.0001
JUDGE	7	18.81	0.0001
BLEND	4	15.64	0.0001
DAY*BLEND	16	0.91	0.5578
JUDGE*BLEND.	28	3.27	0.0001
DAY*JUDGE	28	2.03	0.0028
DAY*JUDGE*BLEND	112	0.67	0.9903

TABLE 26

THE EFFECT OF BLEND ON THE ODOR INTENSITY AFTER FLUORESCENT LIGHT EXPOSURE AT 40°C.

BLENDS	PROPORTION OF CANOLA OIL IN BLEND				
	100%	75%	50%	25%	0%
SUNFLOWER OIL	3.41 ab[1]	3.75 a	3.35 ab	2.56 bc	2.29 c
COTTONSEED OIL	3.41 b	3.66 b	4.92 a	5.17 a	5.46 a

[1] abc : Means in the same row with the same letter are not significantly different ($p \leq 0.05$).

4.3.7.1 Acceptability

The effect of fluorescent light storage on the % acceptability of canola oil/sunflower oil blends and of canola oil/cottonseed oil blends is shown in Figures 31 and 32. The 100% sunflower oil remained 100% acceptable to 4 days, whereas the canola oil was acceptable to 75% of the panel and cottonseed was acceptable to just 56%. A greater proportion of sunflower oil was accompanied by an increase in the number of days the sample was 100% acceptable. The opposite trend was apparent with the cottonseed oil blends, where a decrease in acceptability accompanied increasing amounts of cottonseed oil. A comparison of the proportions of acceptability of the oil blends, however, revealed no significant difference between any of the sunflower oil blends or any of the cottonseed oil blends (See Appendix C).

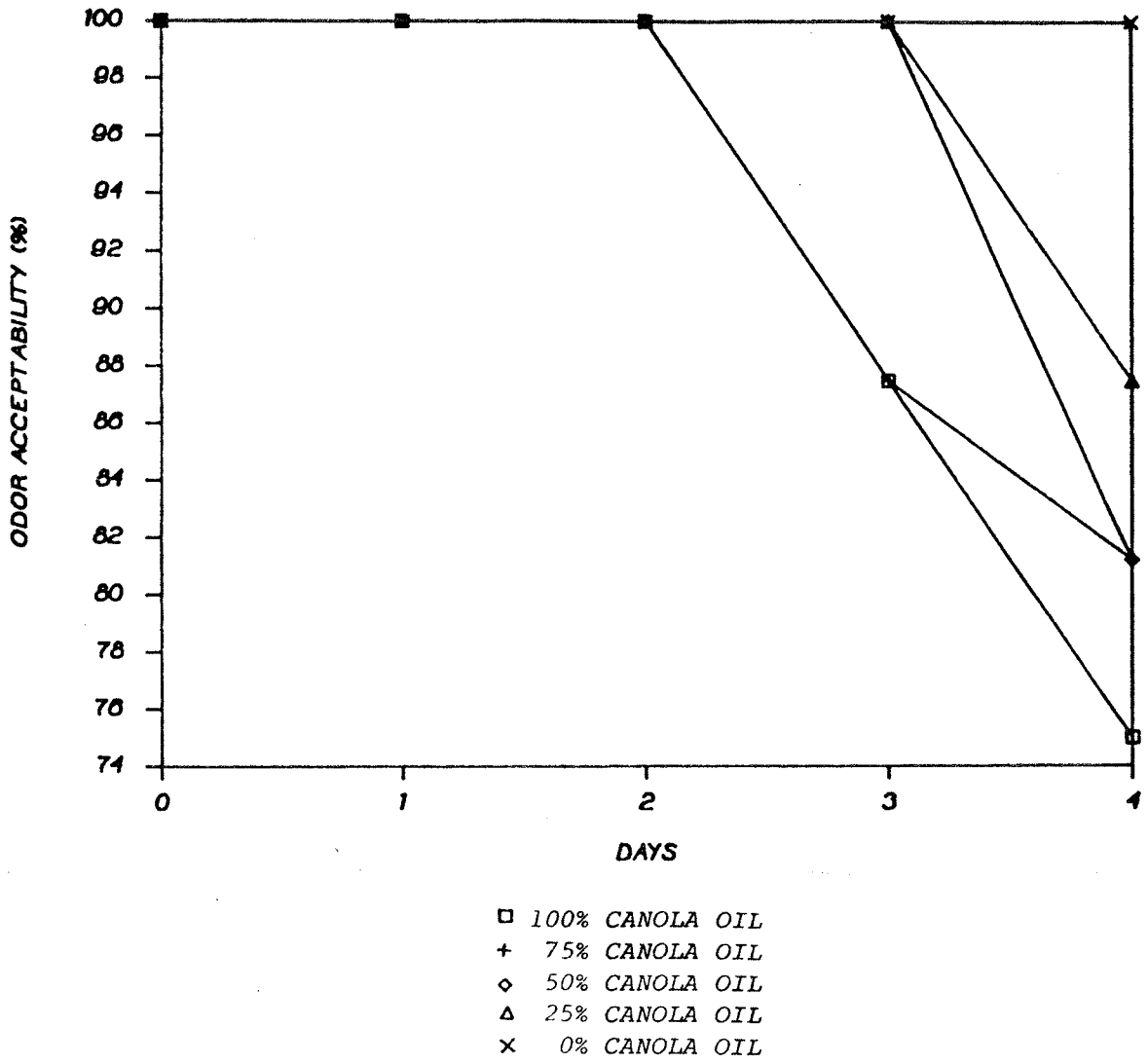

Figure 31: CHANGES IN % ACCEPTABILITY OF CANOLA/SUNFLOWER OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

