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Storage Stability and Frying Performance of Solin and Sunflower Oils

by

Donald Joseph Kibiuk

A Thesis

Submitted to the Faculty of Graduate Studies
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STORAGE STABILITY AND FRYING PERFORMANCE OF SOLIN AND SUNFLOWER OILS

BY

DONALD JOSEPH KIBIUK

**A Thesis/Practicum submitted to the Faculty of Graduate Studies of the University of Manitoba in partial
fulfillment of the requirements for the degree of**

MASTER OF SCIENCE

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ABSTRACT

The development of low linolenic (<5%) flaxseed varieties (solin) has resulted in a new edible oil for use in food applications. Since the fatty acid composition of solin oil (18:1: 16.8%, 18:2: 70.1%, 18:3: 1.9%) is similar to that of sunflower oil (18:1 16.7%, 18:2: 70.3%, 18:3: 0.5%), the two oils were compared for their storage stability and for their use in the frying of potato chips.

Storage stability of the oils was assessed by storing the oils for 0, 1, 2, 4, 6, 8, 12, and 16 days under accelerated heat conditions at 60°C and for 0, 1, 2, 3, 4, 6, and 8 days under accelerated light conditions with an intensity of 4360 lux at 40°C. Solin oil showed greater stability to peroxide development but was less stable to painty odor development than sunflower oil during accelerated heat storage. Both oils showed similar levels of total volatiles and volatile subclasses over the 16 days of storage. Under accelerated light conditions, solin oil showed greater stability to peroxide development and flavor volatiles compared to sunflower oil. Neither oil developed an intense painty odor intensity during the 8 days of storage.

The storage stability of potato chips fried in solin and sunflower oils was compared to potato chips fried in hydrogenated soybean oil (HSO). Chips were fried in a *Garland* institutional fryer at $185 \pm 5^\circ\text{C}$ and packaged into 7.6 x 11.4 cm bags prepared from commercial packaging material comprised of a plastic laminate with a foil lining. Samples were stored for 0, 4, 8, 12, 16, and 20 days at 60°C. All chips had an intense fresh potato chip (FPC) odor at 0 days

which rapidly decreased with storage. Chips fried in solin and sunflower oils showed an increase in stale odor during early storage intervals (4, 8 days) followed by an intense rancid odor by the end of storage. As storage progressed, stale odor increased in chips fried in HSO while sour-cheesy odor peaked at storage day 4. Chips fried in sunflower oil showed an increase in conjugated dienes and total polars at storage day 4 whereas chips fried in solin oil showed an increase at storage day 12. Thus, chips fried in sunflower oil had a significantly ($p \leq 0.05$) greater rate of increase in conjugated dienes during time period I (0, 4, 8 days). This was not observed in time period II (12, 16, 20 days). Chips fried in both oils showed similar rates of development of total polars during time periods I and II. Chips fried in solin and sunflower oils showed rapid increases in total volatiles at storage day 12. Chips fried in sunflower oil had significantly ($p \leq 0.05$) greater rates of development of total volatiles and all volatile sub-classes during time period II (12, 16, 20 days) compared to chips fried in solin oil. Chips fried in HSO showed little change in conjugated dienes and total polars and flavor volatiles during storage.

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Chapter 1

INTRODUCTION

Flax was introduced to North America by early settlers. Cultivated flax, *Linum usitatissimum* L., is grown for two purposes, fibre and oil (linseed oil). Historically, varieties of flax grown for fibre were used to manufacture linen in North America, but due to cotton production in the United States, the growth of flax for this purpose was severely limited (*Flax Council of Canada*, 1991). As a result, the strength of the flax industry in North America was built on the cultivation of oil producing varieties. Industrial linseed oil is used in paints and coatings, linoleum, oil cloth, soap, patent leather, brake linings and herbicide adjuvants (Carter, 1993). Currently, there is no commercial production of fibre flax in North America but flax straw as a by-product of oilseed flax varieties is used as a source of fibre for cigarette and bond papers and will be used in oriented straw board in the future (*Flax Council of Canada*, 1991; B. Hall, personal communication, 1996).

The high linolenic (18:3) acid content of linseed oil (45 - 65%) gives the oil its rapid drying quality making it extremely suitable for paints, inks and varnishes (Haumann, 1990). Due to increased use of synthetic drying agents however, demand for linseed oil as an industrial oil has remained static since the mid-1960's (Haumann, 1990). Because linolenic acid rapidly oxidizes in the presence of oxygen, linseed oil readily develops off-flavors which limits its use in food products (Rowland, 1994). Recently, there has been an increase in the

use of whole and milled flaxseed in bakery products but it is estimated that only 2% of harvested flaxseed is used in this capacity (B. Hall, personal communication, 1996). As a consequence, research efforts have expanded to generate low linolenic flaxseed varieties suitable for use in the food industry (Haumann, 1990).

In 1979, Green of the *Commonwealth Scientific and Industrial Research Organization (CSIRO)* in Australia began a plant breeding program to develop a flaxseed genotype with low levels of linolenic acid (Haumann, 1990). Using the Australian cultivar *Glenelg* and chemical mutagenic agents and gamma radiation, two mutant lines were isolated with reduced levels of linolenic acid and corresponding increases in linoleic (18:2) acid (Haumann, 1990). After recombining the two mutants, a genotype containing less than 2% linolenic acid and 46% linoleic acid was produced (Haumann, 1990). After further genetic modifications, the level of linoleic acid was raised to between 65 and 75% depending on the variety and the growing conditions (Green and Dribnenki, 1994). This new oilseed crop was named *Linola*TM and is being developed exclusively through a joint venture between *CSIRO* and *United Grain Growers (UGG)* of Canada. The fatty acid composition of *Linola*TM is similar to that of sunflower oil and is currently being marketed by *UGG* as a premium polyunsaturated oil (Green and Dribnenki, 1994).

Rowland at the *Crop Development Centre (CDC)* at the *University of Saskatchewan*, has also developed a flax mutagenesis program. Using the

Canadian cultivar *McGregor* and a chemical mutagenic agent, Rowland has developed similar low linolenic lines to those of Green at *CSIRO* (Rowland, 1994). The low linolenic varieties developed at the *CDC* will be marketed by the *Saskatchewan Wheat Pool*. In addition, two other mutant lines have been identified at the *CDC*, one with elevated levels of palmitic (16:0) acid and low linolenic acid levels and one with elevated levels of oleic (18:1) acid and low linolenic acid levels (Rowland, 1994). The high palmitic varieties may be suitable in margarines while both varieties may be suited for frying applications (Rowland, 1994).

In 1994, the *Flax Council of Canada* responded to the developments in flax research by introducing the name *solin* to represent flax varieties with less than 5% linolenic acid. The Canadian Grain Commission in consultation with the flax industry and plant breeders, adopted the specification that solin varieties have yellow seed coats in order to prevent confusion with traditional flax varieties (brown seed coat) in the grain handling system (*Flax Council of Canada*, 1996). In 1994, the first commercial *Linola*TM crop saw 30,000 acres planted in Manitoba and Saskatchewan which translated into 7,000 tons of oil (*Anon.*, 1995). Estimates for the 1995 *Linola*TM plantings were between 220,000 and 250,000 acres (B. Hall, personal communication, 1996). Because of the colour requirement, Rowland of the *CDC* does not expect to release a yellow-seeded variety until 1997 (*Anon.*, 1995).

The development of high-stability edible oils is becoming increasingly

important for use in a variety of applications within the food industry. Currently, no published information exists on the stability of solin oil. If this edible oil is to be used as an alternative to other vegetable oils, research in this area is imperative. Thus, the objectives of this research were: 1) to compare the storage stability of solin and sunflower oils under accelerated heat and accelerated light conditions; and 2) to compare the storage stability of potato chips fried in solin, sunflower and hydrogenated soybean (HSO) oils.

Chapter 2

REVIEW OF LITERATURE

Oil quality and stability are important parameters of edible oils. Oil quality is defined as the present state of oil acceptability whereas oil stability refers to the oil's resistance to future changes (Smouse, 1995). The storage stability of refined edible oils and the storage stability of products fried in edible oils is affected by storage time, storage temperature and conditions (heat, light), the presence of metals and the degree of unsaturation.

2.1 STORAGE STABILITY

During storage, edible oils develop off-flavors resulting from the oxidation of unsaturated fatty acids. Depending on storage conditions, oils can undergo autoxidation and/or photosensitized oxidation.

2.1.1 Autoxidation

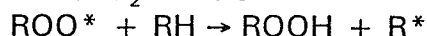
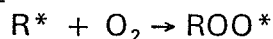
Free radical autoxidation of unsaturated fatty acids is a three step process consisting of: initiation, propagation, and termination (Hawrysh, 1990). During initiation, a free radical (R^*) is formed through the action of heat, light or metal catalysts on the hydrogen atom (RH) adjacent to the double bond in the fatty acid (Hawrysh, 1990). In the propagation step, the free radical (R^*) reacts with oxygen to form unstable peroxy radicals (ROO^*). These products may abstract hydrogen from another unsaturated fatty acid to form a hydroperoxide ($ROOH$) and a new free radical (R^*) (Frankel, 1985; Hawrysh, 1990). Termination can occur with the formation of non-radical products

through the interaction of the free radical (R^*) and peroxy radical (ROO^*) (Frankel, 1985). The process can be summarized as follows:

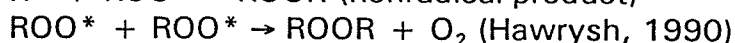
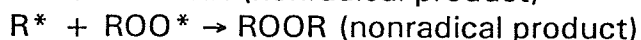
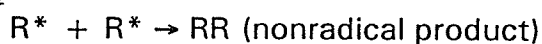
Initiation:



Propagation:



Termination:



Hydroperoxides and free radicals are classified as primary oxidation products (Badings, 1970). Hydroperoxides are flavorless but unstable intermediates that can break down causing the release of volatile decomposition products (VDPs). VDPs include compounds such as: aldehydes, alcohols, ketones, acids, and hydrocarbons (Frankel, 1985; Grosch, 1987). These secondary oxidation products are responsible for the development of off-flavors in vegetable oils (Liu and White, 1992). The specific volatile compounds produced are dependent on the hydroperoxides formed and the fatty acids involved (Przybylski and Eskin, 1995). Volatile compounds formed during free radical autoxidation of oleate, linoleate, and linolenate hydroperoxides are listed in Table 2.1.

Table 2.1 Volatile compounds with flavor significance formed from hydroperoxides during free radical autoxidation (compounds listed in order of decreasing amounts). ¹

Oleate Hydroperoxides (8-,9-,10- and 11-OOH)	Linoleate Hydroperoxides (9-OOH and 13-OOH)	Linolenate Hydroperoxides (9-,12-,13- and 16-OOH)
nonanal octanal 2-decenal heptane decanal octane 1-octanol 2-undecenal heptanol	hexanal 2,4-decadienal pentane 2-nonenal 1-pentanol pentanal	2,4,7-decatrienal ethane/ethene 2,4-heptadienal propanal/propenal 2-/3-hexenal 2-pentenal 3,6-nonadienal

In order to assess the stability of oil to autoxidation, oils are stored in the dark at elevated temperatures (60-65°C) to accelerate the oxidation process (Malcolmson et al., 1994). Samples are removed from storage at pre-determined intervals and assessed for quality using sensory, chemical and gas chromatographic (GC) methods.

Hawrysh (1993a) compared the storage stability of solin, sunflower and canola oils. Samples (68 g) were placed in 100 mL beakers and stored at 65°C, for 0, 4, 8, 12, and 16 days. A 10-member trained sensory panel evaluated the stored oils for overall odor, grassy, painty, rancid, and cardboard intensity using 15 cm unstructured line scales (0 = none, 15 = extreme). At each storage interval, canola oil had higher overall odor intensities than solin and sunflower oils while solin and canola oils had higher grassy odor scores

¹adapted from Przybylski and Eskin (1995)

than sunflower oil. Canola oil had a significantly greater increase in painty and rancid odor intensities throughout storage compared to solin and sunflower oils. Solin and sunflower oils exhibited significantly higher cardboard odor intensities during storage than canola oil. Sunflower oil exhibited greater peroxide formation than solin and canola oils. In addition, sunflower oil showed significantly greater conjugated dienes compared to solin and canola oils at 12 and 16 days of storage. Solin oil had significantly higher levels of total volatiles than canola or sunflower oils. Hawrysh concluded that canola oil developed stronger and more undesirable characteristics during storage than solin and sunflower oils. The chemical data indicated that solin oil was more stable than sunflower oil, however, the GC results suggested that solin oil exhibited greater changes throughout storage.

Warner and colleagues (1989) investigated the stability of soybean, sunflower, and canola oils. Eight ounce (250 mL) glass jars were filled two-thirds full with oil and loosely covered. The samples were stored at 60°C in the dark with and without the addition of citric acid (100 ppm). Samples stored with citric acid were removed from storage at day 0, 4, and 8 while samples stored without citric acid were removed from storage at day 0, 2, and 4. A 15-member trained sensory panel evaluated the oils using the AOCS (1990) ten point flavor/odor intensity scales (10 = bland, 1 = strong) and the flavor/odor descriptor scale which provides the panel with an attribute list and a three point intensity scale (1 = weak, 2 = moderate, 3 = strong). All

freshly deodorized oils were described as nutty and buttery. At storage day 4 for oils without citric acid, soybean oil had significantly higher flavor scores (less overall intensity) than canola and sunflower oils, and sunflower oil had higher flavor scores than canola oil. At storage day 8 for oils containing citric acid, soybean oil had significantly higher flavor scores (less overall intensity) than both canola and sunflower oils. In the early stages of oxidation, soybean oil was described as grassy and beany, sunflower oil as pine/cedar, weedy and acrid while cabbage, sulphur and grassy were descriptors used to characterize canola oil. All oils were described as rancid at later stages of oxidation. Soybean and canola oils which contain high levels of linolenic acid relative to sunflower oil, were also described as painty while only canola oil was reported as having a fishy flavor at later stages of oxidation. At day 8 of storage, the peroxide value for sunflower oil was significantly higher than for either canola or soybean oils. Sunflower oil also developed significantly more volatiles than canola or soybean oils indicating greater formation of secondary oxidation products and therefore greater potential for off-flavor development. Thus, depending on the analyses used to measure stability, there were differences amongst the oils with respect to flavor quality and oxidative stability.

Durance (1986) investigated the effects of accelerated heat storage on the stability of canola/sunflower oil blends. Samples (60 ml) were placed in uncovered 80 mL red pyrex glasses and stored in the dark at 65°C. Samples were removed after 0, 2, 4, 6, 8, 10, and 12 day intervals and underwent

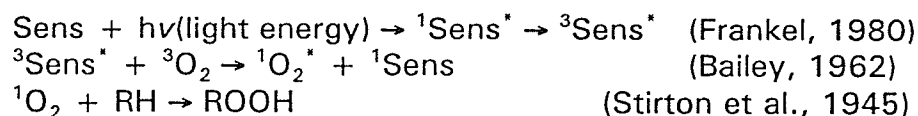
sensory and chemical analyses. Sensory evaluation was carried out by a 10-member trained panel which evaluated the oil samples for overall odor intensity using a 15 cm semi-structured line scale (0 = bland, 15 = strong). After day 4 of storage, the odor intensities of 100% sunflower oil and 100% canola oil began to increase. Malcolmson et al., (1994) termed this a four day induction period. Upon further storage, canola oil had a significantly greater odor intensity than sunflower oil. As the proportion of sunflower oil to canola oil increased, a general decrease in the odor intensity value was observed although the 50% canola oil:50% sunflower oil blend had the lowest odor intensity value overall. The largest final accumulation of volatile carbonyl compounds was found for the 100% canola oil sample. With the addition of sunflower oil, the final carbonyl concentration was reduced. In contrast to the sensory and volatile carbonyl results, three of the chemical indices indicated that sunflower oil exhibited greater changes than canola oil. Sunflower oil had the highest level of peroxides by storage day 12 which was two times higher than canola oil. Generally, as the proportion of sunflower oil to canola increased, there was a consistent increase in peroxide levels at the final day of storage. Furthermore, sunflower oil developed the greatest accumulation of hydroperoxides and exhibited the greatest increase in thiobarbituric acid values. In summary, sunflower oil showed greater formation of primary oxidation products but developed less secondary oxidation products compared to canola oil.

Huang and colleagues (1981) compared the stability of sunflower oil and corn oil to accelerated heat storage. Oil samples were stored in half-filled, clear, pint-sized (500 mL) glass bottles, capped under air and stored at 35°C in the dark for 7, 14, 21, and 28 days. A 7-member trained sensory panel evaluated the samples for odor and flavor strength using a 9-point scale (1 = weak, 5 = moderate, and 9 = strong). Corn oil was found to have higher odor and flavor scores than sunflower oil but sunflower oil developed peroxides more rapidly than corn oil.

2.1.2 *Photosensitized oxidation*

Formation of hydroperoxides can occur when unsaturated fatty acids are exposed to light, in the presence of oxygen and a sensitizer (Frankel, 1985). Sensitizers include chlorophyll and related heme compounds, methylene blue, fluorescein derivatives, and polycyclic aromatic hydrocarbons (Frankel, 1985). Photosensitized oxidation generally involves the light excitation of a sensitizer to the singlet state ($^1\text{Sens}^*$) followed by a intersystem crossing to the triplet state ($^3\text{Sens}^*$) (Frankel, 1980). Energy can be transferred from triplet sensitizer ($^3\text{Sens}^*$) to ground state triplet oxygen ($^3\text{O}_2$) which then can be activated into the singlet state ($^1\text{O}_2$) (Bailey, 1962). The reaction between the singlet state oxygen ($^1\text{O}_2$) and an acceptor (RH) leads to the formation of a hydroperoxide (ROOH) (Stirton et al., 1945).

The reaction can be summarized as follows:



In contrast to free radical autoxidation, singlet state oxygen (${}^1\text{O}_2$) reacts directly with the double bond (Frankel, 1980). Oxygen can be inserted at either carbon of the double bond which becomes shifted and forms a hydroperoxide (Frankel, 1985). In addition, photosensitized oxidation occurs at a much faster rate than autoxidation (Hawrysh, 1990). Singlet state oxygen (${}^1\text{O}_2$) reacts with linoleate at least 1500 times faster than normal triplet state oxygen (${}^3\text{O}_2$) (Rawls and Van Santen, 1970). Photosensitized oxidation, like free radical autoxidation, can result in the breakdown of hydroperoxides to volatile compounds leading to the development of off-flavors. Volatile compounds formed during photosensitized oxidation of oleate, linoleate, and linolenate hydroperoxides are listed in Table 2.2.