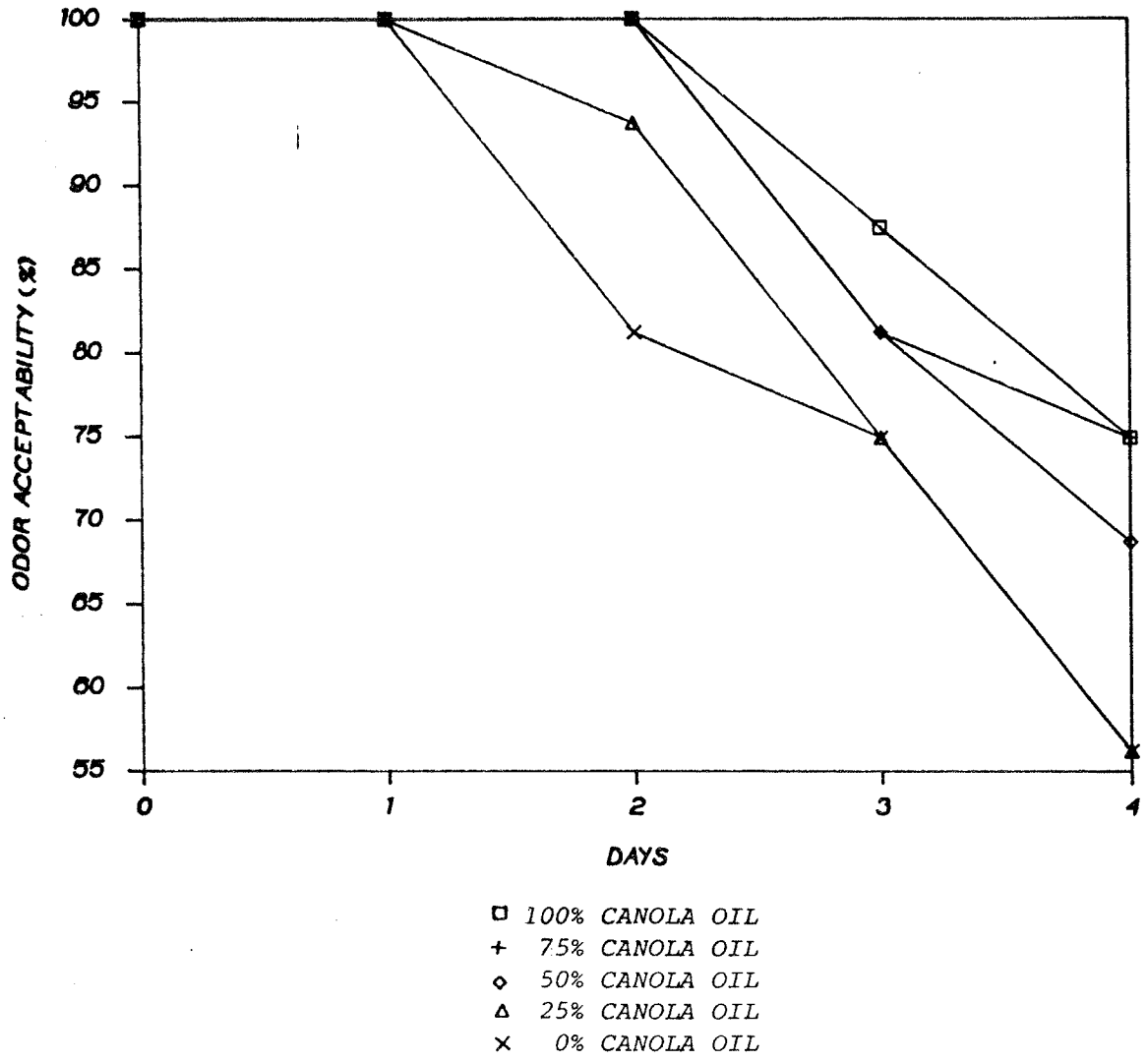

Figure 32: CHANGES IN % ACCEPTABILITY OF CANOLA/COTTONSEED OIL BLENDS DURING FLUORESCENT LIGHT EXPOSURE (250±25 FT.C.) AT 40°C.

4.4 EXPERIMENT 3 : HEATING TO FRYING TEMPERATURE

4.4.1 Chemical Analyses

4.4.1.1 Total Volatile Carbonyl Compounds

All oils and oil blends increased substantially in total volatile carbonyl compounds during the 10 minute heating period, as illustrated in Tables 27 and 28. Both the sunflower oil and the cottonseed oils showed less increase in carbonyl concentration after heating, than did the canola oil. The addition of sunflower oil to canola oil improved the heat stability of canola oil, with a decrease in the accumulation of carbonyl compounds during heating, accompanying an increase in the proportion of sunflower oil.

Relatively little change occurred in carbonyl accumulation as cottonseed oil increased from 0% to 50% of the blend. A dramatic decrease in carbonyl formation on heating was observed, however, as the cottonseed oil was increased to 75% of the blend.

4.4.1.2 Furfural

The change in furfural concentration after heating to 185^{o}C ± 5^{o}C for either the sunflower oil or the cottonseed oil was relatively small as compared to that for the canola oil. A reduction in furfural accumulation occurred, as the proportion of canola oil decreased, upon blending with either sunflower oil or cottonseed oil (Tables 27 and 28).

TABLE 27

THE EFFECT OF HEATING ON THE ACCUMULATION OF VOLATILE CARBONYL COMPOUNDS AND FURFURAL OF CANOLA OIL / SUNFLOWER OIL BLENDS.

BLEND	TOTAL CARBONYLS (µg/100µl) UNHEATED (U)	HEATED (H)	H-U	FURFURAL (µg/100µl) UNHEATED (U)	HEATED (H)	H-U
100% CANOLA OIL	0.906	8.405	7.499	0.011	2.193	2.182
75% CANOLA : 25% SUNFLOWER OIL	0.565	7.797	7.232	0.008	1.360	1.352
50% CANOLA : 50% SUNFLOWER OIL	0.518	6.660	6.142	0.008	0.309	0.301
25% CANOLA : 75% SUNFLOWER OIL	0.654	5.676	5.022	0.010	0.227	0.217
100% SUNFLOWER OIL	0.555	4.498	3.943	0.008	0.100	0.092

TABLE 28

THE EFFECT OF HEATING ON THE ACCUMULATION OF VOLATILE CARBONYL COMPOUNDS AND FURFURAL OF CANOLA OIL / COTTONSEED OIL BLENDS.

BLEND	TOTAL CARBONYLS (µg/100µl)			FURFURAL (µg/100µl)		
	UNHEATED (U)	HEATED (H)	H-U	UNHEATED (U)	HEATED (H)	H-U
100% CANOLA OIL	0.906	8.405	7.499	0.011	2.193	2.182
75% CANOLA OIL 25% COTTONSEED OIL	0.570	8.399	7.829	0.008	0.408	0.400
50% CANOLA 50% COTTONSEED OIL	0.508	8.734	8.226	0.010	0.285	0.275
25% CANOLA 75% COTTONSEED OIL	0.523	5.262	4.739	0.013	0.179	0.166
100% COTTONSEED OIL	0.382	4.608	4.226	0.002	0.113	0.111

4.4.2 Sensory Evaluation

4.4.2.1 Judge Consistency

Pearsons correlation coefficients for individual judges' performances over the two replications are presented in Table 29. All judges had correlation coefficients within the range r = 0.75 ± 0.25.

TABLE 29

CONSISTENCY OF JUDGES' MEASUREMENTS OF ODOR INTENSITY FOR EXPERIMENT 3

JUDGE	r (REP 1 VS REP 2)
1	0.65
2	0.75
3	0.76
4	0.87
5	0.72
6	0.95
7	0.55
8	0.72
9	0.82
10	0.71

4.4.2.2 Total Odor Intensity Value

All oils and oil blends except 100% cottonseed oil increased in odor intensity value (OIV) over the heating period (Tables 30 and 31).

Cottonseed oil remained relatively unchanged in OIV after heating to frying temperature. Sunflower oil developed a less intense odor upon heating than did canola oil. Addition of sunflower oil to canola oil improved the OIV as did the addition of cottonseed oil. The 100% cottonseed oil remained at the same odor intensity as the unheated sample. It should also be noted that the unheated odor intensity increased with the proportion of cottonseed oil.

TABLE 30

THE EFFECT OF HEATING ON THE ODOR INTENSITY VALUE AND ACCEPTABILITY OF CANOLA OIL / SUNFLOWER OIL BLENDS.

BLEND	MEAN ODOR INTENSITY VALUE(cm)			% ACCEPTABILITY		
	UNHEATED (U)	HEATED (H)	H-U	UNHEATED (U)	HEATED (H)	H-U
100% CANOLA OIL	1.3	10.8	9.5	95%	10%	85%
75% CANOLA : 25% SUNFLOWER OIL	0.8	9.3	8.5	95%	30%	65%
50% CANOLA : 50% SUNFLOWER OIL	0.4	8.7	8.3	100%	35%	65%
25% CANOLA : 75% SUNFLOWER OIL	0.7	8.3	7.6	100%	25%	75%
100% SUNFLOWER OIL	0.8	8.2	7.4	100%	45%	55%

TABLE 31

THE EFFECT OF HEATING ON THE ODOR INTENSITY VALUE AND ACCEPTABILITY OF CANOLA OIL / COTTONSEED OIL BLENDS.

BLEND	MEAN ODOR INTENSITY VALUE(cm) UNHEATED (U)	HEATED (H)	H-U	% ACCEPTABILITY UNHEATED (U)	HEATED (H)	H-U
100% CANOLA OIL	1.3	10.8	9.5	95%	10%	85%
75% CANOLA OIL 25% COTTONSEED OIL	1.6	10.9	9.3	95%	5%	90%
50% CANOLA 50% COTTONSEED OIL	3.0	10.4	7.4	75%	20%	55%
25% CANOLA 75% COTTONSEED OIL	3.6	7.3	3.7	80%	35%	45%
100% COTTONSEED OIL	4.8	5.3	0.5	70%	65%	15%

4.4.3 Analysis of Variance

The results of the separate Analyses of Variance (ANOVA) for odor intensity values (OIV) of the sunflower oil blends and the cottonseed oil blends are presented in Tables 32 and 33. The main sources of variation for the sunflower oil set were Heating, Judge, Blend, and a Heating*Judge interaction. The major effects for the cottonseed oil blends were Heated, Judge, a Heated*Judge interaction and a Heated*Blend interaction. The effect of blend on odor development after heating to 185^{0}C for 10 minutes, although it was significant ($p \leq 0.05$) for both sunflower oil and cottonseed oil blends, could not be investigated further due to the significant Blend*Judge interactions ($p \leq 0.05$) The relatively large F values for Heating*Judge interactions appeared to be caused by the fact that the panelists had differing perceptions of the magnitude of difference between unheated and heated samples. The differences in the individual judges' scores for unheated vs. heated samples are illustrated in Figure 33.

4.4.3.1 Acceptablility

All oils and oil blends experienced a decline in acceptability after heating for 10 minutes, (Tables 30 and 31). Canola oil had the least acceptable heated odor of the parent oils, followed by sunflower oil and then cottonseed oil. The level of acceptability was improved as the proportion of sunflower oil is increased. The 75% sunflower oil blend appeared to be out of sequence, being less acceptable after heating than either the 25% sunflower oil or 50% sunflower oil blends. An increase in the proportion of judges reporting acceptability was observed as more

cottonseed oil was added, although, the 25% cottonseed oil was slightly less acceptable than the 100% canola oil.