Table 2.2 Volatile compounds with flavor significance formed from hydroperoxides during photosensitized oxidation (compounds listed in order of decreasing amounts)²

Oleate Hydroperoxides (9-OOH and 10-OOH)	Linoleate Hydroperoxides (9-,10-,12- and 13-OOH)	Linolenate Hydroperoxides (9-,10-,12-,13-,15- and 16-OOH)
2-decenal nonanal octane 1-octanol	hexanal 2-heptenal 2,4-decadienal pentane 2-nonenal pentanal 1-octen-3-ol 2-octen-1-ol 1-pentanol	2-butenal propanal/propenal 2,4-heptadienal 2,4,7-decatrienal 2-/3-hexenal ethane/ethene 3,6-nonadienal 2-pentenal

Photosensitized oxidation and free radical autoxidation may act synergistically (R. Przybylski, personal communication, 1994). Photosensitized oxidation may initiate free radical autoxidation through the formation of peroxy and alkoxy radicals and act to accelerate the rate of autoxidation (Frankel, 1985).

In order to assess the stability of oil to photosensitized oxidation, oils are stored under light conditions and removed from storage at pre-determined intervals and assessed for quality using sensory, chemical and GC volatile methods. A variety of sample sizes, light intensities and temperatures have been employed to accelerate this process (Malcolmson et al., 1994). Storage temperatures ranging from ambient temperature to 40°C and light intensities

²adapted from Przybylski and Eskin (1995)

from 1200 lux to 7535 lux have been used. Such variation in testing conditions makes comparisons between studies difficult (Malcolmson et al., 1994).

Warner et al. (1989) studied the stability of soybean, canola and sunflower oils to fluorescent light. Oil samples were placed in eight oz (250 mL) narrow-mouthed, clear, glass bottles (two-thirds full) and exposed to fluorescent light with an intensity of 7535 lux at 30°C. Samples without citric acid were removed from storage at 0, 4, and 8 hours while samples containing citric acid were removed from storage after 0, 8, and 16 hours. The oils were evaluated by a 15-member trained panel using a 10-point flavor/odor score and a 3-point flavor/odor descriptor scale, both described previously. In the absence of citric acid, sunflower oil had significantly higher flavor scores (less overall intensity) than canola or soybean oils. Canola and sunflower oils containing citric acid were judged to have similar flavor scores and were significantly less intense in overall flavor than the soybean oil. Flavor/odor descriptors used to characterize the oils exposed to fluorescent light were distinctly different than those used to describe the oils subjected to accelerated heat storage in the dark. Soybean and canola oils stored under light were described as grassy, sour, metallic or buttery, while sunflower oil was described as stale or sour. Peroxide values were not significantly different between the three oils. Volatile analysis indicated that sunflower and soybean oils developed significantly more total volatiles than canola oil with or without

citric acid. Thus, for oils containing citric acid, both sunflower and canola oils were more stable than soybean oil whereas in the absence of citric acid, both sunflower and soybean oils were more stable than canola oil.

Morrison et al. (1981) investigated the effects of storage under different light conditions and container types on the stability of sunflower oil. Three storage treatments were compared: 1) dark storage at room temperature using clear glass bottles; 2) light storage (1400 lux) at room temperature using clear glass bottles; and 3) light storage (1400 lux) at room temperature using amber glass bottles. Eight oz (250 mL) bottles were filled with 180 mL aliquots of oil, tightly capped and stored for 0, 4, 8, 12, and 16 weeks. The samples were evaluated by a 10-member trained panel for flavor/odor intensity using 10 point intensity scales (5 = extreme, 1 = bland with 0.5 increments). Panelists also checked the appropriate flavor/odor descriptor (i.e. buttery, green beany, green creamy, nutty, rancid, or painty) and rated the intensity of the descriptor as either weak, moderate or strong. The flavor/odor descriptor scale was quantified as the flavor intensity value (FIV). FIV equalled the intensity-weighted summations of the flavor responses divided by the number of panelists (n):
$$FIV = [(no. \text{ of weak responses}) + 2(no. \text{ of moderate responses}) + 3(no. \text{ of strong responses})]/n.$$
 FIVs range from 0.0 to 3.0 (Cowan, 1970). As the storage time increased, the flavor/odor intensity score increased, corresponding to an increase in FIVs for rancid and painty and a decrease in FIVs for buttery and green beany. Not surprisingly, samples stored in clear

bottles in the light received higher flavor/odor intensity scores than samples stored in amber bottles exposed to light or in clear bottles stored in the dark.

Durance (1986) examined the effects of fluorescent light exposure on the stability of canola/sunflower oil blends. Aliquots (50 mL) of each oil were placed in petri dishes (8.6 cm x 1.2 cm) and exposed to fluorescent light (2690 lux) at 40°C for 0, 1, 2, 3, and 4 days. A 10-member trained panel used a 15 cm semi-structured line scale (0 = bland, 15 = strong) to rate overall odor intensity. Sunflower oil (100%) had the lowest odor intensity scores over storage than all sunflower/canola oil blends examined. Canola oil (100%) had the highest final volatile carbonyl level of all oil blends and this level was twice the final volatile carbonyl level found in 100% sunflower oil. In contrast, the peroxide and hydroperoxide values of sunflower oil were twice those of canola oil at every storage interval.

Huang et al. (1981) investigated the stability of sunflower and corn oils to photosensitized oxidation. Two storage conditions were used to examine light stability: 1) room temperature under diffused daylight for 0, 3, 7, 14, 21, and 28 days; 2) room temperature in a box lit with fluorescent light for 12, 24, 32, 40, and 48 hours. Corn oil exhibited higher odor and flavor intensities than sunflower oil whereas sunflower oil developed peroxides more rapidly than corn oil.

2.2

THERMAL OXIDATION

During heating and deep-fat frying, fats and oils are subjected to elevated temperatures (180-190°C) in the presence of air and moisture (Hawrysh, 1990). Under these conditions, thermolytic and oxidative reactions proceed rapidly resulting in the formation of both volatile (VDPs) and non-volatile decomposition products (NVDPs) (Paradis and Nawar, 1981; Stevenson et al., 1984; White, 1991). VDPs are unstable compounds which include hydrocarbons, aldehydes, ketones, furans, and carboxylic acids (White, 1991). VDPs contribute greatly to the odor of the oil and to the odor and flavor of lipid-containing foods (Stevenson et al., 1984). NVDPs include polar and non-polar material such as cyclic and noncyclic monomers, dimers, trimers, and high molecular weight compounds (White, 1991). NVDPs are reliable indicators of frying oil deterioration because of their steady accumulation and low volatility (Paradis and Nawar, 1981).

2.2.1

Thermolytic reactions

Thermolytic reactions during frying occur both in the presence and absence of water. In the absence of moisture, triacylglycerols (TAG) in saturated systems can form a "6-atom ring closure" by way of a hydrogen bridge caused by the presence of a hydrogen on the TAG (Hurd, 1938). This intermediate compound can result in the formation of hydrocarbons and ketones as well as fatty acids which are the major product of the reaction (Nawar, 1985). In the absence of moisture, thermolytic reactions occur in

unsaturated systems producing hydrocarbons, fatty acid esters as well as acyclic and cyclic dimeric compounds (Nawar, 1985). These compounds can result from the combining of free radicals (C^*) formed via carbon-carbon cleavages near the double bond and/or hydrogen abstraction (Nawar, 1985). Dimers and polymers contribute to flavor, texture and appearance of fried foods and are responsible for increasing the viscosity of the frying oil (Nawar, 1985).

The presence of moisture in the foods being fried, can result in the formation of free fatty acids via hydrolysis of ester linkages (Stevenson et al., 1984). Because of their greater solubility in water, unsaturated fatty acids and short chain fatty acids are more prone to hydrolysis (Nobel et al., 1967; Buziassy and Nawar, 1968).

2.2.2

Oxidative reactions

Because temperature is a major factor in oxidation rate, the high temperatures used during frying (180 - 190°C) greatly increase the rate of lipid oxidation (Nawar, 1985). In saturated systems, hydroperoxides are formed which rapidly decompose giving rise to aldehydes, carboxylic acids, ketones, and hydrocarbons (Nawar, 1985). The principal reaction pathways for the oxidation of unsaturated fatty acids are similar to those which occur in autoxidation. However, the rate of hydroperoxide formation and destruction is substantially increased at frying temperatures (Hawrysh, 1990). In addition, primary decomposition products are unstable and rapidly undergo further oxidative decomposition (Nawar, 1985). Volatile decomposition products from

the oxidation of unsaturated fatty acids include aldehydes, hydrocarbons, and alcohols.

Oxidative polymerization results in the production of NVDPs, mainly dimer and polymeric compounds as well as cyclic monomers (Nawar, 1985). The primary products produced in the presence of oxygen are alkyl hydroperoxides and dialkyl hydroperoxides which readily decompose forming oxy- and peroxy- radicals (Nawar, 1985). Through a series of reactions involving the radicals, oxydimers or polymers are formed (Nawar, 1985). Some of the major volatile compounds formed during thermal oxidation of oleate, linoleate, and linolenate are listed in Table 2.3.

Table 2.3 Volatile compounds with flavor significance formed from hydroperoxides during thermal oxidation (compounds listed in order of decreasing amounts)³

Oleate Hydroperoxides	Linoleate Hydroperoxides	Linolenate Hydroperoxides
heptane octane octanal nonanal decanal decenal undecenal	hexanal pentane 2,4-decadienal 2-heptenal pentyl furan	3,6-nonadienal hexenal 2,4-heptadienal pentene propanal

In order to assess the stability of oil to thermal oxidation, and to assess the storage stability of the fried product, a variety of methods are used. Oils are heated to frying temperatures typically $185^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and potato slices, french fries or bread cubes are fried for a specified time. Frying may be carried

³adapted from Nawar (1985)

out for one day or can span several days. Frying performance of the oil is determined by removing samples of the fried product and samples of the frying oil from the fryer at pre-determined intervals and assessing for quality using sensory, chemical and GC methods. To determine the storage stability of the fried product, the product is packaged using a variety of materials and is stored under accelerated heat conditions (60 - 65°C). Samples are removed at specified intervals and assessed for quality using sensory, chemical and GC methods.

Few published studies have examined the thermal oxidation of sunflower oil and the storage stability of products fried in sunflower oil. No studies have been undertaken to examine the thermal oxidation of solin oil nor the storage stability of products fried in solin oil.

Robertson and Morrison (1977) compared the frying performance of partially hydrogenated sunflower oil with a standard cottonseed/corn (70:30) oil blend. Potato chips fried in each of the oils were evaluated after 0, 2, 4, 6, 8, and 10 weeks of storage at room temperature. Sensory evaluation indicated that stored chips from both oils had no significant flavor differences throughout the 10 week storage period.

Robertson and Morrison (1978) compared the frying performance of sunflower, cottonseed, and palm oils over a 12 hour period and the storage stability of potato chips fried in each of the oils. Potato chips were collected after frying for 12 hours and bagged in waxed-coated glassine bags before

storing at 31°C for 10 weeks. A 10-member trained sensory panel evaluated the chips using a 5 point flavor quality scale where 1 = fresh (good chip flavor, no off-flavors), 2 = heated (good quality but flavor indicating some storage), 3 = stale (fair, not fresh, flat or tasteless from aging), 4 = off-flavor (poor, undesirable flavor e.g. grassy), and 5 = rancid (bad, old oil flavor). Panelists also rated the intensities of each odor/flavor descriptors using a three-point scale (1 = weak, 2 = moderate, and 3 = strong). These values were used to calculate flavor intensity values (FIV) as described in Section 2.1. Not surprisingly, the flavor quality of chips fried in all three oils gradually decreased throughout storage and differed significantly between 0 and 10 weeks of storage. FIV for stale increased for all chips as storage time increased. Cowan et al. (1970) stated that FIV's > 0.7 (out of a possible 3.0) are considered to be relatively intense odor/flavor descriptors. Chips fried in palm and sunflower accumulated FIV's > 0.7 for stale, off-flavor, and rancid at 10 weeks of storage. In general, the chemical indices indicated that there were no differences in the frying performance among the oils. Free fatty acids, peroxide values, and anisidine values of the oils extracted from the chips varied among the oils but no trend was evident. The authors concluded that the response of chips to accelerated storage was not significantly affected by the oils used for frying.

2.3 *SIGNIFICANCE OF UNSATURATION ON OIL STABILITY*

The rate of oxidation can be significantly affected by the degree of unsaturation of the fatty acid (Liu and White, 1992). The relative reaction rate with oxygen and the hydroperoxide decomposition rate of linolenate (18:3) are much faster than those of linoleate (18:2) and oleate (18:1) (Frankel, 1985; Gunstone and Hilditch, 1945). Labuza (1971) reported that the rate of oxidation of linolenic acid was twice that of linoleic acid and 25 times that of oleic acid. Linolenic acid makes up 9 - 15% of the fatty acids in canola oil, 7% soybean oil, and 45% - 65% in linseed oil (Ackman, 1983). It has been reported that linolenic acid is responsible for initiating oxidation of other fatty acids in edible oils due to its own instability (Smouse, 1979). As a result, the high linolenic acid content of these oils is problematic in terms of increased rates of oxidation; therefore reducing the linolenic acid content would appear to be advantageous. Reduction in linolenic acid levels in edible oils has been accomplished through hydrogenation, blending and more recently through breeding.

2.3.1 *Low linolenic acid oils - storage stability*

White and Miller (1988) compared the storage stability of five varieties of soybean oil with linolenic acid contents ranging from 4.2% to 9.2%. Samples were stored at 60°C for 0, 2, 4, 6, and 8 days. Sensory evaluation was carried out by a trained panel using the AOCS (1990) 10-point flavor intensity scale (10 = bland and 1 = strong). Few differences were found

among the oils in flavor intensity. After 8 days of storage, the peroxide value was significantly higher for the variety with 7.2% linolenic acid compared to the variety with the lowest linolenic acid content (4.2%) and a second variety with 7.2% linolenic acid. However, this variety had substantially less linoleic acid and oleic acid than all other soybean oils which may account for its stability to increased flavor scores and peroxide development.

Mounts et al. (1988) compared the storage stability of three low linolenic soybean oils (18:3: 3.3%, 4.2%, 4.8%) to regular soybean oil (18:3: 7.7%).

Oils were stored at 60°C for 0, 4, and 8 days. Sensory evaluation was carried out by a trained panel using the AOCS (1990) 10-point flavor intensity scale. The low linolenic oils stored for 8 days had improved flavor scores compared to regular soybean oil. No significant differences in peroxide development were observed between the low linolenic acid oils and regular soybean oil.

Liu and White (1992) compared the storage stability of canola (18:3: 10.3%), two regular soybean (18:3: 5.7% and 6.5%), three low linolenic soybean (18:3: 1.5%, 1.5%, 2.0%), and one intermediate linolenic soybean (18:3: 4.0%) oils. The oils were stored at 60°C for 0, 2, 7, and 15 days. Sensory evaluation was carried out by a trained panel using the AOCS (1990) 10-point flavor intensity scale. During storage, canola oil had significantly lower (stronger) flavor scores compared to all other oils. On storage day 15, flavor scores tended to decrease in relation to the order of increasing linolenic acid levels of the oils. Similarly, the peroxide values tended to increase with

increasing levels of linolenic acid.

Przybylski et al. (1993) compared the stability of low linolenic canola oil (LLCO) (18:3: 3.1%) and regular canola oil (RCO) (18:3: 11.5%). The oils were stored at 60°C for 12 days. Sensory evaluation was carried out by 10-member trained panel using two, semi-structured line scales: overall odor intensity (0 = bland, 8 = moderate, 15 = extremely strong) and pleasantness (0 = very pleasant, 8 = neutral, 15 = very unpleasant). The overall odor intensity increased and pleasantness decreased for RCO over the storage period, but this trend did not occur for LLCO. Peroxide value, hydroperoxide value, and thiobarbituric acid values for RCO exhibited greater changes over the storage period compared to LLCO. Volatile analysis indicated that there was a slower formation of dienals and total volatile compounds in LLCO than in RCO. The authors concluded that there was a marked improvement in the odor and flavor stability of genetically reduced LLCO compared to RCO after accelerated heat storage at 60°C.

2.3.2 *Low linolenic acid oils - storage stability of fried products*

Miller and White (1988) compared the storage stability of bread cubes fried in four different soybean oils with linolenic acid levels ranging from 3.5 to 8.1%. Fried bread cubes were stored at 60°C for 14 days. Ten trained panelists evaluated the bread cubes for oxidized flavor using the AOCS (1990) 10-point flavor intensity scale. At storage day 14, bread cubes fried in the low linolenic (18:3: 3.5%) and intermediate linolenic (18:3: 5.9%) soybean oils had

significantly less overall flavor intensity than the two regular soybean oils (18:3 6.9% & 8.1%). The oil containing the intermediate level of linolenic acid also had the lowest level of linoleic acid which may explain why this oil had similar flavor scores to the low linolenic soybean oil. Furthermore, bread cubes fried in low linolenic and intermediate linolenic oils developed significantly less peroxides at storage day 14 compared to bread cubes fried in regular soybean oils.

Liu and White (1992) compared the storage stability of bread cubes fried in canola (18:3: 10.3%) and soybean oils with linolenic acid levels ranging from 1.8 to 6.8%. Fried bread cubes were stored at 60°C for 7 days. Twelve trained panelists evaluated the bread cubes for intensity of oxidized flavor using the AOCS (1990) 10-point flavor intensity scale. Stored bread cubes fried in oils with low and intermediate levels of linolenic acid had significantly less overall flavor intensity compared to cubes fried in canola and regular soybean oils. The oil with the intermediate amount of linolenic acid (4.1%) also had less polyunsaturated fatty acids (18:2 + 18:3) than all other soybean oils which may explain why bread cubes fried in this oil had similar flavor scores to bread cubes fried in low linolenic acid soybean oils. Peroxide values determined on oil extracted from the bread cubes tended to be higher with increasing amounts of linolenic acid.

Hawrysh (1993b) compared the storage stability of potato chips fried in regular canola oil (RCO) (18:3: 9.3%) with chips fried in partially hydrogenated

canola oil (PHCO) (18:3: 1.7%). Chips were fried at 185°C and were then stored under one of the following conditions: 1) Time 0 - flushed with nitrogen and stored at -25°C; 2) Schaal storage for 6 d (S6) at 60°C; and 3) Schaal storage for 12 d (S12) at 60°C. An 8-member trained panel evaluated the chips for six odor and six flavor attributes using 15 cm unstructured lines scale (0 = absent, 15 = extreme). At Time 0, chips fried in RCO had higher characteristic potato chip odor/flavor and lower off-odor/flavor than chips fried in PHCO. Chips fried in PHCO had a pronounced buttery odor/flavor at Time 0 and this odor/flavor became more intense with storage. At S12, chips fried in RCO had the highest painty odor scores which was significantly higher than chips fried in PHCO. Anisidine values for chips fried in PHCO were significantly lower than chips fried in RCO throughout storage. At S12, chips fried in RCO had significantly higher levels of pentane than chips fried in PHCO. Even though there were large increases with storage, no significant differences were found in total volatiles and 2,4-decadienals between chips fried in RCO and PHCO.

Hawrysh (1995) compared the storage stability of tortilla chips fried in regular canola oil (RCO) (18:3: 9.9%), partially hydrogenated canola oil (PHCO) (18:3 1.2%), and low linolenic acid canola oil (LLCO) (18:3: 3.4%). Chips were fried at 185°C and were stored under one of the following conditions: 1) Time 0 - flushed with nitrogen and sealed in commercial foil potato chip bags at -25°C; 2) Schaal storage for 8 d (S8) at 60°C; and 3) Schaal storage for 16

and seven flavor attributes using 15 cm unstructured line scales (0 = absent, 15 = extreme). Time 0 chips fried in RCO and LLCO had significantly higher characteristic tortilla chip odor/flavor intensities compared to chips fried in PHCO which had the highest off-odor/flavor and buttery odor/flavor. At S16, chips fried in RCO had significantly higher off-odor/flavor, rancid odor/flavor and painty odor/flavor compared to chips fried in PHCO and LLCO. Chips fried in PHCO had greater buttery odor/flavor than chips fried in LLCO and RCO. Chips fried in PHCO were the most stable to peroxide development followed by chips fried in LLCO during storage. Chips fried in RCO had significantly greater levels of conjugated dienes compared to chips fried in LLCO and PHCO. At S8, chips fried in RCO had significantly greater pentane levels than chips fried in LLCO and PHCO. No significant differences in 2,4-decadienals or total volatiles were found among the chips.

Chapter 3

STORAGE STABILITY OF SOLIN AND SUNFLOWER OILS

3.1

INTRODUCTION

Linolenic (18:3) acid rapidly oxidizes in the presence of oxygen and therefore plays an important role in off-flavor development in edible oils. Linseed oil contains between 45% and 65% linolenic acid and as a consequence, has limited use in food applications. Through extensive breeding research, low linolenic (<5%) varieties of flaxseed have been produced. The name solin refers to these new low linolenic varieties which have fatty acid profiles similar to those of sunflower. Sunflower oil, a major commodity oil, currently ranks fourth on the world market surpassed only by soybean, palm, and canola/rapeseed oils (Anon., 1994). Research has shown that sunflower oil with its low linolenic acid content, is relatively stable to flavor and oxidative deterioration in accelerated heat and accelerated light storage tests (Warner et al., 1989; Durance, 1986). Further evidence of this can be seen in studies with genetically modified low linolenic (<5%) canola and soybean oils. These oils have exhibited greater storage stability compared to regular canola (18:3: 9-15%) and soybean (18:3: 7-9%) oils (Przybylski et al., 1993; Liu and Miller, 1992). Studies done on solin oil have shown that it is stable to off-odor and peroxide development during accelerated heat storage when compared to sunflower and canola oils (Hawrysh, 1993a). No other research has been undertaken to examine the stability of solin oil. Therefore, it was the purpose

of this research project to compare the stability of solin and sunflower oils to both accelerated heat and accelerated light storage conditions.

3.2 *EXPERIMENTAL DESIGN*

3.2.1 *Materials*

Pilot plant, refined, bleached and deodorized (RBD) solin oil (*POS Pilot Plant Corp.*, Saskatoon, SK) and commercially RBD sunflower oil (*CanAmera Foods*, Altona, MB) were selected for the study. The oils contained no additives.

3.2.2 *Sample Preparation and Storage Protocol*

Oil samples were stored under accelerated heat and accelerated light conditions. For accelerated heat storage, samples were stored in a forced draft oven at $60^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 0, 1, 2, 4, 6, 8, 12, and 16 days. For each storage interval, 270 g of each oil was stored in 3-125 mL uncovered glass jars (90 g/jar) ($\text{SA:OV}^1 = 0.19$). Positioning of the jars on the oven shelves was randomized. Upon removal from the oven, the 3 jars of oil were combined with a recovery of approximately 268 g of oil. Aliquots of oils were then removed from the composite sample as follows: 1 g placed in a 4 mL vial for GC analysis, 8 g placed in a 20 mL vial for chemical analysis, and the remainder (approximately 259 g) was divided among 3-125 mL jars for sensory evaluation. All vials and jars were flushed with nitrogen to exclude oxygen, capped with lined, plastic lids and stored at -25°C until analysis could be

¹SA:OV = surface area to oil volume ratio

carried out (approximately 6 months).

For accelerated light storage, samples were stored in a specially built storage cabinet using a light intensity of 4360 lux at $40^{\circ}\text{C} \pm 5^{\circ}\text{C}$. The fluorescent tubes in the cabinet had a color rendering index of 62 and a light temperature of 4100° K (Wesco Ltd., Winnipeg, MB, 1996). For each storage interval, 261 g of oil was placed in a clear, uncovered 125 x 65 mm glass crystallizing dish ($\text{SA:OV}^2 = 0.39$) for 0, 1, 2, 3, 4, 6, and 8 days. Positioning of the dishes on the shelves was randomized. Upon removal from the cabinet, the following amounts were removed from each dish: 1 g placed in a 4 mL vial for GC analysis, 8 g placed in a 20 mL vial for chemical analyses, and the remainder (approximately 249 g) placed in 3-125 mL jars for sensory evaluation. All vials and jars were flushed with nitrogen to exclude oxygen, capped with lined, plastic caps and stored at -25°C until analysis could be carried out (approximately 6 months).

3.2.3 *Methods of Analysis of Fresh Oils*

Fatty Acid Composition

The fatty acid composition of the oils was determined using AOCS official method Ce 1-62 (AOCS, 1990) with minor modifications. To carry out the procedure, acid catalyzed transesterification was used. Samples (approximately 50 mg) were weighed into threaded 25 mL capacity test tubes and 1 mL of petroleum ether was added to produce a monophasic system.

²SA:OV = surface area to oil volume ratio

Methanolic HCl (12 mL) was added and the tubes mixed on a vortex before being placed in an oven (70°C) for 1 hour. The tubes were removed from the oven and mixed frequently on a vortex during the first 10 minutes of heating. The tubes were cooled to room temperature and then 6 mL of water and 5 mL of *iso*-octane were added. The samples were left to form a clear upper layer (approximately 1 hour) before being injected in the GC. A *Hewlett Packard* model 5890 GC (*Hewlett Packard Inc.*, Avondale, USA) was used with a capillary column (Supelcowax 10, 30 m x 0.25mm, phase coating thickness of 0.15 μ m, *Supelco* Canada, Mississauga, ON). Samples (2.0 μ l) were injected and the initial time and initial column temperature used was 175°C for 2 min which was increased to 235°C at a rate of 3°C/min. The final time was 5 min which produced a total run time of 27 min. Fatty acid composition was determined using reference standards which allowed for peak identification. Analysis was carried out in duplicate.

Peroxide Value

Peroxide values were determined using AOCS official method Cd 8-53 (AOCS, 1990) but due to a limited amount of oil, 2.5 g samples were used instead of 5.0 g. Analysis was carried out in duplicate.

Free Fatty Acids

Free fatty acids were determined using AOCS official method Ca 5a-40 (AOCS, 1990). Analysis was carried out in duplicate.

Tocopherols

Tocopherols were determined using AOCS official method Ce 8-89 (AOCS, 1990).

Sterols

Saponification of the oils was necessary for the extraction of sterols. The saponification procedure was based on the method described by Losano (1993). The sterols were separated using a *Hewlett Packard* model 5890 GC (*Hewlett Packard Inc.*, Avondale, USA) with a fused silica capillary column (Rtx-5, 30 m x 0.25 mm i.d., film thickness of 0.15 μ m) (*Resteck*, Bellefonte, PA). The initial time and temperature of the column was 8 min at 90°C. The temperature was increased to 210°C at a rate of 30°C/min and was held at 210°C for 1 minute before being increased to 280°C at a rate of 5°C/min. This temperature was held for 40 min. Hydrogen was used as the carrier gas and the injector temperature was 260°C. Analysis was carried out in duplicate.

Metals

Copper, iron, and nickel were measured in the oils by atomic absorption spectroscopy using methods developed by van Loon (1980) and Cassetta and Aldrighectti (1992). The analysis was performed by E. Gawalko and C. Jarrin at the *Grain Research Laboratory* (Winnipeg, MB).

3.2.4

Methods of Analysis of Stored Oils

Sensory Evaluation

Odor evaluation of the stored oils was carried out using a trained odor profile panel. Ethics approval (Appendix A) was granted by the Faculty of Human Ecology Ethics Committee before panelists were recruited from staff and students in the Faculty of Human Ecology by letters of invitation (Appendix A). Twenty-four persons agreed to take part in three screening sessions over three days. Panelist selection was based on odor acuity, availability and a desire to take part in a sensory evaluation project. To determine odor acuity, panelists completed six triangle tests (2 tests per day). Fresh and stored (60°C) solin and sunflower oils were used in the triangle tests as follows:

Day #1	2d and 16d sunflower oil 0d and 16d solin oil
Day #2	0d and 12d sunflower oil 2d and 16d sunflower oil
Day #3	0d and 16d solin oil 0d and 12d sunflower oil

At each triangle test, the panelists were presented with three coded samples, two of the samples were the same and one was different. The panelists' task was to determine which one of the three coded samples was different from the other two samples presented. Samples were labelled with 3-digit codes and the order of presentation was randomized for each panelist. Panelists carried out the evaluations in a sensory panel room equipped with individual computerized sensory booths under red light to mask any color differences.

Samples (10 g) were placed in 125 mL glass jars and capped with lined, plastic caps. The jars were placed in a water bath to ensure a sample temperature of $50^{\circ}\text{C} \pm 2^{\circ}\text{C}$. This temperature is recommended for oil evaluations according to AOCS official method Cg 2-83 (AOCS, 1990). *Compusense* version 4.1 (*Compusense Inc.*, Guelph, ON) a sensory evaluation software package, provided panelists with on-screen instructions, sample presentations and recording of judgements. The criterion used for selection was four correct tests out of six tests which represents a 66.6% success rate. This exceeded the *American Society for Testing Materials* (ASTM, 1981) suggested success rate of 60% for the selection of panelists. Of the 24 persons who completed the screening sessions, 15 achieved a success rate of 66.6% or greater. Of the 15 persons, 3 could not take part in the training due to time constraints resulting in a final panel of 12 persons for training. Panelists who were not selected for training were notified by a letter, thanking them for their efforts.

Training

Training sessions took place over a two week period with each session lasting approximately 30 minutes. The initial training session had three objectives: to introduce the panelists to one another and to the panel leader, to explain and demonstrate the evaluation technique, and to become familiar with odor attributes to be evaluated in the oil. The evaluation technique which was agreed upon by all panelists, was as follows: panelists were to remove the jar from the waterbath, swirl the jar gently, remove the cap, hold the jar close

to the nose and take three short sniffs.

At the first training session, the panel evaluated a set of heat stored coded sunflower oil samples which covered a wide range of storage intervals. The panel's task was to describe the odor of the coded samples. The term painty was frequently used by the panelists to describe the odor property present in the stored samples, therefore the next phase of the training focused on the identification and assessment of painty odor. To confirm that panelists were correctly identifying painty odor in the samples, a canola oil sample (stored 10 days at 60°C) which had an intense painty odor was presented to the panel as a coded sample along with the coded sunflower oil samples. Since all panelists considered the odor in the sunflower oil sample to be the same odor present in the canola oil sample, this confirmed that panelists were in fact identifying painty odor in the sunflower oil samples.

The next step in the training was to introduce stored solin oil samples to determine if painty odor was also present in these samples. To achieve this objective, a 20-day sunflower oil sample was provided as a reference sample for painty and panelists were asked to rate coded sunflower and solin oil samples in relation to the reference sample. The panel agreed that the painty note was similar in both oils but the 20-day solin oil sample was considered more painty than the 20-day sunflower oil sample. Therefore, it was decided that a 20-day solin oil sample would serve as the painty reference for the remaining training and testing sessions. A 0-day sunflower oil sample was

selected to serve as the bland reference.

The panel was then introduced to the concept of intensity scaling using an unstructured line scale by completing the scaling exercise provided in Appendix B. Through this activity, the panelists gained an understanding of how to use the line scale as a method for rating intensity. From here the panelists went on to rate the intensity of painty odor in the oil samples using a 15 cm line scale where: 0 = *NONE*, 15 = *STRONG*. The panel agreed that the bland reference (R1) would be placed at the 0 cm (*NONE*) endpoint of the scale and the painty reference (R2) would be placed at the 15 cm (*STRONG*) endpoint of the scale. The final ballot agreed upon by the panelists is presented in Figure 3.1.

Figure 3.1 Final ballot used in the evaluation of stored oil

Method for Evaluation: Remove the sample from the water bath, swirl the jar gently, remove the lid and take three short sniffs. Replace the lid and put the jar back into the water bath. Wait at least 15 seconds between each evaluation.

Today's task: Smell references R1 and R2, noting the presence and intensity of the PAINTY odor. These references represent the endpoints of the line scale. Evaluate the coded samples in the order listed below. Rate the intensity of PAINTY for these samples by placing a vertical line at the point on the scale that represents the intensity of PAINTY present in the samples.

SAMPLE:

R1		R2
↓		↓
None		Strong

During training, values from the line scale were obtained by measuring in centimetres from the left (R1) endpoint to the vertical line on the scale for each sample evaluated. During test sessions, the panelists recorded their evaluations on the computer screen with the use of a mouse and the software package automatically calculated the values.

In subsequent training sessions, additional samples were presented to give the panelists' practice to ensure that they were in agreement and were consistent in their judgements. Samples representing the range of samples that they would receive during the testing sessions were presented at this time. This ensured that no samples would exceed the limits of the scale and that R1 and R2 were correctly placed on the line scale. The final training sessions were held to determine if the painty note could be perceived in light stored samples and if the same reference samples could be used in the evaluation of these samples. It was found that painty odor could be perceived in the light stored samples and the same references could be used.

Testing

Eight test sessions were required to evaluate the painty odor intensity of all heat and light stored samples. On test days one and two, all heat stored solin and sunflower oil samples were evaluated. The 14 samples (2 oils x 7 storage days) were randomly ordered and coded with three digit codes. The first seven samples in the randomized order were evaluated on test day one and the second seven samples on test day two. Test days three and four repeated

the evaluations from test days one and two but the sample order was re-randomized for the replication. On each test day, panelists evaluated four samples, took a five minute break, then evaluated the remaining three samples. The sample order within the block of seven samples was randomized for each panelist. On test days five and six, all light stored solin and sunflower oil samples were evaluated. The 14 samples (2 oils x 7 storage days) were randomly ordered and coded with three digit numbers. The procedure followed was the same as described for the heat stored samples. Test days seven and eight served as replications for test days five and six.

Because the heat and light stored samples were only evaluated for painty odor intensity, information on additional odor attributes, specifically odor attributes which may have been present at early storage intervals was obtained by holding four additional testing sessions. For light stored oils, samples stored 1, 2, 3, 4, 6 and 8 days were evaluated and for heat stored oils, samples stored 0, 1, 2, 4, 6, and 8 days were evaluated. On test day one, panelists evaluated light stored solin oil, on test day two, light stored sunflower oil, on test day three, heat stored solin oil, and on test day four, heat stored sunflower oil. At each testing session, panelists evaluated the coded samples and described any odors present using the ballot provided in Figure 3.2.

Figure 3.2. Ballot used for descriptive test sessions.

Method of Evaluation: Remove the sample from the water bath, swirl the jar gently, remove the lid and take three short sniffs. Replace the lid and put the jar back into the water bath. Wait at least 15 seconds between each evaluation.

Today's task: Evaluate the coded samples in the order listed below. Describe the odor of the sample by recording your observations in the appropriate space below.

SAMPLE: _____

The odor descriptors recorded by the panelists were tabulated for each sample in terms of the frequency of each particular odor descriptor.

Peroxide Value

Peroxide values were determined using AOCS official method Cd 8-53 (AOCS, 1990) but due to a limited amount of oil, 2.5 g samples were used instead of 5.0 g. Analysis was carried out in duplicate.

Volatile Analysis

Volatile analysis was carried out on the oils using the method developed by Przybylski et al. (1993). A *Perkin-Elmer* gas chromatograph (*Perkin-Elmer Inc.*, Norwalk, CT) with a capillary column (DB-5, 60 m x 32 mm, , phase coating thickness of 1 μ m) (*J&W*, Folsom, CA) was used for the analysis. The

column temperature was programmed in the following sequence from 45°C, 85°C, 125°C, 235°C at rates of 2, 3, 4, 5°C/min respectively. The temperature was held at lower and upper regions for 2 min and 15 min respectively. The injector temperature was set at 125°C while the flame ionization detector (FID) was set at 250°C. Helium was used as the carrier gas. To carry out the analysis, 15 cm glass tubes were used. Each tube was packed with one - 2 cm glass wool plug that was placed approximately 1.5 cm from the trap column end. Samples (100 μ L) from each treatment were injected into separate glass tubes using a micropipetter. Dodecane (C₁₂) served as the internal standard for the analysis and was injected (5 μ L, 187 ng) into the trap column end of the glass tube. The trap column was cooled using liquid nitrogen and the samples were purged for 15 minutes using helium gas. Following purging, the trapped volatiles were separated and the total run time was 70 minutes. Standard reference samples containing hydrocarbons, dienals, saturated carbonyls, monounsaturated carbonyls, pentyl furan, and 1-octen-3-ol were used to identify peaks using relative retention times.

3.2.5

Statistical analysis

Sensory Evaluation Data

Data from heat and light stored oils was analyzed separately using analysis of covariance (ANCOVA) by the PROC MIXED procedure of SAS (SAS Institute, Cary, NC, 1992). Oil type and storage interval were used as the predictor variables. The first step in the analysis of the sensory data was the

determination of statistical models (one for heat and one for light) to account for the variability in the data. Analysis of the full models was done initially followed by the development of reduced models. Reduced models were tested for loss of information against full models and were also tested for any significant improvement over the null models. This model building process resulted in appropriate reduced models for both heat and light stored oils (Appendix C).

Fixed effects of oil type ('Oil'), storage interval ('INT') and 'Oil x INT' were also determined and are found in Tables C.1 and C.2 in Appendix C. From the fixed effects tables, equations of lines were produced and tests for significant differences in slopes were carried out using t-tests. In addition, 95% confidence intervals were calculated on the difference in slopes. Sample calculations are presented in Appendix C.

Chemical and Volatile Data

ANCOVA was used to analyze the chemical and volatile data using the regression procedure of *Minitab version 8* (Addison-Wesley Publishing Inc, Reading, MA, 1992). Similar to the analysis of the sensory results, oil type and storage interval were used as the predictor variables. Fixed effects of oil type ('Oil'), storage interval ('INT') and 'Oil x INT' were also determined and are found in Tables D.1 to D.14 in Appendix D. Equations of lines, t-tests for significant differences in slopes, and 95% confidence intervals were calculated from the fixed effects tables.