There was insufficient evidence ($p \leq 0.05$) to reject the null hypothesis that the sunflower oil blends were equal in acceptability after heating (See Appendix C). In contrast, the cottonseed oil blends were significantly different ($p \leq 0.0001$), although they did not increase linearly with the proportion of cottonseed oil.

TABLE 32

ANALYSIS OF VARIANCE OF THE ODOR INTENSITY VALUES FOR THE SUNFLOWER OIL BLENDS UPON HEATING TO 185°C.

SOURCE OF VARIATION	DF	F VALUE	PR > F
HEATING	1	1117.65	0.0001
JUDGE	9	15.50	0.0001
BLEND	4	5.24	0.0007
HEATING*BLEND	4	2.08	0.0887
HEATING*JUDGE	9	12.62	0.0001
JUDGE*BLEND	36	2.42	0.0003
HEATING*JUDGE*BLEND	36	1.18	0.2593

TABLE 33

ANALYSIS OF VARIANCE OF THE ODOR INTENSITY VALUES FOR THE COTTONSEED OIL BLENDS UPON HEATING TO 185°C.

SOURCE OF VARIATION	DF	F VALUE	PR > F
HEATING	1	370.63	0.0001
JUDGE	9	23.24	0.0001
BLEND	4	2.76	0.0320
HEATING*BLEND	4	35.67	0.0001
HEATING*JUDGE	9	8.10	0.0001
JUDGE*BLEND	36	1.70	0.0202
HEATING*JUDGE*BLEND	36	2.23	0.0009

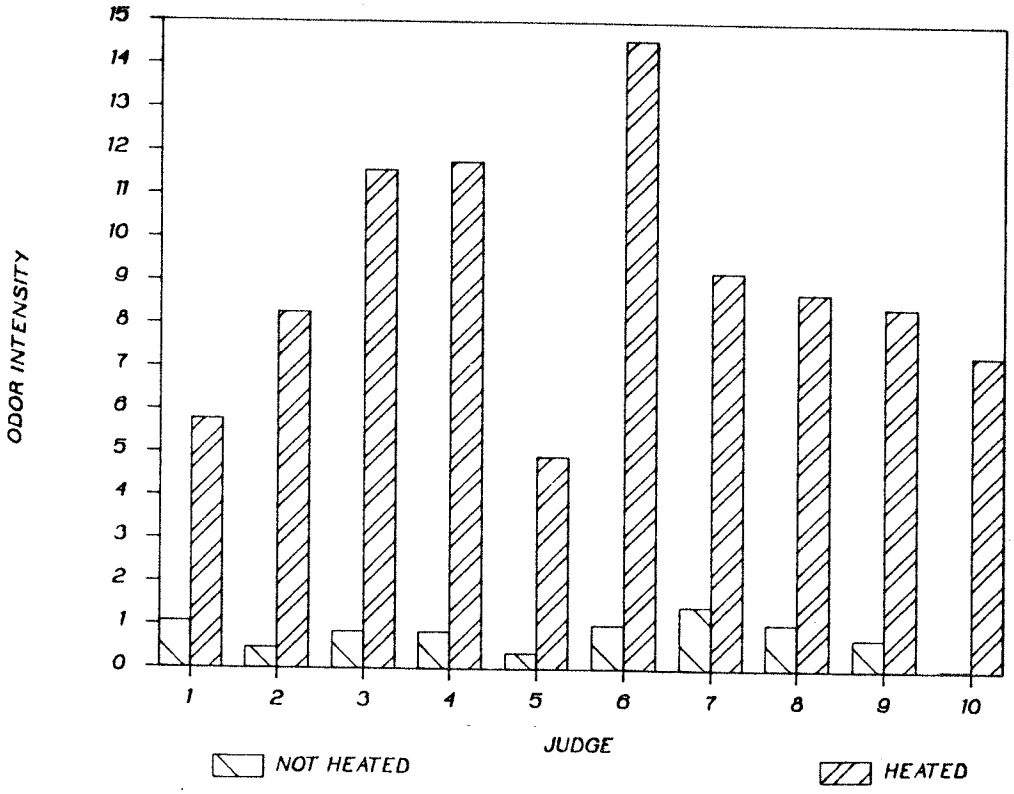

Figure 33: INDIVIDUAL JUDGES' PERCEPTIONS OF MEAN ODOR INTENSITY OF HEATED OILS

4.4.4 The Effect Of Heating Under Nitrogen

A substantial positive effect was evident from the chemical and sensory parameters, upon heating canola oil under nitrogen to exclude the oxygen (Table 34). A summary of the ANOVA (Table 35) indicates a significant difference ($p \leq 0.05$) in odor intensity for the two treatment conditions. The canola oil heated under nitrogen was also significantly more acceptable ($p \leq 0.05$) than that heated in air (See Appendix C).