Pearson's correlation coefficients were calculated between painty odor scores and chemical and volatile data using *Minitab*.

3.3

RESULTS

3.3.1

Fresh oils

Tables 3.1 to 3.5 present results from the analysis of the fresh oils. The fatty acid compositions of the two oils were similar but solin oil had greater levels of linolenic (18:3) acid compared to sunflower oil (Table 3.1). Linoleic (18:2) acid was the predominant fatty acid in both oils followed by oleic (18:1), palmitic (16:0) and stearic (18:0) acids.

Table 3.1. Relative fatty acid composition (%) of fresh oils

Fatty Acid	Solin	Sunflower
14:0	0.06	0.06
15:0	0.01	----
16:0	6.06	5.76
16:1	0.10	0.07
17:0	0.07	0.05
17:1	0.05	0.03
18:0	4.33	4.93
18:1	16.80	17.04
18:2	69.97	69.91
18:3	1.86	0.47
20:0	0.16	0.35
20:1	0.16	0.19
22:1	0.22	0.89
24:0	0.16	0.26
24:1	----	0.01

Both oils were of good initial quality as indicated by low peroxide values and free fatty acids (Table 3.2). Sunflower oil had greater total tocopherols, predominantly α - tocopherol compared to solin oil, which had predominantly γ - tocopherol (Table 3.3). Sunflower oil had greater total sterols than solin oil with β - sitosterol being the major sterol present in both oils (Table 3.4). Neither oil contained significant amounts of copper, iron or nickel (Table 3.5).

Table 3.2. Peroxide values and free fatty acids determined for fresh oils

	Solin	Sunflower
Peroxide value (meq/kg)	0.59	0.61
Free fatty acids (% as oleic)	0.04	0.05

Table 3.3. Tocopherols in fresh solin and sunflower oils

Type	Solin (ppm)	Sunflower (ppm)
α - tocopherol	10.4	232.6
β - tocopherol	----	10.1
γ - tocopherol	134.6	13.4
δ - tocopherol	----	5.1
Total	145.0	261.2

Table 3.4. Sterols in fresh solin and sunflower oils

Sterol	Solin (ppm)	Sunflower (ppm)
Campesterol	526.3	376.6
β - Sitosterol	1263.3	1910.1
Stigmasterol	108.9	158.7
Total	1898.5	2445.4

Table 3.5. Metals in fresh solin and sunflower oils

Metal	Solin (ppm)	Sunflower (ppm)
Copper	<0.02	<0.02
Iron	<0.02	<0.02
Nickel	<0.02	<0.02

3.3.2. *Heat stored oils*

Results from the two descriptive test sessions are presented in Tables 3.6 and 3.7. Figures 3.3 to 3.10 show the data for painty odor intensity, peroxide values, total volatiles, hydrocarbons, dienals, monounsaturated carbonyls, saturated carbonyls, and other volatiles plotted against storage days.

Sensory Evaluation

Descriptive data

Results from the descriptive analysis test sessions highlighted odor differences between the two oils at early storage intervals. Fresh (Od) solin oil was described as 'bland/fresh' with a 'vegetable/cereal/grassy' note (Table 3.6). However, the 'vegetable/cereal/grassy' note diminished quickly since few panelists were detecting it by storage day 1. In contrast, fresh (Od) sunflower oil was described as 'buttery/sweet' and 'rancid/painty' by the majority of the panelists (Table 3.7). At storage day 4, panelists detected all four odor descriptors in solin oil with 'buttery/sweet' being selected slightly more often than the other three descriptors. Sunflower oil at day 4 was described as 'bland/fresh' by half the panel, but one-third of the panel also described this sample as 'painty/rancid'. By day 8, solin oil was described as 'bland/fresh' and 'painty/rancid' by an equal number of panelists, while almost the entire panel described sunflower oil as 'painty/rancid'.

Table 3.6. Odor descriptors for heat stored solin oil

<i>DESCRIPTOR</i>	<i>NUMBER of RESPONSES</i>					
	0d	1d	2d	4d	6d	8d
bland/fresh	5	8	5	3	3	5
buttery/sweet	3	4	1	4	4	1
vegetable/cereal/grassy	5	2	1	3	1	2
rancid/painty	1	3	4	2	4	5

Table 3.7. Odor descriptors for heat stored sunflower oil

<i>DESCRIPTOR</i>	<i>NUMBER of RESPONSES</i>					
	0d	1d	2d	4d	6d	8d
bland/fresh	2	4	4	7	1	1
buttery/sweet	6	3	1	3	2	1
rancid/painty	4	3	7	5	9	8

Painty odor evaluation

Transformation of the painty odor scores was necessary to achieve a linear response. The data was transformed into natural logarithms (Ln) using the equation: $\text{Ln}(\text{painty odor score} + 0.5)$ since taking a natural logarithm of 0 is not possible. Sunflower oil had a higher painty odor score initially compared to solin oil but this difference was not evident by storage day 2 (Figure 3.3). Overall, solin oil had a significantly ($p \leq 0.04$) greater rate of painty odor development over the 16 days of storage compared to sunflower oil (Table 3.8).

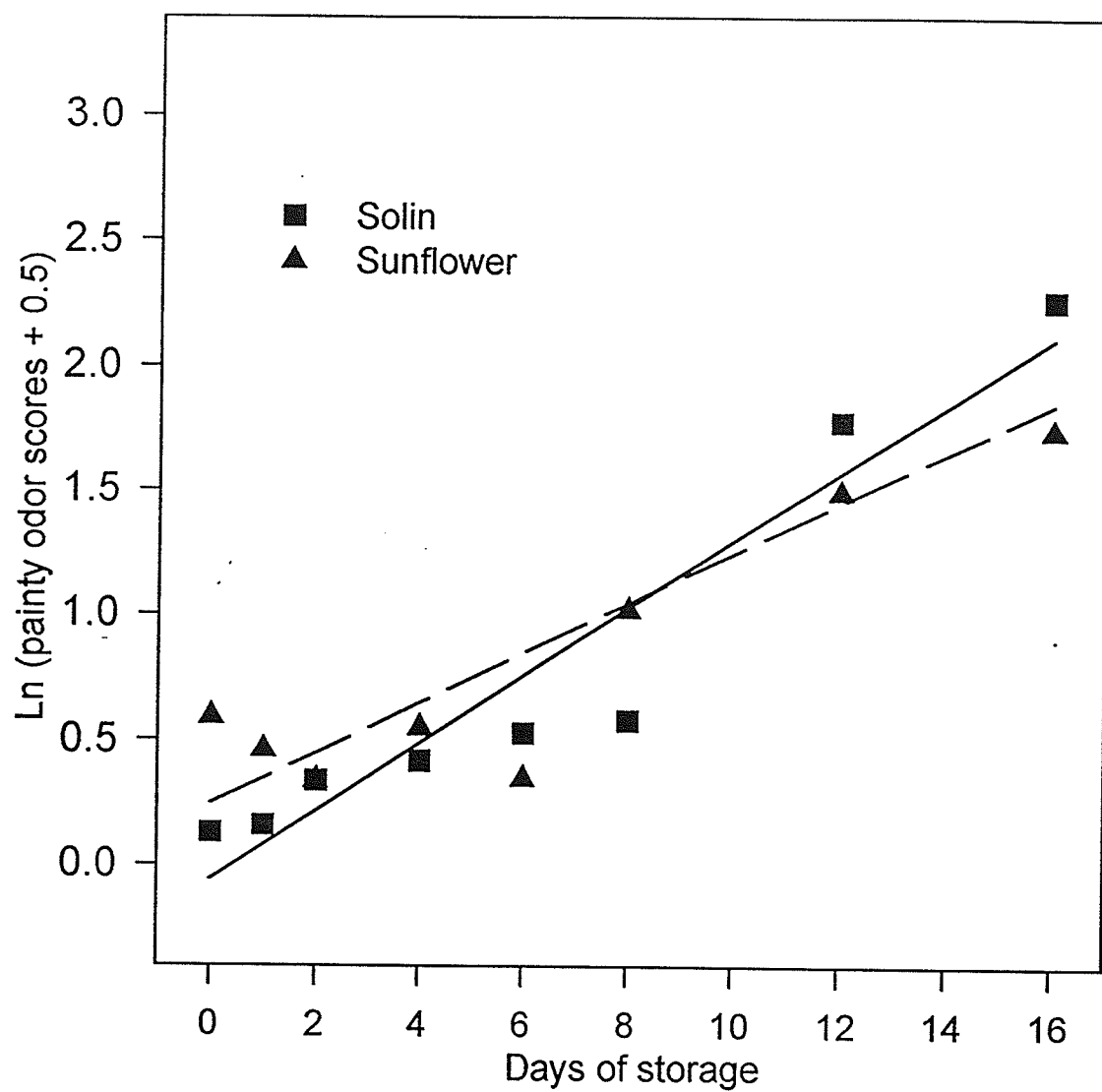


Figure 3.3. Ln (painty odor scores + 0.5) of heat stored oils

Table 3.8. Summary of all response parameters for heat stored oil

Parameter	Oil	Equation ²	Difference in slopes ³ (p-value)	Confidence interval (C.I. ⁴) (95%)
Painty odor score ¹	Solin	$-0.05 + 0.14(\text{INT})$	$p \leq 0.04$	(0.51,0.57)
	SFO	$0.25 + 0.10(\text{INT})$		
Peroxide Value	Solin	$-5.45 + 3.15(\text{INT})$	$p \leq 0.01$	(-1.96,-0.44)
	SFO	$-0.83 + 4.35(\text{INT})$		
Total Volatiles	Solin	$156.99 + 72.20(\text{INT})$	$p \leq 1.00$	(-22.0,22.0)
	SFO	$176.69 + 72.20(\text{INT})$		
Hydro-carbons	Solin	$-11.28 + 21.30(\text{INT})$	$p \leq 0.35$	(-4.36,11.44)
	SFO	$12.74 + 24.84(\text{INT})$		
Dienals	Solin	$3.18 + 18.01(\text{INT})$	$p \leq 0.40$	(-5.53,12.87)
	SFO	$12.61 + 21.68(\text{INT})$		
Monounsaturated Carbonyls	Solin	$8.07 + 17.49(\text{INT})$	$p \leq 0.02$	(1.30,12.64)
	SFO	$33.11 + 10.52(\text{INT})$		
Saturated Carbonyls	Solin	$158.57 + 9.38(\text{INT})$	$p \leq 0.57$	(-4.65,8.03)
	SFO	$115.59 + 11.07(\text{INT})$		
Other Volatiles	Solin	$-1.53 + 6.04(\text{INT})$	$p \leq 0.08$	(-0.24,4.08)
	SFO	$2.70 + 4.12(\text{INT})$		

¹ Painty odor score = $\text{Ln}(\text{Painty odor score} + 0.5)$

² INT in the equation represents storage interval

³ t-test for significant difference between the slopes of the oils.

⁴ significant ($\alpha = 0.05$) difference in slope if zero is not included in the C.I.

The 95% confidence interval provides information on the difference in painty odor intensity development between the oils. The painty odor intensity of solin oil increased by between 0.51 and 0.57 POS³ more per storage day compared

³POS = painty odor score units

to sunflower oil.

Peroxide Value

Sunflower oil had higher peroxide values (Figure 3.4) and a significantly ($p \leq 0.01$) greater rate of peroxide value development than solin oil over the 16 days of storage (Table 3.8). Sunflower oil developed between 0.44 and 1.96 meq/kg more peroxides per storage day than solin oil (Table 3.8).

Volatile Analysis

Both oils had similar levels (Figure 3.5) and exhibited similar ($p \leq 1.00$) rates of development of total volatiles throughout storage (Table 3.8).

Sunflower oil developed higher levels of hydrocarbons (mainly pentane) (Figure 3.6) compared to solin oil throughout storage. However, the rates of development were similar ($p \leq 0.35$) between the oils (Table 3.8).

Sunflower oil had higher levels of dienals (mainly 2,4-decadienal) for storage days 6, 8, and 12 compared to solin oil but this difference was not evident by day 16 (Figure 3.7). Thus, the rates of development of dienals were considered to be similar ($p \leq 0.40$) for the two oils throughout storage (Table 3.8).

Both oils had similar levels of monounsaturated carbonyls (mainly 2-heptenal) but by storage day 12, solin oil had higher levels compared to sunflower oil (Figure 3.8). The rate of development was considered to be significantly ($p \leq 0.02$) greater for solin oil which developed between 1.30 and

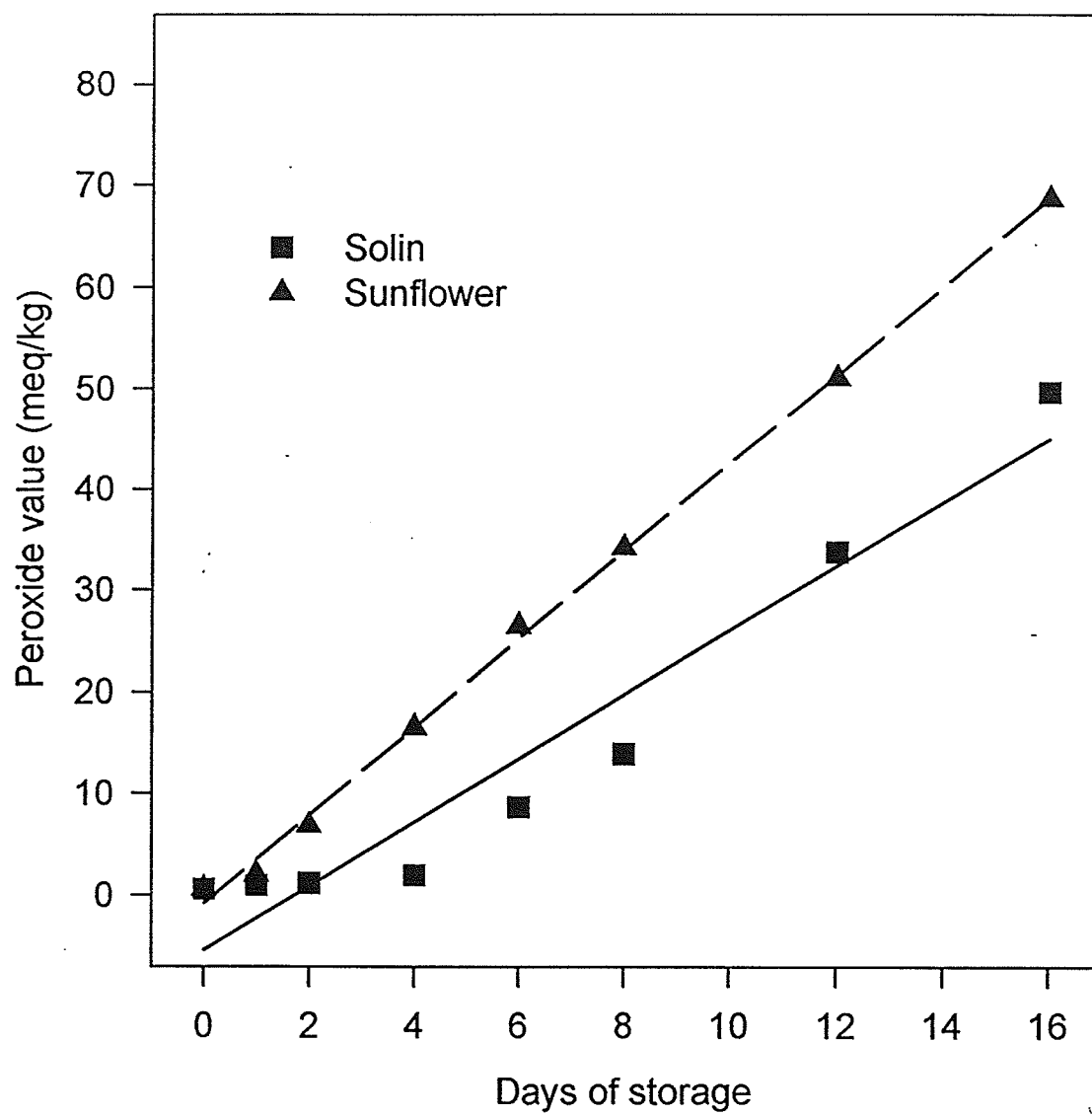


Figure 3.4. Peroxide values of heat stored oils

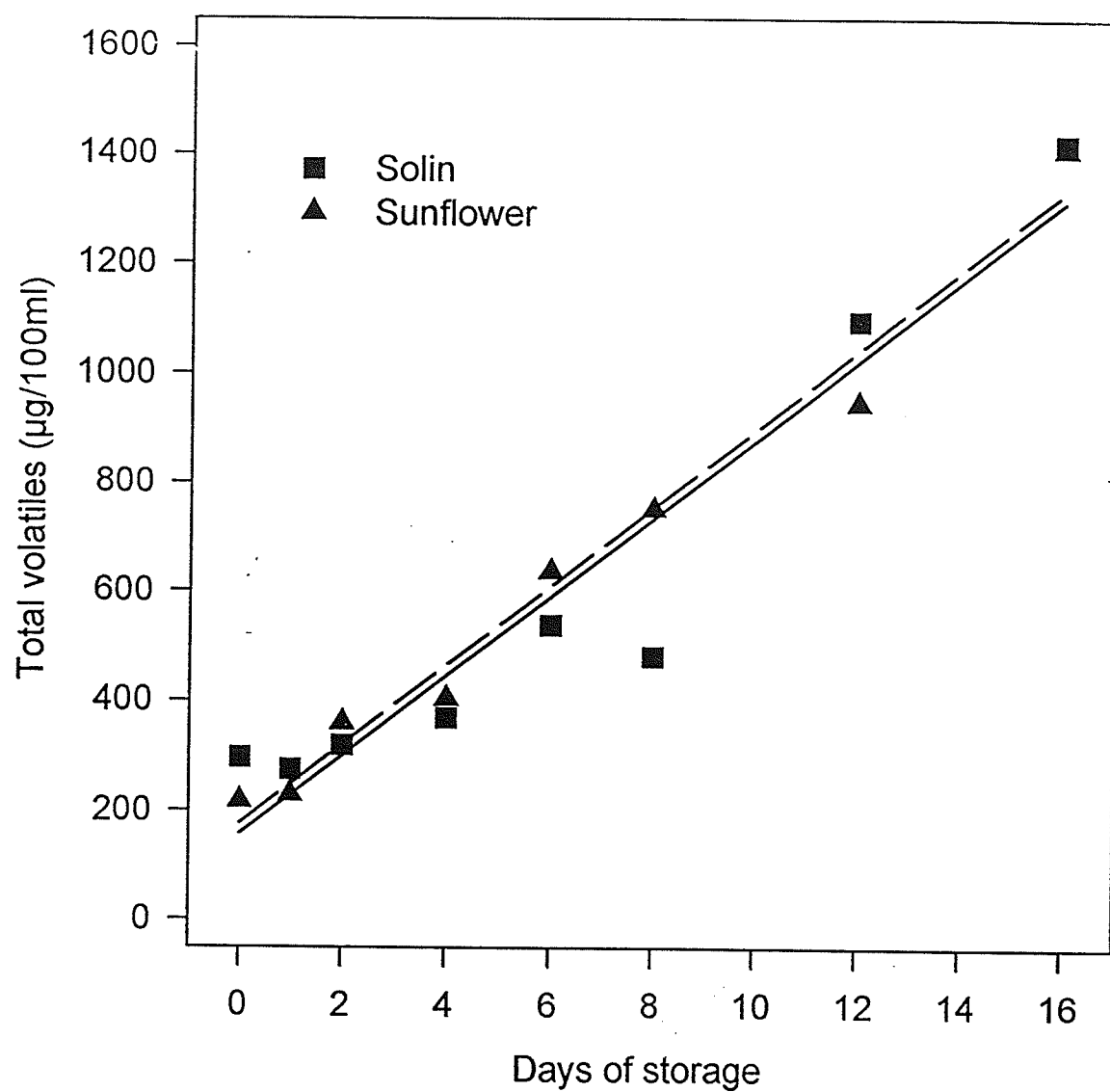


Figure 3.5. Total volatiles in heat stored oils

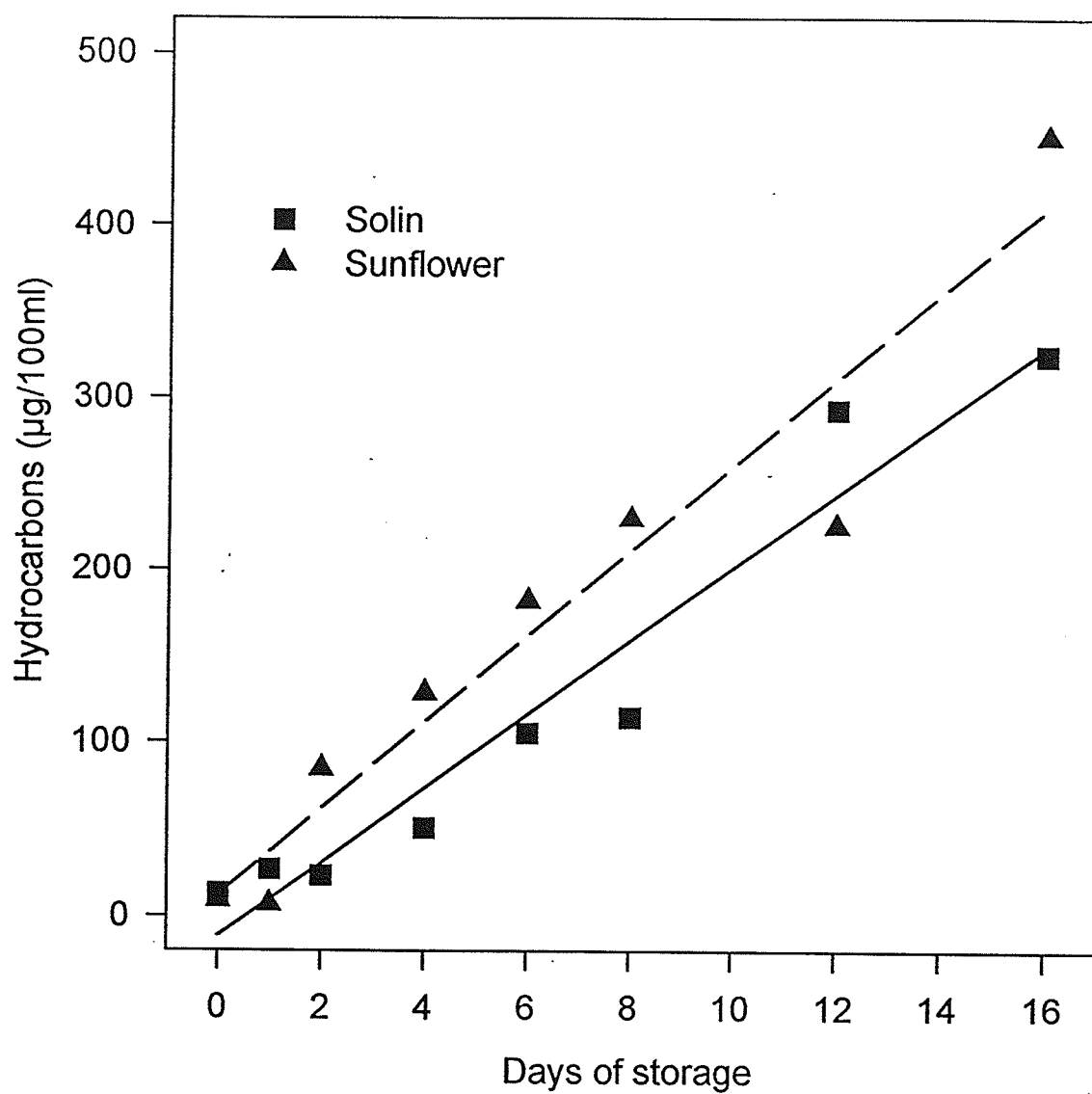


Figure 3.6. Hydrocarbons in heat stored oils

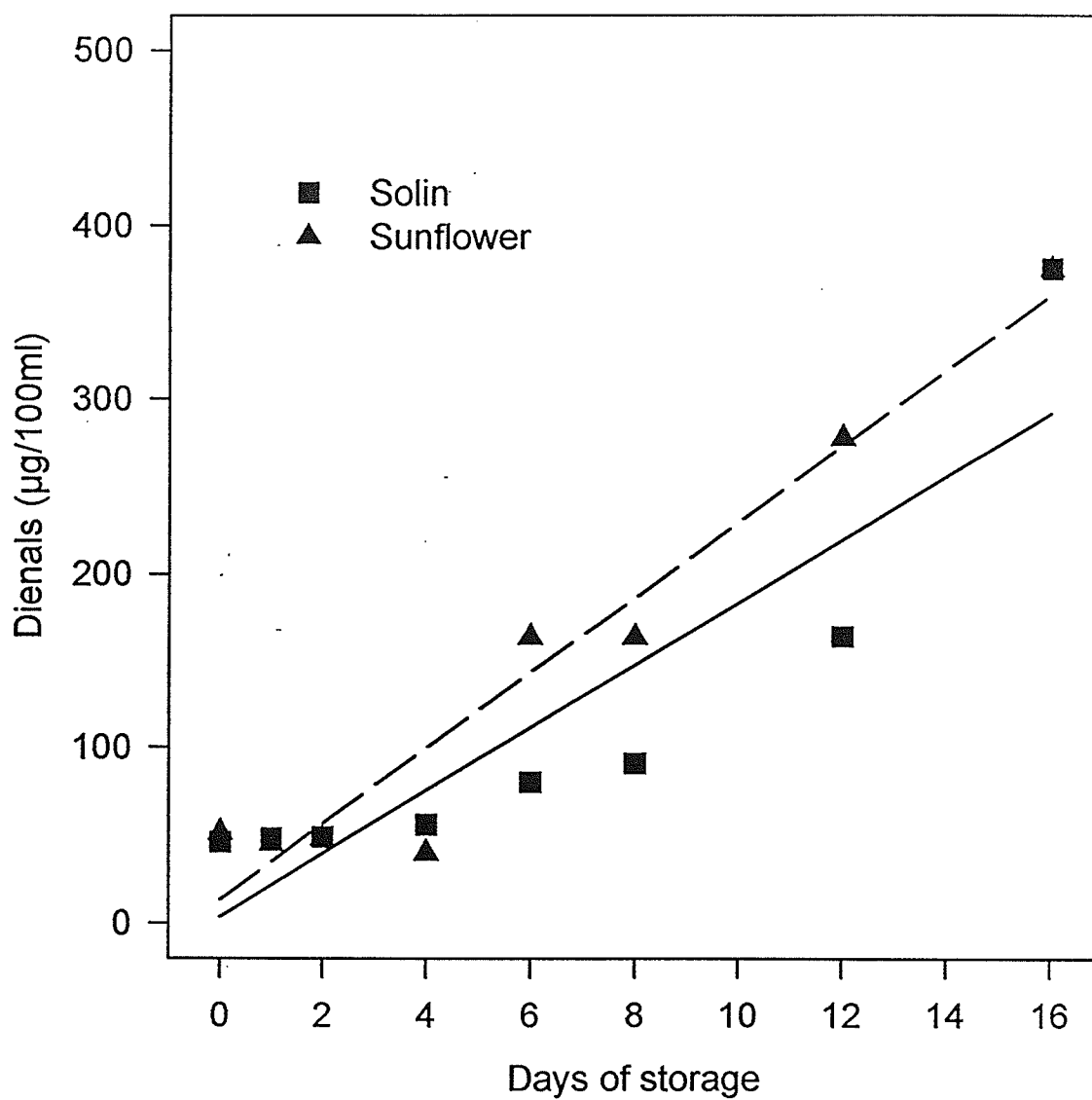


Figure 3.7. Dienals in heat stored oils

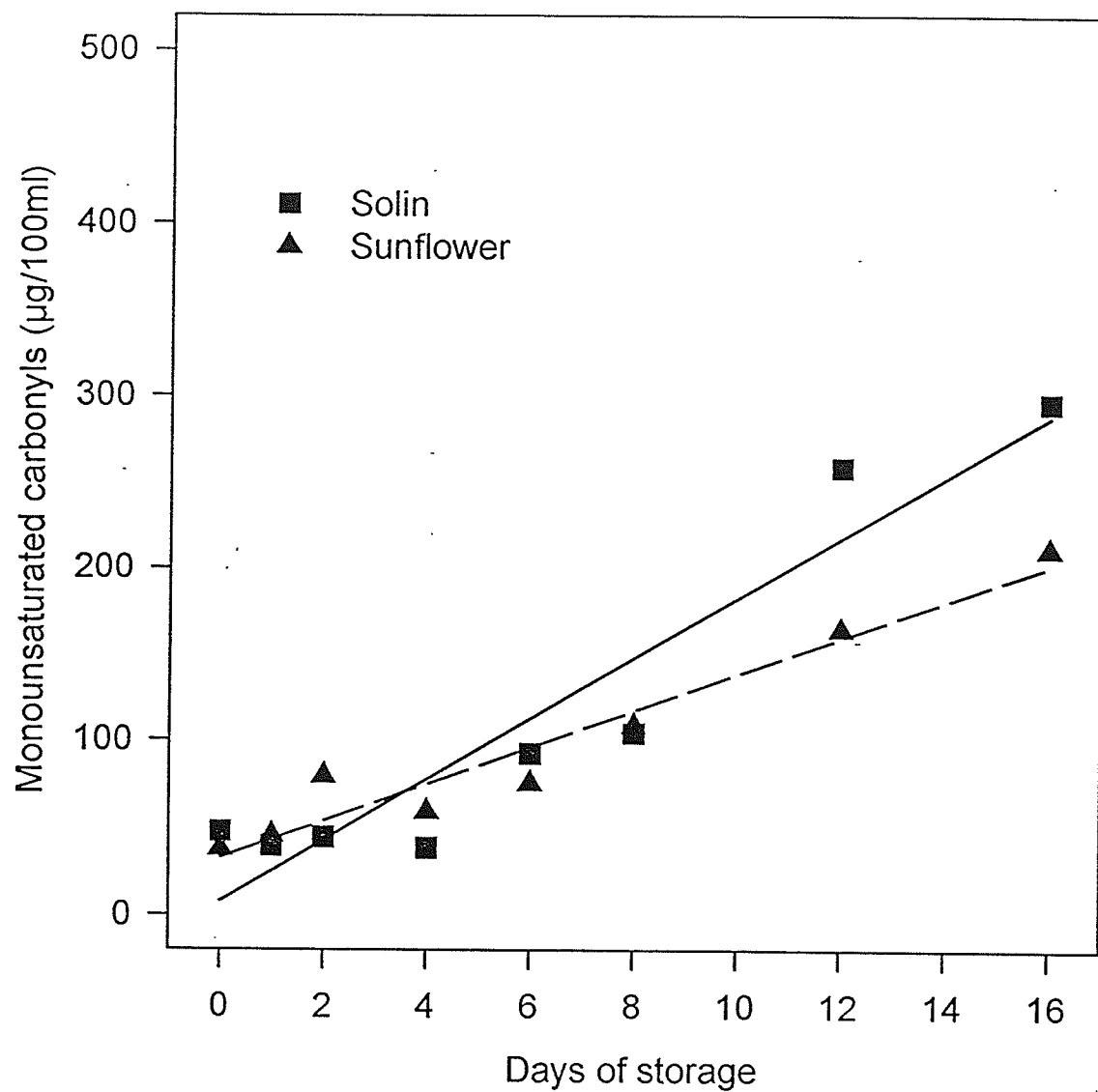


Figure 3.8. Monounsaturated carbonyls in heat stored oils

12.64 $\mu\text{g}/100\text{ mL}$ more of monounsaturated carbonyls per storage day than sunflower oil (Table 3.8).

Solin oil displayed higher levels of saturated carbonyls (mainly hexanal, nonanal, and pentanal) compared to sunflower oil throughout storage (Figure 3.9) Both oils had similar ($p \leq 0.57$) rates of development of saturated carbonyls (Table 3.8).

Solin oil had higher levels of other volatiles (mainly pentyl furan) by storage day 12 compared to sunflower oil (Figure 3.10). Both oils had similar ($p \leq 0.08$) rates of development of other volatiles (Table 3.8).

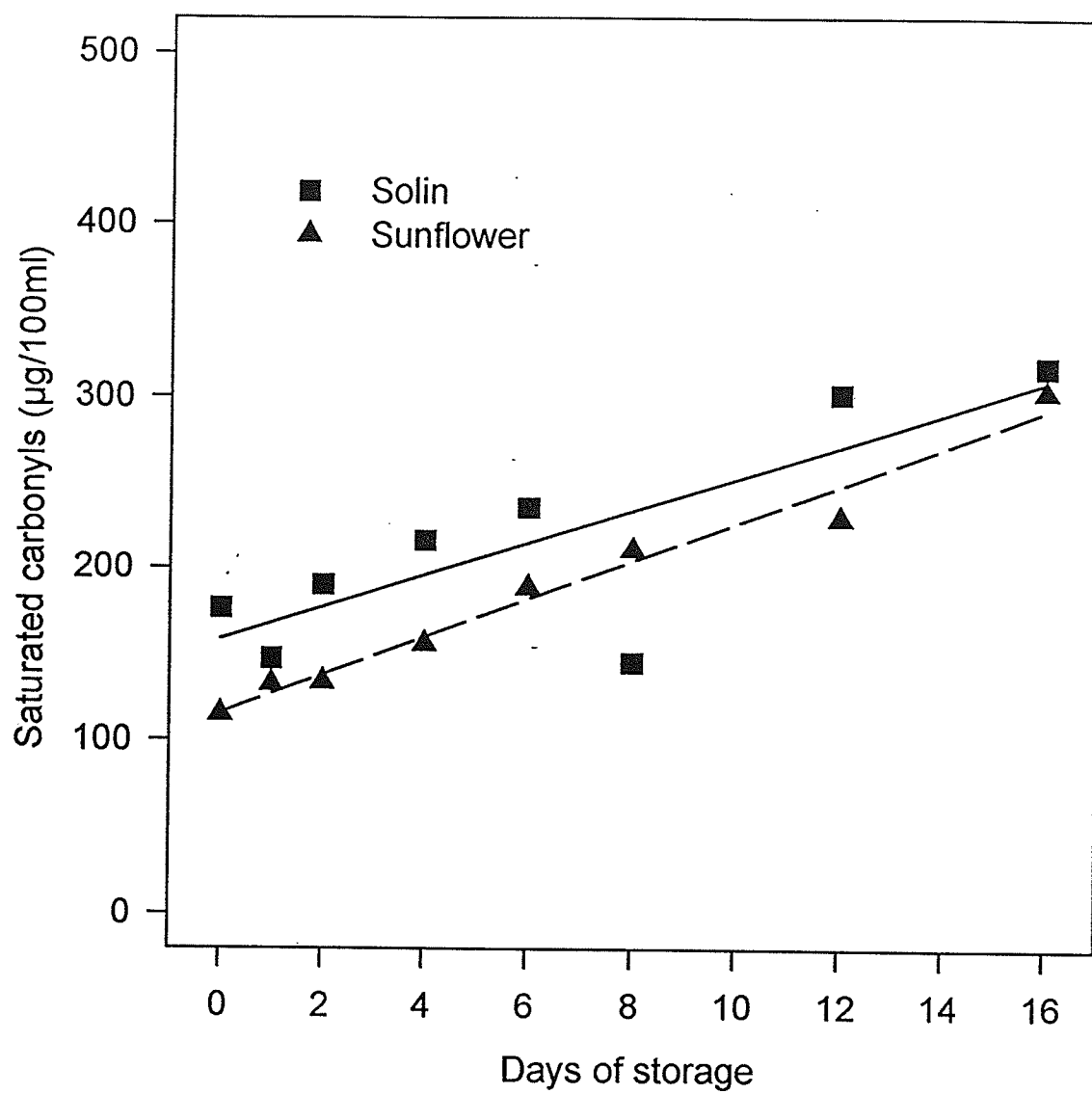


Figure 3.9. Saturated carbonyls in heat stored oils

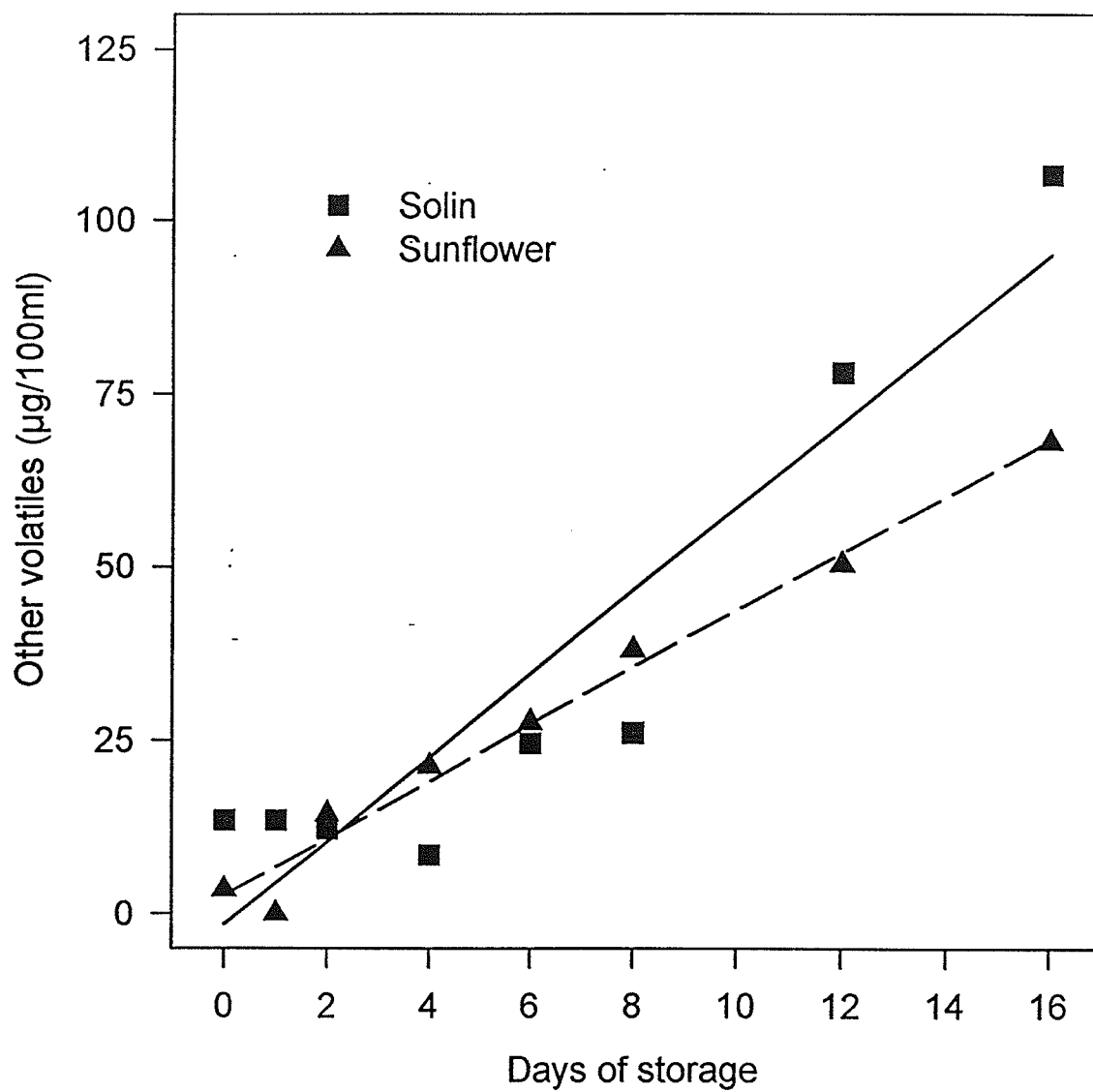


Figure 3.10. Other volatiles in heat stored oils

3.3.3. *Light stored oils*

Results from the two descriptive test sessions are presented in Tables 3.9 and 3.10. Figures 3.11 to 3.18 show the data for painty odor intensity, peroxide values, total volatiles, monounsaturated carbonyls, other volatiles, hydrocarbons, dienals, and saturated carbonyls plotted against storage days.