TABLE 34

THE EFFECT OF HEATING CANOLA OIL AT 185°C UNDER NITROGEN

PARAMETER	UNHEATED (U)	HEATED IN N_2 (H_N)	H_N-U	HEATED IN AIR (H_A)	H_A-U
TOTAL CARBONYLS	0.906	0.958	0.052	8.405	7.458
FURFURAL	0.011	0.045	0.034	2.193	2.182
ODOR INTENSITY VALUE	1.3	8.2	6.9	9.5	8.2
% ACCEPTABILITY	95%	35%	60%	10%	85%

TABLE 35

ANALYSIS OF VARIANCE OF THE ODOR INTENSITY VALUES OF CANOLA OIL HEATED AT 185°C UNDER NITROGEN

SOURCE OF VARIATION	DF	F VALUE	PR > F
TREATMENT	1	4.77	0.0410
JUDGE	9	1.97	0.0996
TREATMENT*JUDGE	9	0.34	0.9484

Chapter V

DISCUSSION

The effect of blending canola oil with two low linolenate oils, namely, sunflower oil and cottonseed oil, on its stability to (1) accelerated storage at 65°C; (2) fluorescent light exposure at 40°C; and (3) heating to frying temperature (185°C) was examined. Stability to these conditions was monitored by sensory and chemical measurements. Since the correlation coefficients between all chemical parameters were high, only one (TBA value) was selected for statistical analysis. The effect of the proportion of canola oil on the odor development of the blend was determined and, as well, the final levels of acceptability for each blend were compared.

5.1 EXPERIMENT 1 : STABILITY TO ACCELERATED STORAGE AT 65°C

The linolenate contents and the final odor intensity values for the oils stored for 12 days at 65°C are presented in Table 36. The addition of either sunflower oil or cottonseed oil to canola oil appeared to retard odor development upon storage in the dark for 12 days at 65°C, with a decrease in C18:3 from 6.4% to 5.7% or less appearing sufficient to cause a significant improvement ($p \leq 0.05$) in odor stability. No significant difference ($\alpha = 0.05$) in acceptability after storage was apparent with the addition of sunflower oil but, in contrast, cottonseed oil did significantly increase ($p \leq 0.001$) the level of acceptability in

a linear fashion. Had a larger population been used, a significant difference in the acceptability of the sunflower oil blends may have been evident. The small sample size of 20 observations, however, meant that one judgement either way caused a 5% change in the proportion, making it more difficult to reject the null hypothesis of equality (Appendix C).

The chemical tests supported the trend of odor intensity development. The slopes of the regression lines for TBA value decreased in order of increased sunflower oil (to 50%) or increased cottonseed oil. While 50% sunflower oil was required for significant difference ($p = 0.012$) in TBA value, only 25% sunflower oil was sufficient for significant improvement of odor intensity. In the case of the cottonseed oil blends, the results from the regression analysis of TBA values, support the results of the sensory analysis without exception.

The TBA test and furfural concentration appeared to correlate the best with odor intensity value (OIV) as would be expected, due to the fact that these chemical tests measure the accumulation of secondary oxidation products which are largely responsible for flavor and odor deterioration (Gunstone, 1984). The low mean correlation coefficients between each of the chemical tests and OIV for the cottonseed oil blends may be due to the strong initial cottonseed oil odor perceived by many of the panelists, but not measured by any of the chemical tests. This phenomenon is supported by the reduction of the Day*Blend interaction upon the removal of the 0 Day cottonseed oil values from the Analysis of Variance. The high Judge*Blend and Judge*Day interactions may be related to the relatively low correlation coefficients for judge consistency.

TABLE 36

FINAL ODOR INTENSITY VALUES AFTER ACCELERATED STORAGE AT 65°C AND LINOLENATE CONTENTS OF THE OIL BLENDS

BLEND	C18:3 CONTENT (%w/w)	FINAL ODOR INTENSITY VALUE (cm)
100% SUNFLOWER OIL	0.4	6.8
75% SUNFLOWER OIL : 25% CANOLA OIL	1.9	6.2
50% SUNFLOWER OIL : 50% CANOLA OIL	4.1	7.5
25% SUNFLOWER OIL : 75% CANOLA	5.2	7.7
100% CANOLA OIL	6.4	8.2[1]
25% COTTONSEED OIL : 75% CANOLA OIL	5.7	6.2
50% COTTONSEED OIL : 50% CANOLA OIL	4.2	5.6
75% COTTONSEED OIL : 25% CANOLA OIL	3.4	4.5
100% COTTONSEED OIL	1.9	3.5

[1] The final OIV for canola oil is a calculated mean for the two samples of stored canola oil.

The relatively high oxidative stability of the cottonseed oil, as shown in this study, is in support of an investigation by Evans et al (1973) into the storage stability of cottonseed oil and hydrogenated soybean oil. Upon storage of the oils for up to one year at 38°C, the cottonseed oil was found to have a better flavor score than the soybean oil.

The quadradic nature of the TBA values of the 75% and 100% sunflower oil samples was not expected. It is possible that the antioxidant mixture added (BHA, BHT, propyl gallate, and citric acid) was not appropriate for sunflower oil, and was not able to protect the oil after 10 days accelerated storage. Morrison et. al. (1981) reported the peroxide value of stored sunflower oil with the same mixture was much greater than with BHA, BHT, and TBHQ or with TBHQ alone. TBHQ was also shown by Sherwin and Luckadoo (1970) and Campbell (1983) to be more effective in limiting peroxide formation of sunflower oil than either BHA or BHT. Alternatively, it is known (deMan, 1980) that antioxidants in high concentrations may exhibit a prooxidant effect. Since sunflower oil naturally contains a relatively high level of tocopherols (Campbell, 1983), the addition of 0.04% of the antioxidant mixture may have caused a greater then optimal concentration of antioxidants.

5.2 EXPERIMENT 2 : STABILITY TO FLUORESCENT LIGHT EXPOSURE AT 40°C

A 50% increase in sunflower oil, from 25% to 75% and from 0% to 50% of the blend, significantly improved ($p \leq 0.05$) the odor stability to light. The 100% canola oil, though, was not significantly different ($\alpha = 0.05$) in odor stability from any of the sunflower oil blends but was less stable than the 100% sunflower oil. The blending of 50-100%

cottonseed oil with canola oil caused a significant increase ($p \leq 0.05$) in the odor intensity. It is possible that this was related to the development of a "light-struck" flavor in cottonseed oil, as described by Fan et. al. (1983), which is caused by the formation of 1-decyne as a result of the photodegradation of the cyclopropenoid fatty acids naturally present in cottonseed oil. The % acceptability of stored canola oil was, however, not significantly affected by the blending with either cottonseed or sunflower oil ($\alpha = 0.05$). This may again be attributable to the small sample size of 16 observations.