Sensory Evaluation

Descriptive data

Fresh (0d) solin oil was described as 'bland/fresh' with a 'vegetable/cereal/grassy' note (Table 3.9). In contrast, fresh (0d) sunflower oil was described as 'buttery/sweet' and 'rancid/painty' by a majority of panelists (Table 3.10). At storage day 2, solin oil retained the 'vegetable/cereal/grassy' note but this note diminished with storage. By day 4, half the panelists described solin oil as having a 'painty/rancid' odor. At day 4, the panel was divided in their description of the sunflower oil odor with slightly more panelists describing the odor as 'buttery/sweet' with the remainder of the panelists describing it as 'painty/rancid'. At day 8 of storage, one-third to one-half of the panelists described solin oil as having a 'painty/rancid' odor while almost the entire panel described sunflower oil as 'painty/rancid'.

Table 3.9. Odor descriptors for light stored solin oil

<i>DESCRIPTOR</i>	<i>NUMBER of RESPONSES</i>						
	0d	1d	2d	3d	4d	6d	8d
bland/fresh	5	6	4	4	4	4	2
buttery/sweet	3	4	6	5	2	4	3
veg./cer./grass	5	2	4	1	2	2	3
rancid/painty	1	4	3	5	8	6	5

Table 3.10. Odor descriptors for light stored sunflower oil

<i>DESCRIPTOR</i>	<i>NUMBER of RESPONSES</i>						
	0d	1d	2d	3d	4d	6d	8d
bland/fresh	2	6	7	8	2	0	0
buttery/sweet	6	2	5	4	5	1	1
rancid/painty	4	6	4	3	4	8	11

Painty odor evaluation

Although a majority of panelists described light stored solin and sunflower oils as having a 'painty/rancid' odor during the descriptive test sessions, when this odor was evaluated by the panel using the line scale, neither oil was judged to have an intense painty odor. This indicates that panelists detected 'painty/rancid' odor in the two oils but that it was present at a low intensity. This finding was supported by a non-significant ($p \leq 0.32$) non-zero slope (Appendix C, Table C.2). Both oils had similar painty odor scores throughout storage (Figure 3.11) and had similar ($p \leq 0.44$) rates of painty odor development (Table 3.11).

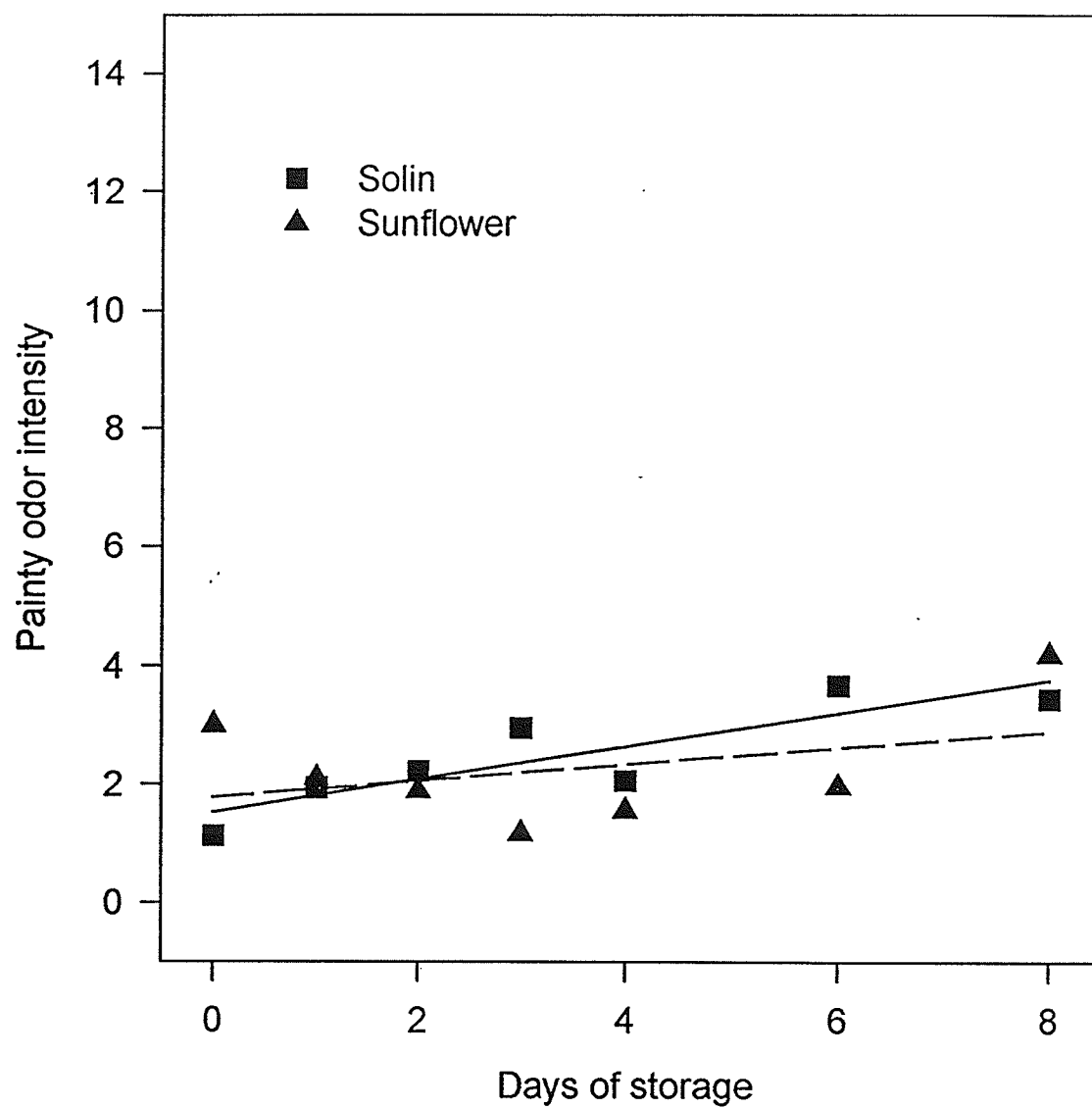


Figure 3.11. Painty odor scores of light stored oils

Table 3.11. Summary of all response parameters for light stored oil

Parameter	Oil	Equation ¹	Difference in slopes ² (p-value)	Confidence interval (C.I. ³) (95%)
Painty odor intensity	Solin	$1.53 + 0.28(\text{INT})$	$p \leq 0.44$	$(-0.51, 0.23)$
	SFO	$1.78 + 0.14(\text{INT})$		
Peroxide Value	Solin	$1.00 + 4.54(\text{INT})$	$p \leq 0.07$	$(-0.23, 6.33)$
	SFO	$9.74 + 7.59(\text{INT})$		
Total Volatiles	Solin	$269.4 + 122.57(\text{INT})$	$p \leq 0.02$	$(26.80, 231.50)$
	SFO	$65.30 + 251.72(\text{INT})$		
Hydro-carbons	Solin	$13.02 + 29.95(\text{INT})$	$p \leq 0.01$	$(16.56, 82.06)$
	SFO	$-9.24 + 79.26(\text{INT})$		
Dienals	Solin	$23.23 + 25.42(\text{INT})$	$p \leq 0.01$	$(11.96, 50.26)$
	SFO	$14.22 + 56.53(\text{INT})$		
Monounsaturated Carbonyls	Solin	$61.32 + 21.40(\text{INT})$	$p \leq 0.03$	$(2.04, 37.44)$
	SFO	$7.85 + 41.14(\text{INT})$		
Saturated Carbonyls	Solin	$158.23 + 39.72(\text{INT})$	$p \leq 0.28$	$(-18.39, 56.83)$
	SFO	$60.46 + 58.94(\text{INT})$		
Other Volatiles	Solin	$13.62 + 6.07(\text{INT})$	$p \leq 0.02$	$(2.33, 17.19)$
	SFO	$-7.97 + 15.83(\text{INT})$		

¹ INT in the equation represents storage interval

² t-test for significant difference between the slopes of the oils.

³ significant ($\alpha = 0.05$) difference in slope if zero is not included in C.I.

Peroxide Value

Sunflower oil had higher peroxide values at every storage interval compared to solin oil (Figure 3.12) but both oils had similar ($p \leq 0.07$) rates of development throughout the storage period (Table 3.11).

Volatile Analysis

Both oils had similar levels of total volatiles (Figure 3.13), monounsaturated carbonyls (mainly 2-heptenal) (Figure 3.14), and other volatiles (mainly 1-octen-3-ol) (Figure 3.15) until day 6, after which sunflower oil exhibited higher levels. Sunflower oil had significantly greater rates of development of total volatiles ($p \leq 0.02$), between 26.80 and 231.50 $\mu\text{g}/100\text{mL}$ more per storage day, monounsaturated carbonyls ($p \leq 0.03$), between 2.04 and 37.44 $\mu\text{g}/100\text{mL}$ more per storage day, and other volatiles ($p \leq 0.02$), between 2.33 and 17.19 $\mu\text{g}/100\text{ mL}$ more per storage day compared to solin oil (Table 3.11).

After day 1 of storage, sunflower oil accumulated higher levels of hydrocarbons (mainly pentane) (Figure 3.16) and dienals (mainly 2,4-decadienal) (Figure 3.17) throughout storage. Sunflower oil exhibited significantly greater rates of development of hydrocarbons ($p \leq 0.01$), between 16.56 and 82.06 $\mu\text{g}/100\text{mL}$ more per storage day and dienals ($p \leq 0.01$), between 11.96 and 50.26 $\mu\text{g}/100\text{mL}$ more per storage day (Table 3.11).

Both oils had similar levels of saturated carbonyls (mainly hexanal and nonanal) until day 4 of storage (Figure 3.18). At storage day 6, solin oil had