Although there was a high degree of correlation between the chemical measurements and odor intensity values for the stored samples from both oil blend sets, the results from the regression analysis did not entirely support the results of the multiple comparison of odor intensity values. For the sunflower oil blends, a similar trend was seen for both the chemical and odor measurements, in that greater odor stability, as well as, a less rapid development of malonaldehyde, occured with decreased canola oil. Significant differences ($p \leq 0.05$) in TBA values over time, were seen between 25% and 50% sunflower oil and between 50% and 75% sunflower oil. The quadradic nature of the sunflower oil exhibited in Experiment 1, was not repeated in Experiment 2.

In the case of the cottonseed oils blends, the significant increase ($p \leq 0.05$) in odor intensity development as cottonseed oil was increased to 50% could be related to a significant increase ($p \leq 0.01$) in the rate of oxidation as measured by TBA value. While the odor intensity continued to increase, although not significantly ($\alpha = 0.05$), the TBA values decreased significantly ($p \leq 0.05$) as cottonseed oil completely replaced canola oil.

Since methyl linolenate has been reported to produce more hydroperoxides, upon photooxidation, than methyl linoleate or methyl oleate (Gunstone, 1984), the sunflower oil and cottonseed oils were expected to be more stable than the canola oil. Sattar and deMan (1976a), however, did not find the photooxidative stability of edible oils and fats to correlate well with the degree of unsaturation. Low erucic acid rapeseed oil had a greater content of C18:3 (12.0%), followed by soybean oil (8.4%) and then corn oil (0.8%). The oxidative stability as measured by flavor score, however, was greatest for the corn oil, followed by the low erucic rapeseed oil, and the soybean oil. It has been suggested that erucic acid may be responsible for the increased stability of rapeseed oil as compared to soybean oil (Roy Carr, personal communication).

5.3 EXPERIMENT 3 : STABILITY TO HEATING TO FRYING TEMPERATURE

Odor stability to heating to 185°C generally increased as sunflower oil or cottonseed oil was added to canola oil. In addition, accumulation of volatile carbonyl compounds and furfural during heating decreased with the addition of sunflower oil. Furfural concentration also decreased with increased cottonseed oil, but accumulation of total volatile carbonyl compounds peaked slightly at the 50% cottonseed oil level and then quickly decreased to 100% cottonseed oil.

The acceptability of the odor of heated canola oil was not significantly affected (α = 0.05) by the addition of sunflower oil, but was significantly improved (p = 0.0001), by the addition of cottonseed oil, although this did not appear to be a linear effect. Dilution of canola

oil with cottonseed oil, in general, had a more pronounced effect on the odor of heated canola oil than did the sunflower oil. The strong initial odor intensity of cottonseed oil was again percieved by many of the panelists and this also affected its initial (unheated) acceptability.

The sunflower oil and cottonseed oil were expected to produce less odor upon heating, than the canola oil, due to their lower C18:3 contents. The results of this study tend to support those of Evans et al (1972) who investigated the room odor of oils and fats, including soybean and cottonseed oils, heated to 192°C. These researchers concluded that the high linolenate content of soybean oil was responsible for its more intense room odor as compared to oils, such as cottonseed, which are high in oleic acid.

5.3.1 The Effect of Heating Under Nitrogen

The exclusion of oxygen during heating of canola oil by nitrogen appeared to reduce significantly ($p \leq 0.05$) the odor of heated canola oil and the odor acceptability. A substantial improvement was also evident in terms of the reduced accumulation of volatile carbonyl compounds and furfural. This is an indication that oxidation was a primary factor in heated oil odor and is in agreement with work carried out by Peers and Swoboda (1982), who used argon to exclude the oxygen.

Chapter VI

CONCLUSIONS

Canola oil was blended with sunflower oil and with cottonseed oil. The blends were subjected to (1) accelerated storage at 65°C; (2) exposure to fluorescent light at 40°C; and (3) heating to frying temperature (185°C). The effect of lowering the linolenic acid (C18:3) content on odor stability, odor acceptability, and, in the first two experiments, on malonaldehyde production, was examined.

6.1 EXPERIMENT 1 : STABILITY TO ACCELERATED STORAGE AT 65°C

1. A decrease in C18:3 content in the blends from 6.4% to 5.7% or less by blending of either 25% sunflower oil or 25% cottonseed oil to canola oil, caused a significant reduction ($p \leq 0.05$) in the rate of increase of odor intensity during the 12 days storage at 65°C.

2. A reduction of C18:3 content from 6.4% to 4.1% by blending canola oil with 50% sunflower oil, or to 5.7% with 25% cottonseed oil, was sufficient to cause a significant decrease ($p \leq 0.05$) in malonaldehyde production, upon accelerated storage at 65°C.

3. The TBA values of the 100% sunflower oil and the 75% sunflower:25% canola oil blend, stored for 12 days at 65°C, were observed to fit a quadradic model, while all other oils and blends were linear in nature. This may have been a result of the antioxidant mixture used.

4. The addition of sunflower oil to canola oil did not cause a significant change ($\alpha = 0.05$) in odor acceptability upon accelerated storage, but the addition of cottonseed oil did significantly increase ($p \leq 0.001$) the level of acceptability after storage, and in a linear fashion.