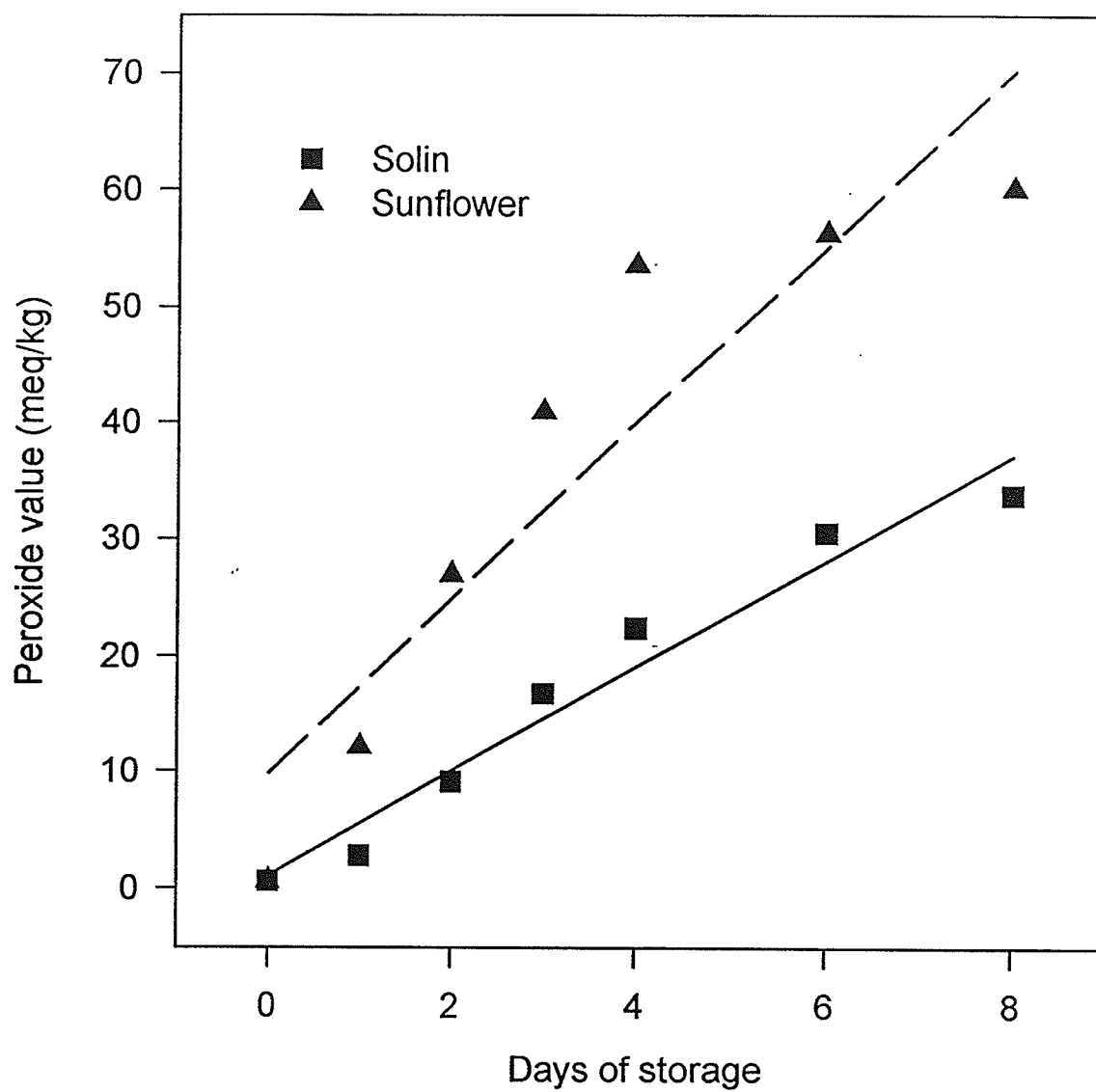


Figure 3.12. Peroxide values of light stored oils

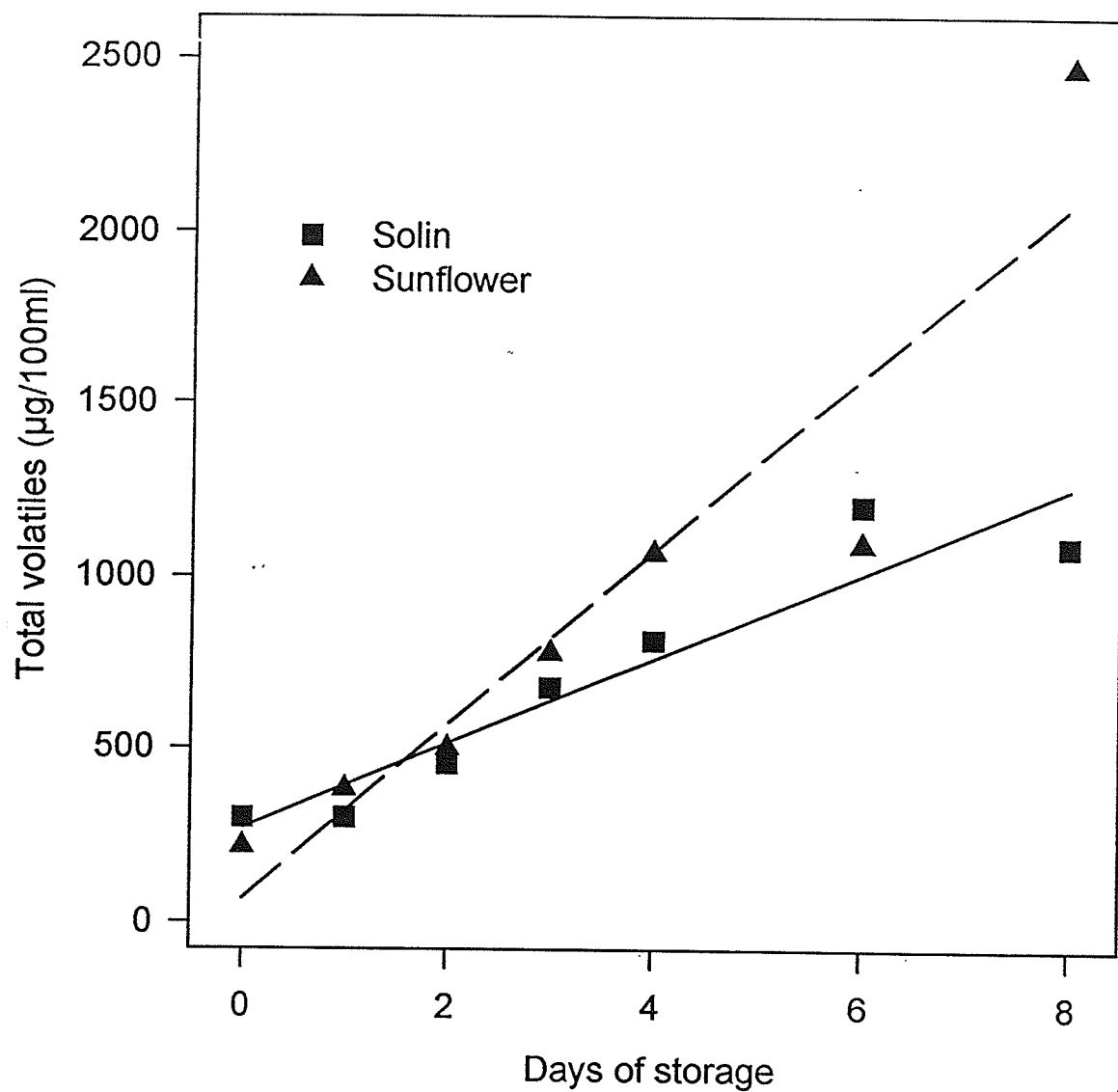


Figure 3.13. Total volatiles in light stored oils

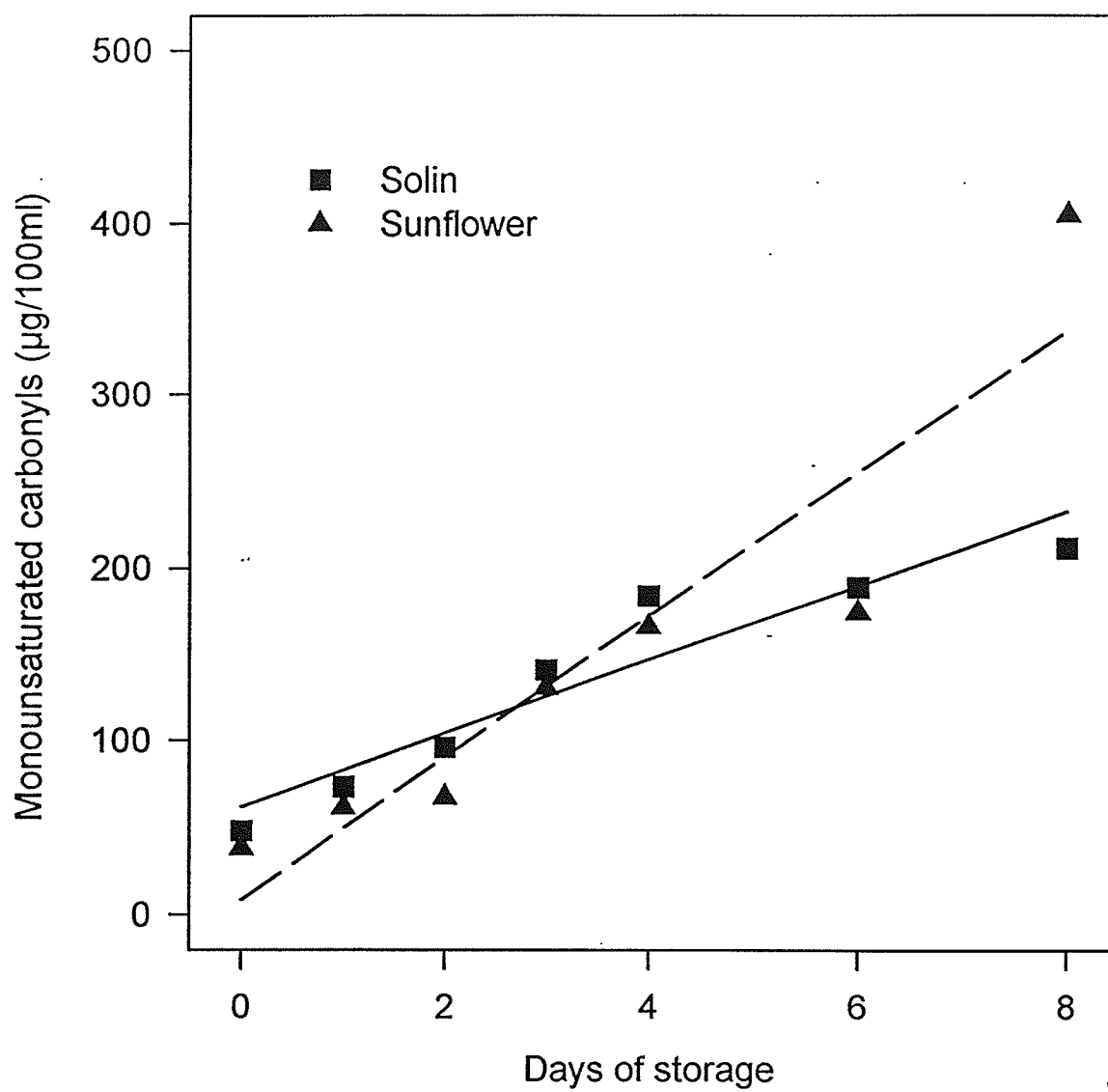


Figure 3.14. Monounsaturated carbonyls in light stored oils

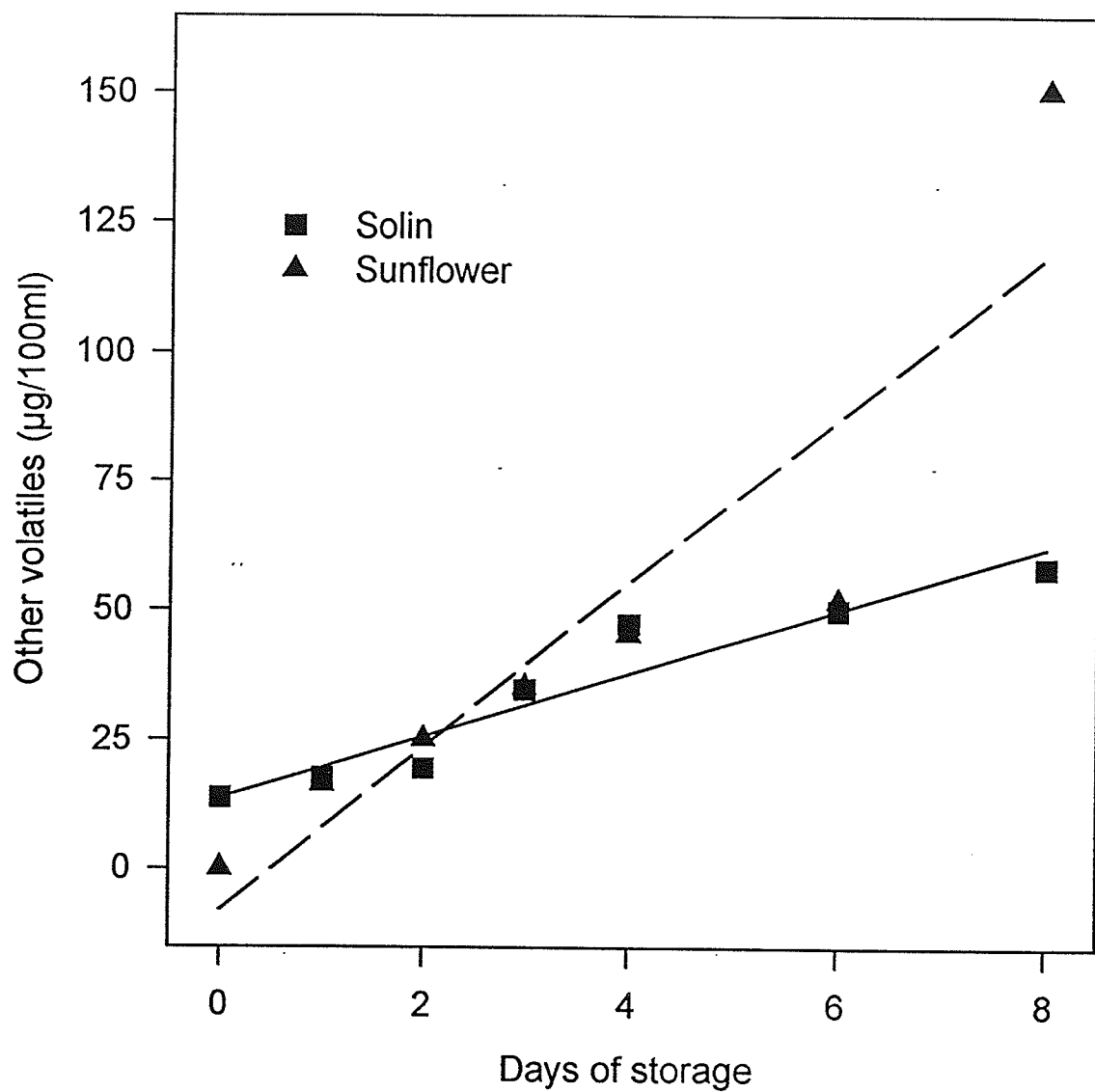


Figure 3.15. Other volatiles in light stored oils

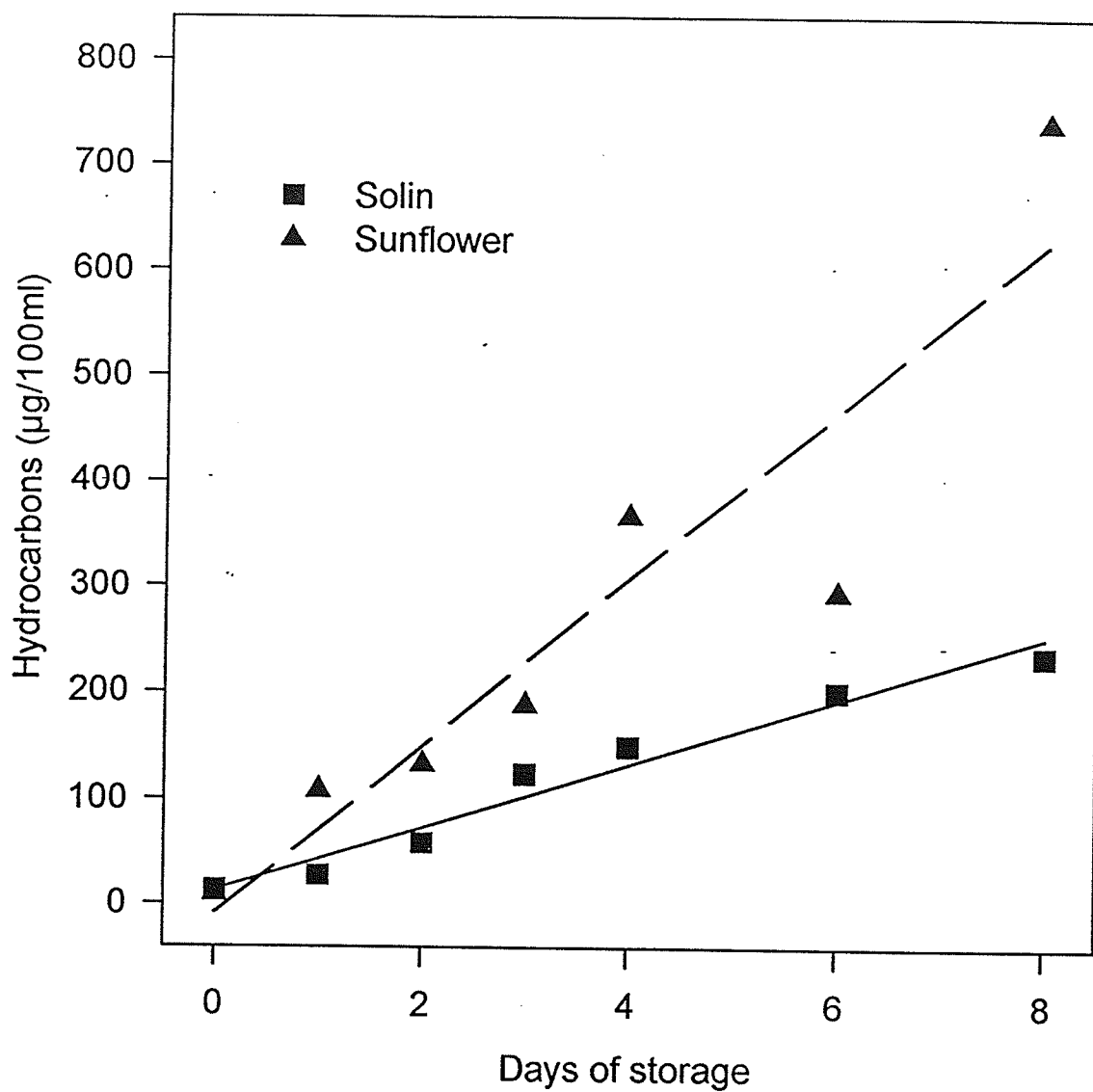


Figure 3.16. Hydrocarbons in light stored oils

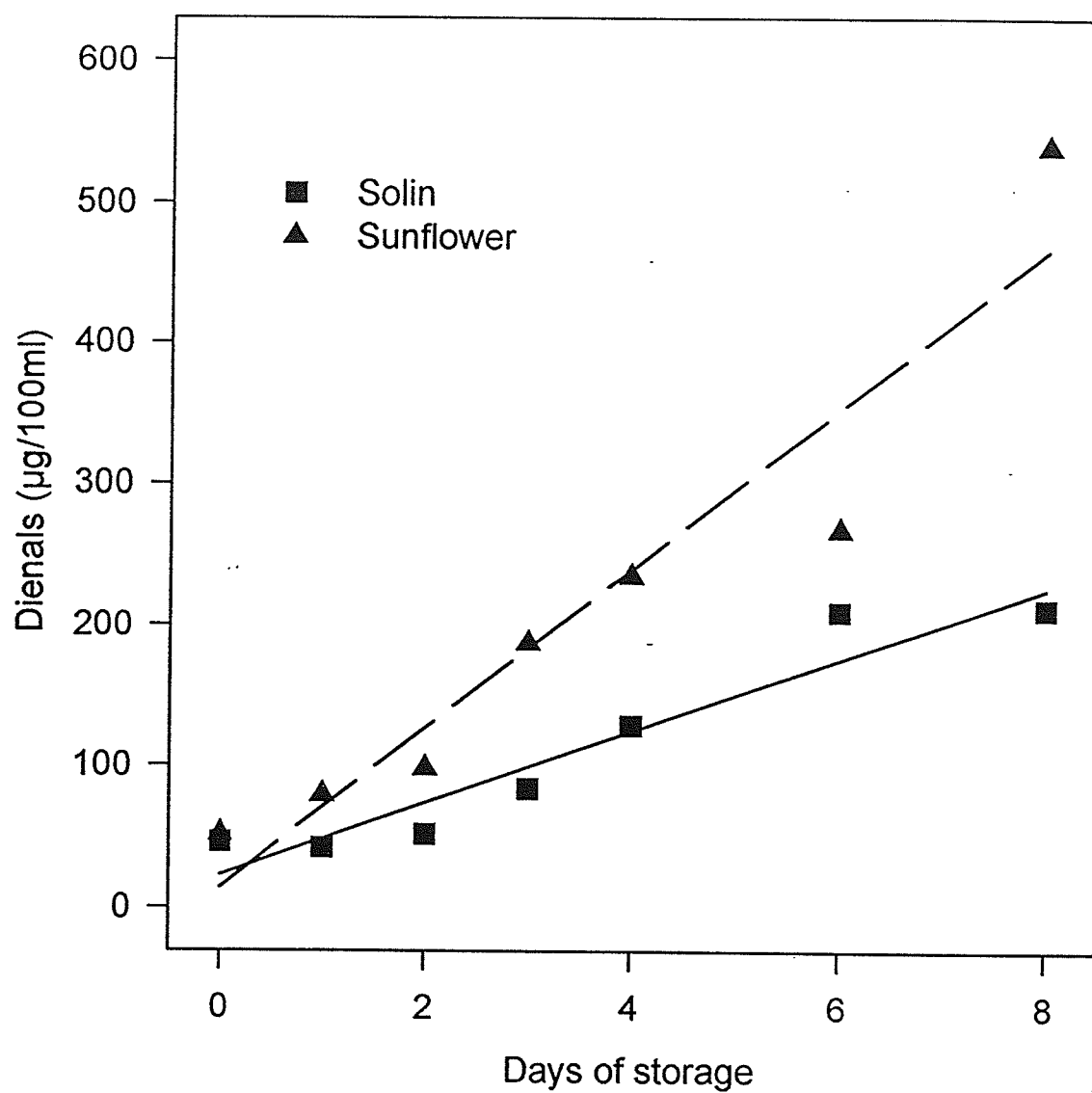


Figure 3.17. Dienals in light stored oils

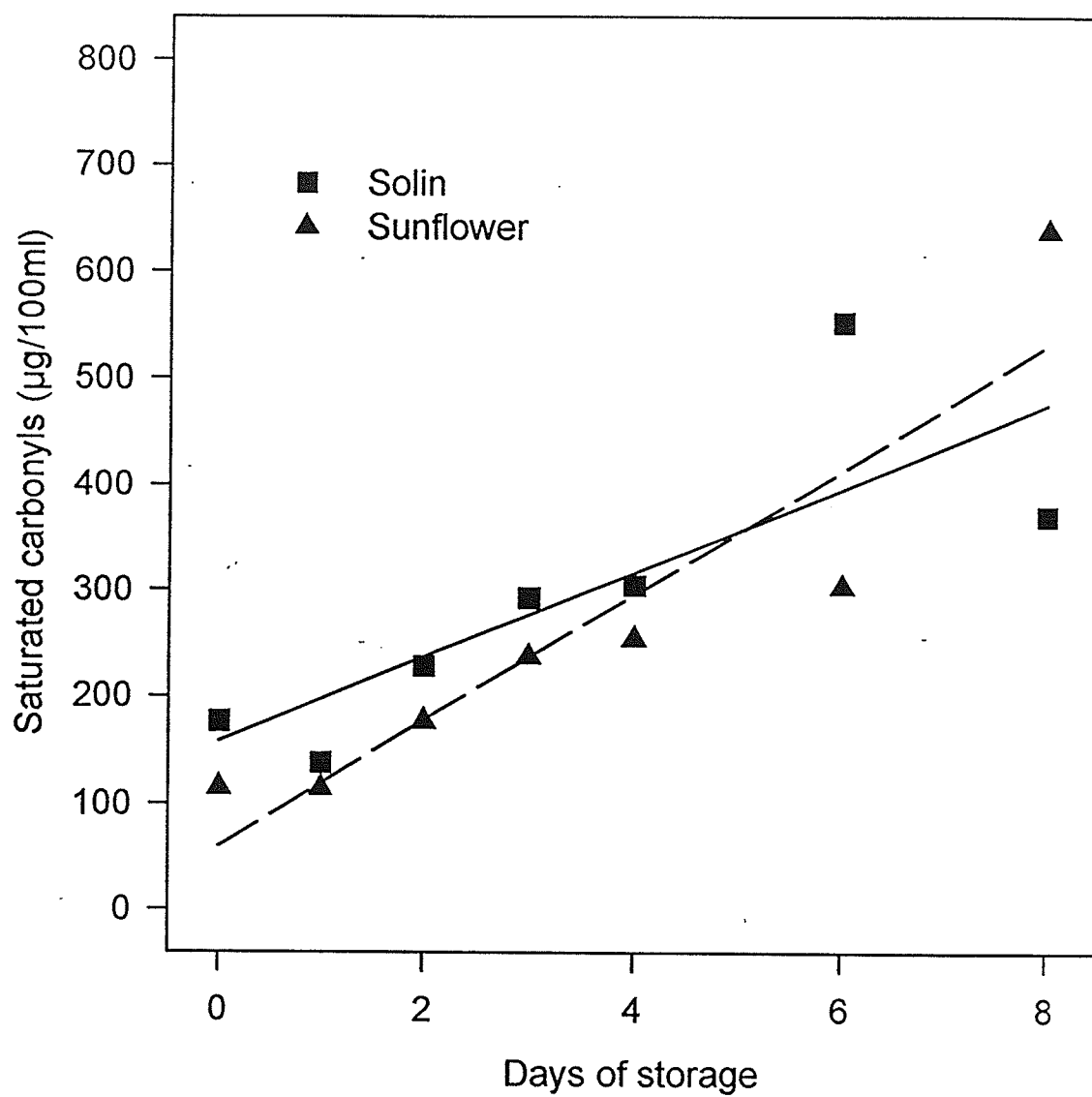


Figure 3.18. Saturated carbonyls in light stored oils

a higher level of saturated carbonyls while at day 8, sunflower oil had a greater level. Both oils exhibited similar ($p \leq 0.28$) rates of development of saturated carbonyls throughout storage (Table 3.11).