5. High positive correlations were seen for all methods of measurement of oxidation, during accelerated storage at 65°C, for the sunflower oil blends; those that measured secondary oxidation products (ie. TBA and Furfural) correlated the best with odor intensity value.

6. High positive correlations were also seen for the chemical tests of oxidation for the cottonseed oil, during 12 days storage at 65°C. However, the strong initial odor of the oil, as perceived by many of the panelists, was reflected in poor correlations of odor intensity value with the chemical tests, as well as, a high F value for the Day*Blend interaction in the ANOVA.

6.2 EXPERIMENT 2 : STABILITY TO FLUORESCENT LIGHT EXPOSURE AT 40°C

1. With fluorescent light exposure at 40°C, no significant improvement ($\alpha = 0.05$) in the odor intensity of canola oil was evident upon blending with sunflower oil, although the two parent oils were significantly different ($p \leq 0.05$) and significant differences in odor intensity were seen between certain blends of canola and sunflower.

2. The cottonseed oil blends exhibited a significant increase ($p \leq 0.05$) in odor intensity, during fluorescent light exposure at 40°C, as

cottonseed oil was increased. This is suggested to be due to development of "light-struck" flavor.

3. A significant decrease ($p \leq 0.05$) in TBA value over time of fluorescent light exposure was observed as the C18:3 content was reduced from 6.4% to 4.1% by blending 50% sunflower oil with canola oil.

4. A significant increase ($p \leq 0.01$) in malonaldehyde formation over time of fluorescent light exposure was the result of addition of cottonseed oil to 50%, afterwhich, a significant decrease occured ($p \leq 0.05$).

5. Blending with either sunflower or cottonseed oil exhibited no significant effect on the odor acceptability ($\alpha = 0.05$) after fluorescent light exposure.

6.3 EXPERIMENT 3 : STABILITY TO HEATING TO FRYING TEMPERATURE

1. The addition of sunflower oil or cottonseed oil to canola oil caused a reduction in the heated odor intensity, as well as the accumulation of volatile carbonyl compounds and furfural.

2. Acceptability of heated canola oil was significantly increased by blending with cottonseed oil ($p = 0.0001$) but was not significantly affected by blending with sunflower oil ($\alpha = 0.05$).

3. The exclusion of oxygen by nitrogen significantly improved the heated odor and level of acceptability ($p \leq 0.05$) of canola oil and also reduced the accumulation of total volatile carbonyl compounds and furfural.

6.4 GENERAL SUMMARY AND RECOMMENDATIONS

In general, the stability of canola oil to accelerated storage in heat and in light, as well as, during heating to frying temperature, was improved by the lowering of the linolenic acid content. With one exception, blends which contained 25% canola oil, and which could be compared statistically, were not significantly different (in terms of odor development or rate of change in TBA value upon accelerated storage in heat or light) from their parent sunflower or cottonseed oil. The exception was in the case of the TBA values of the cottonseed oil blends stored under fluorscent light at 40°C. Blending with 50% canola oil, did not cause a significant difference in (1) odor development of the sunflower oil blends during accelerated storage at 65°C; and (2) odor development of the cottonseed oil blends exposed to fluorescent light at 40°C. Odor acceptability, under any of the experimental conditions, seemed to be unaffected by blending sunflower oil with canola oil. Odor acceptability was significantly improved by blending cottonseed oil with canola oil under all of the experimental conditions, except upon fluorescent light exposure where no significant changes in acceptability were observed.

Based on the results from this study, 25% canola oil can be successfully blended with 75% sunflower oil or cottonseed oil to produce oils which are close in odor stability to that of the original parent sunflower or cottonseed oil.

Recommendations for further research include the use of a larger population for the determination of odor acceptability; examination of the role of antioxidants on the accelerated storage of sunflower oil at

65°C; and verification of 1-decyne as the cause of the low photooxidative stability of cottonseed oil in this study. The stability of oil blends containing between 25% and 50% canola oil also merits investigation.

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Appendix A

BARTLETT'S TEST FOR HOMOGENEITY OF VARIANCE.

H_0: $r_1^2 = r_2^2 = r_3^2 = \ldots r_r^2$

H : not all r_i^2 equal

$$\hat{\chi}_0^2 = 2.3026 \frac{q}{c} \qquad \text{with } r-1 \text{ df}$$

where $$q = (N-2r)\log_{10} Sp^2 - \sum_{i=1}^{r}(n_i - 2)\log S_i^2$$

$$c = 1 + \frac{1}{3(r-1)}\left[\sum_{i=1}^{r}(n-2)^2 - (N-2r)^{-1}\right]$$

$$Sp^2 = \frac{\sum (n_i - 2)S_i^2}{\sum (n_i - 2)}$$

A1. EXPT. 1

$r = 8$

$n = 7 \times 2 = 14$

$N = 8 \times 7(2) = 112$

Calculation:

$Sp^2 = 0.0043313$

$q = 5.39609$

$c = 1.0312$

$\hat{\chi}_0^2 = 12.0491$

$\hat{\chi}^2_{.95,7} = 14.0671$

$p = .10$ $\therefore$ Fail to reject H_0 : variances are equal.

Appendix A. continued
A2. EXPT. 2

All Blends:

$r = 9$

$n_i = 5 \times 2 = 10$

$N = 9 \times 10 = 90$

Calculation:

$Sp^2 = 2.6869 \times 10^4$

$q = 13.8945$

$c = 1.0463$

$\chi_0^2 = 30.58$

$\chi^2_{.95,8} = 15.51$

$p = 0.01$

$\therefore$ Reject H_0 : variances are not equal

All Blends - D and E:

$r = 7$

$n_i = 5 \times 2 = 10$

$N = 7 \times 10 = 70$

Calculation:

$Sp^2 = 3.3620134$

$q = 3.7783$

$c = 1.0476$

$\chi_0^2 = 8.3046$

$\chi^2_{.95,6} = 12.592$

$p = 0.22$

$\therefore$ Fail to reject H_0: variances are equal.

Appendix B

T STATISTIC FOR COMPARISON OF TBA REGRESSION SLOPES.

$$T = \frac{\hat{m}_1 - \hat{m}_2}{\sqrt{Sp^2 \left(\frac{1}{\Sigma (X_{1i} - \bar{X}_1)^2} + \frac{1}{\Sigma (X_{2i} - \bar{X}_2)^2} \right)}}$$

Appendix C

CHI SQUARE CALCULATIONS OF DIFFERENCES IN % ACCEPTABILITY.

* H_{01}: proportions are equal
* H_{02}: acceptability varies linearly with amount of canola oil in blend
* H_{03}: slope of line = 0

C1 ACCEPTABILITY OF SUNFLOWER OIL BLENDS STORED 12 DAYS AT 65°C.

OIL BLEND	NUMBER OF OBSERVATIONS	PROPORTION OF PANEL REPORTING ACCEPTABILITY
100% CANOLA OIL	20	.40
75% CANOLA : 25% SUNFLOWER OIL	20	.55
50% CANOLA : 50% SUNFLOWER OIL	20	.70
25% CANOLA : 75% SUNFLOWER OIL	20	.55
100% SUNFLOWER OIL	20	.45

$\chi^2 = 4.26$

$p = 0.37$

$\therefore$ Fail to reject H_0 : prorportions are equal.

Appendix C. continued.

C2. ACCEPTABILITY OF COTTONSEED OIL BLENDS STORED 12 DAYS AT 65°C.

OIL BLEND	NUMBER OF OBSERVATIONS	PROPORTION OF PANEL REPORTING ACCEPTABILITY
100% CANOLA OIL	20	.45
75% CANOLA : 25% COTTONSEED OIL	20	.60
50% CANOLA : 50% COTTONSEED	20	.75
25% CANOLA : 75% COTTONSEED OIL	20	.85
100% COTTONSEED OIL	20	1.00

$\chi^2 = 18.54$

$p = 0.001$

$\therefore$ Reject Ho; proportions are not equal.

$\chi^2 = 0.0913$

$p = 0.997$

$\therefore$ Fail to reject Ho; % acceptability increases linearily with % cottonseed oil.

$\chi^2 = 18.49$

$P = 0.00001$

$\therefore$ Reject Ho; slope $\neq 0$.

Appendix C continued.

C3 ACCEPTABILITY OF SUNFLOWER OIL BLENDS STORED UNDER FLUORESCENT LIGHT

OIL BLEND	NUMBER OF OBSERVATIONS	PROPORTION OF PANEL REPORTING ACCEPTABILITY
100% CANOLA OIL	16	.75
75% CANOLA : 25% SUNFLOWER OIL	16	.81
50% CANOLA : 50% SUNFLOWER OIL	16	.81
25% CANOLA : 75% SUNFLOWER OIL	16	.87
100% SUNFLOWER OIL	16	1.00

$\chi^2 = 4.59$

$p = 0.33$

$\therefore$ Fail to reject H_0 : proportions are equal.

Appendix C. continued.

C4. ACCEPTABILITY OF COTTONSEED OIL BLENDS STORED UNDER FLUORESCENT LIGHT

OIL BLEND	NUMBER OF OBSERVATIONS	PROPORTION OF PANEL REPORTING ACCEPTABILITY
100% CANOLA OIL	16	.75
75% CANOLA : 25% COTTONSEED OIL	16	.75
50% CANOLA : 50% COTTONSEED	16	.69
25% CANOLA : 75% COTTONSEED OIL	16	.56
100% COTTONSEED OIL	16	.56

$\chi^2 = 2.654$

$p = 0.62$

$\therefore$ Fail to reject H_0 : proportions are equal.

Appendix C continued.

C5. ACCEPTABILITY OF HEATED SUNFLOWER OIL BLENDS.

OIL BLEND	NUMBER OF OBSERVATIONS	PROPORTION OF PANEL REPORTING ACCEPTABILITY
100% CANOLA OIL	20	.10
75% CANOLA : 25% SUNFLOWER OIL	20	.30
50% CANOLA : 50% SUNFLOWER OIL	20	.35
25% CANOLA : 75% SUNFLOWER OIL	20	.25
100% SUNFLOWER OIL	20	.45

$\chi^2 = 6.508$

$p = 0.16$

$\therefore$ Fail to reject H_0 : proportions are equal.

Appendix C. continued.

C6. ACCEPTABILITY OF HEATED COTTONSEED OIL BLENDS.

OIL BLEND	NUMBER OF OBSERVATIONS	PROPORTION OF PANEL REPORTING ACCEPTABILITY
100% CANOLA OIL	20	.10
75% CANOLA : 25% COTTONSEED OIL	20	.05
50% CANOLA : 50% COTTONSEED	20	.20
25% CANOLA : 75% COTTONSEED OIL	20	.35
100% COTTONSEED OIL	20	.65

$\chi^2 = 23.67$

$p = 0.0001$

$\therefore$ Reject H_0; proportions are not equal.

Appendix C. continued.

C7. MEAN ACCEPTABILITY OF CANOLA OIL HEATED IN TWO MEDIA.

TREATMENT	NUMBER OF OBSERVATIONS	PROPORTION OF PANEL REPORTING ACCEPTABILITY
HEATED IN AIR	20	.10
HEATED IN N_2	20	.35

$\chi^2 = 4.06$

$p = 0.045$

$\therefore$ Reject H_0 : proportions are not equal.