3.6.

DISCUSSION

Fresh solin oil was described as 'bland/fresh' but with a detectable 'vegetable/cereal' note whereas fresh sunflower oil was described as 'buttery/sweet'. Hawrysh (1993a) reported that fresh solin oil had a higher grassy odor intensity than sunflower oil. Hawrysh (1993a) also noted the presence of rancid and fishy odors in fresh solin oil. Similar to this study, Warner (1989) described fresh sunflower oil as buttery and nutty whereas Hawrysh (1993a) described fresh sunflower oil as bland.

Results from the accelerated heat storage test indicated that there were differences in stability between solin and sunflower oils depending on the method of evaluation used. Sensory results showed that solin oil had a greater rate of painty odor development throughout storage compared to sunflower oil. This resulted in a higher painty odor score for solin oil at 16 days of storage. Hawrysh (1993a) found that solin oil had a significantly higher painty odor score compared to sunflower oil after 16 days of storage at 60°C. Hawrysh (1993a) also showed that there were no significant differences in rancid odor between solin and sunflower oils over 16 days of storage. Warner (1989) reported that in later stages of storage, sunflower oil developed a rancid odor as opposed to a painty odor which developed in soybean and canola oils by day

16 of accelerated heat storage. The distinction between rancid and painty odors is difficult for panelists which may mean that the results from the Warner (1989) study are in agreement with the results of this study.

In contrast to the sensory findings, sunflower oil had a higher rate of peroxide development over storage and had greater peroxide values at every storage interval compared to solin oil. Similarly, Hawrysh (1993a) found that sunflower oil exhibited higher peroxide values compared to solin oil over 16 days of storage. In addition, both studies showed an induction period of approximately 4 days for solin oil. In contrast, the induction period for sunflower oil was 1 day in this study similar to that reported by Warner (1989). Because the earliest storage interval for Hawrysh (1993a) was day 4 and the peroxide value of sunflower oil had increased substantially by that point, it is difficult to determine the exact induction period in her study, but it likely occurred before day 4 of storage. This situation did not occur with solin oil as the increase in peroxide value for solin oil was not as substantial as it was for sunflower oil at storage day 4. Warner (1989) reported a 24 meq/kg increase in peroxide value for sunflower oil after 6 days of storage similar to the 26 meq/kg increase for the same time period found in this study. However, these increases are less than the 35 meq/kg increase reported by Durance (1986) for sunflower oil for the same storage period.

Volatile analysis indicated that both oils showed similar levels and rates of development of total volatiles throughout accelerated heat storage. Hawrysh

(1993a) reported no significant differences in total volatiles throughout 16 days of storage. In the Warner (1989) study, sunflower oil showed a 7 fold increase in total volatiles after 8 days of storage compared to a 4 fold increase found in this study for the same time period. In this study, no one particular oil showed greater rates of development in all volatile subclasses. Sunflower oil had higher levels of hydrocarbons (mainly pentane) throughout storage but both oils showed similar rates of development. Hawrysh (1993a) reported no significant differences in pentane level throughout 16 days of storage both oils. In this study, sunflower oil had higher levels of dienals (mainly 2,4-decadienal) at days 6, 8, and 12 compared to solin oil but this difference was not evident by storage day 16. Thus, the rates of development of dienals were considered to be similar ($p \leq 0.40$). Hawrysh (1993a) reported no significant differences in 2,4-heptadienals, and 2-4 decadienals at 0, 4, 8, and 16 days of storage between solin and sunflower oils.

The differences observed between solin and sunflower oils in their stability to accelerated heat storage are surprising since the two oils had similar fatty acid compositions. Thus, other factors must be influencing the storage stability of these oils. Differences were observed between the two oils in the type of tocopherols present. Gamma-tocopherol was the predominant tocopherol found in solin oil whereas α -tocopherol was the predominant tocopherol present in sunflower oil. Lea and Ward (1959) reported that α -tocopherol had the lowest antioxidant activity when α -, β -, γ -, and δ -

tocopherols were compared in methyl linoleate held at 50°C. Jung and Min (1990) have also shown that α -, γ -, and δ -tocopherol have optimum concentrations for antioxidant activity and concentrations in excess of these levels resulted in lowered antioxidant activities in soybean oil stored at 55°C. The level of α -tocopherol found in fresh sunflower oil was 233 ppm which is double the level found by Jung and Min (1990) to have optimal antioxidant activity for sunflower oil.

Research has also shown that the position of fatty acids on the triacylglycerol molecule can influence the stability of oils to accelerated heat storage (Neff et al., 1992). The triacylglycerol structure of the oils used in this study is not known, but it is possible that the positional effects may account for some of the differences observed between the two oils in their stability to accelerated heat storage. The role of sterols in the oxidation of edible oils is not clearly understood making it difficult to determine their impact on storage stability (Przybylski, personal communication, 1995). Differences were found in the two oils in the amount of total sterols present. β -sitosterol was the major sterol found in both oils but sunflower oil had greater total sterols compared to solin oil.

Strong correlations were found between painty odor scores and chemical and volatile parameters performed on the heat stored oils. Correlation coefficients were as follows: monounsaturated carbonyls (0.94), total volatiles (0.93), other volatiles (0.93), dienals (0.90), peroxide value (0.86),

hydrocarbons (0.84), and saturated carbonyls (0.82). These strong coefficients suggest that the chemical and volatile parameters were paralleling changes in painty odor development in these two oils stored under accelerated heat storage conditions.

Sunflower oil exhibited greater deterioration during accelerated light storage than solin oil. Sunflower oil accumulated higher levels of peroxides at every storage interval although the rate of peroxide development was not significantly ($p \leq 0.07$) different between the two oils. This lack of significant difference may have been due to the relatively high standard deviation caused by the lack of fit of the regression line at days 4 and 8 for sunflower oil. Hawrysh (1993a) reported the peroxide value of sunflower oil to be 10 times that of solin oil after 6 days of storage under light with an intensity of 1400 lux. Durance (1986) reported that the peroxide value of sunflower oil increased by approximately 110 meq/kg after 4 days of light storage with an intensity of 2690 lux. In this study, the peroxide value of sunflower oil increased by 50 meq/kg after 4 days of storage.

Volatile results indicated that both oils had similar levels of total volatiles and all volatile sub-classes until storage day 6. Sunflower oil had higher levels for all volatile indices at day 8 of storage and had significantly greater rates of development for total volatiles and all volatile sub-classes than solin oil. Since the first and last storage intervals (0, 8 day) are the most influential in the fit of the regression line (Hair et al., 1992), day 8 likely influenced the significant

differences found in the rates of development for each parameter. In contrast, Hawrysh (1993a) reported no significant differences in total volatiles, pentane, 2,4-heptadienals, and 2,4-decadienals between oils or between storage days within each oil treatment. In this study, sunflower oil exhibited a 3 fold increase in total volatiles after 4 days of storage which is similar to the findings of Durance (1986) where a 2 fold increase in volatile carbonyls was reported after 4 days of light storage.

Neither solin or sunflower oils showed a significant increase in painty odor scores throughout 8 days of accelerated light storage and there was no significant difference in the rate of painty odor development between the two oils. It is possible that additional odors may have masked the painty odor and resulting in lower painty odor scores. In addition, a longer storage period may have been required for full development of a painty odor. Similar to this study, Hawrysh (1993a) found that painty odor was present only in low levels in light stored solin and sunflower oils. Hawrysh (1993a) also reported the presence of similar levels of rancid, nutty, and cardboard odors in light stored solin and sunflower oils. Morrison (1981) reported a decrease in the flavor intensity value (FIV) for buttery with a subsequent increase in FIV for rancid and painty for sunflower oil stored 16 weeks under light with an intensity of 1400 lux. Warner (1989) described light-exposed sunflower oil as having a stale or sour flavor when exposed to a light intensity of 7535 lux.

Jung et al. (1991) reported that α - tocopherol had greater antioxidant

activity compared to γ - tocopherol in soybean oil exposed to light (4000 lux) whereas Lea and Ward (1959) found little difference in antioxidant activity between α - and γ - tocopherol in methyl linoleate exposed to light (5900 lux). Since γ - tocopherol was the predominant tocopherol type found in fresh solin oil and α - tocopherol was the predominant tocopherol type found in fresh sunflower oil, the previous research does not explain the difference in light stability between the oils.

Neff et al. (1993) has shown that triacylglycerol structure can influence the stability of oils to accelerated light storage. Positional effects may account for some of the differences between the two oils in terms of their stability to accelerated light storage.

Since painty odor was not found to increase significantly throughout accelerated light storage, marginal correlations were found between painty odor scores and chemical and volatile parameters thus limiting their use as predictors. Correlation coefficients were as follows: saturated carbonyls (0.68), monounsaturated carbonyls (0.57), total volatiles (0.54), other volatiles (0.53), dienals (0.43), hydrocarbons (0.41), and peroxide value (0.13).

3.7**CONCLUSIONS**

Fresh solin oil was described as having a bland odor with a vegetable/cereal/grassy note. Solin oil showed greater stability to peroxide development but was less stable to painty odor development than sunflower oil during accelerated heat storage. Both oils showed similar accumulation of flavor volatiles throughout storage. Under accelerated light conditions, solin oil showed greater stability to peroxide development and accumulation of flavor volatiles than sunflower oil. Painty odor intensity did not increase for either oil throughout the 8 days of light storage. This finding may have been due to insufficient storage time which did not permit adequate development of a painty odor. Since the fatty acid compositions of the two oils were similar, the differences in storage stability are somewhat unexpected suggesting that other factors may have influenced their storage stability. Differences in tocopherol type between the oils may be one possible explanation for the observed differences in storage stability between solin and sunflower oils. Further research is needed to determine the exact role of tocopherols on storage stability and whether there are differences in triacylglycerol structure which may account for the differences in storage stability between solin and sunflower oils.

Chapter 4

STORAGE STABILITY OF POTATO CHIPS FRIED IN SOLIN, SUNFLOWER AND HYDROGENATED SOYBEAN OILS

4.1

INTRODUCTION

During deep-fat frying, oils are exposed to elevated temperatures (180 - 190°C) in the presence of air and moisture (Hawrysh, 1990). Under such conditions, thermolytic and oxidative reactions occur in the oil causing the formation of both volatile and non-volatile decomposition products. Volatile decomposition products contribute to the odor of the oil and to the odor and flavor of the fried product. Since fried products absorb a significant amount of frying oil e.g. potato chips (30-40% by weight), the storage stability of these products is largely a function of the stability of the frying oil. During potato chip storage, oxidative reactions occur in the oil causing the development of off-odors and off-flavors. Previous research has shown that genetically modified canola and soybean oils with reduced linolenic acid levels have improved the storage stability of fried products (Hawrysh, 1995; Liu and White, 1992). Recently, through breeding, the relatively high linolenic acid content of traditional flax (45 - 65%) has been reduced to less than 5%, thus increasing the potential for its use in food applications. The name solin refers to these new low linolenic varieties which have fatty acid profiles similar to those of sunflower.

Few studies have examined the storage stability of potato chips fried in

sunflower oil and no studies are available on the storage stability of potato chips fried in solin oil. Robertson and Morrison (1978) reported that potato chips fried in sunflower oil exhibited similar storage stability to potato chips fried in cottonseed oil. Cottonseed oil is considered a high quality frying oil and is used extensively by the potato chip industry. It was the purpose of this research project to compare the storage stability of potato chips fried in solin, sunflower, and hydrogenated soybean oils. Partially hydrogenated soybean oil was included in this study, since it is used in commercial frying operations and is considered a stable frying oil.

4.2 *EXPERIMENTAL DESIGN*

4.2.1 *Materials*

Pilot plant refined, bleached and deodorized (RBD) solin oil (*POS Pilot Plant Corp.*, Saskatoon, SK), commercially RBD sunflower oil (SFO) (*CanAmera Foods*, Altona, MB) and commercially RBD partially hydrogenated soybean oil (HSO) (*CanAmera Foods*, Dundas, ON) were used in the study. Dimethylpolysiloxane (Dow Corning, Toronto, ON) was added (2 ppm) to solin and SFO while HSO already contained the antifoaming agent dimethoxysiloxane (2 ppm).

4.2.2 *Frying and Storage Protocol*

Frying took place over seven days using a 11-kg capacity *Garland* fryer (Model 80-03; Toronto, ON). Solin and HSO were each fried for two days whereas SFO was fried for three days. Potato chips produced from the first

day of frying for each oil were collected for chemical, GC and sensory analyses. Potato chips produced from the second day of frying for each oil were collected for sensory training sessions while chips from the third day of frying from SFO were used in the screening of panelists for sensory evaluation. Chips fried in partially hydrogenated canola and low linolenic canola oils from a concurrent study in the Department of Foods and Nutrition were also used in the screening of panelists.

The fryer was filled with $11 \text{ kg} \pm 100 \text{ g}$ of oil. On day one of frying for each oil, the oil was heated to $185^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 30 minutes to season the oil. *Norchip* variety potatoes (*Southern Potato Co.*, Winkler, MB) were washed and sliced to 1.3 mm thickness using an Omega slicer (Toronto, ON). The slices ($100 \text{ g} \pm 5 \text{ g}$) were soaked in water for 4 minutes to remove surface starch. Potato slices were blotted dry before being placed in the bottom of the wire basket with minimal overlapping. The potatoes were fried until bubbling ceased and potatoes were uniformly light brown (2.5 - 3.0 minutes). The basket was then removed and allowed to drain for 2 minutes. The chips were placed on paper towels for 5 minutes before being put into a large bowl. Batches of potato chips were fried every 9 minutes $\pm$ 30 seconds. At the end of the frying day, the pooled chips were placed in large plastic bags (double bagged) and placed in the freezer at -25°C . Within seven days of freezer storage, potato chips ($4.25 \text{ g} \pm 0.25 \text{ g}$) were packaged into bags (7.6 cm x 11.4 cm) formed from potato chip packaging material comprised of plastic laminate with

foil lining and heat sealed. Fifty-four batches of potato chips were fried on the first day of frying for each oil, forty-five batches were fried on the second day of frying for each oil, and forty batches were fried on the third day of frying (SFO only).

The sealed bags were placed in a forced draft oven at $60^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 0, 4, 8, 12, 16, and 20 days. On each of the five cabinet shelves, four racks were used to hold the chip bags upright to allow for air flow between the bags. Because of space limitations, all bags required for the study could not be stored at the same time. Set one included all samples required for chemical and GC analysis, screening, reference and test samples needed for sensory evaluation (900 bags). Set two included all bags required for training the sensory panel (800 bags). The bags were randomly placed in the cabinet and were removed from the cabinet using the following protocol:

- 1) Oil type was chosen using a random numbers table.
- 2) Shelf number in cabinet was chosen using a random numbers table.
- 3) Rack number on shelf was chosen using a random numbers table.
- 4) Moved along the row of bags on the rack until two bags of desired oil type were located.
- 5) Repeated procedure from step #2 onward until required number of bags had been removed for one oil type.
- 6) Repeated procedure from step #2 onward for second oil type.

Upon removal from the cabinet, bags were stored at -25°C until analysis could be carried out (approximately 6 months).

4.2.3 *Methods of Analysis for Fresh Oils*

Fatty Acid Composition

The fatty acid composition of the oils was determined using AOCS official method Ce 1-62 (AOCS, 1990) with minor modifications. To carry out the procedure, acid catalyzed transesterification was used. Samples (approximately 50 mg) were weighed into threaded 25 mL capacity test tubes and 1 mL of petroleum ether was added to produce a monophasic system. Methanolic HCl (12 mL) was added and the tubes mixed on a vortex before being placed in an oven (70°C) for 1 hour. The tubes were removed from the oven and mixed frequently on a vortex during the first 10 minutes of heating. The tubes were cooled to room temperature and then 6 mL of water and 5 mL of *iso*-octane were added. The samples were left to form a clear upper layer (approximately 1 hour) before being injected in the GC. A *Hewlett Packard* model 5890 GC (*Hewlett Packard Inc.*, Avondale, USA) was used with a capillary column (Supelcowax 10, 30 m x 0.25mm, phase coating thickness of $0.15\ \mu\text{m}$, *Supelco* Canada, Mississauga, ON). Samples ($2.0\ \mu\text{l}$) were injected and the initial time and initial column temperature used was 175°C for 2 min which was increased to 235°C at a rate of $3^{\circ}\text{C}/\text{min}$. The final time was 5 min which produced a total run time of 27 min. Fatty acid composition was determined using reference standards which allowed for peak identification.

Analysis was carried out in duplicate.

Peroxide Values

Peroxide values were determined using AOCS method Cd 8-53 (AOCS, 1990) except that 2.5 g of oil was used instead of 5.0 g. Analysis was carried out in duplicate.

Free Fatty Acids

Free fatty acids were determined using AOCS method Ca 5a-40 (AOCS, 1990). Analysis was carried out in duplicate.

Metals

Copper, iron, and nickel were measured in the oils by atomic absorption spectroscopy using methods developed by van Loon (1980) and Cassetta and Aldridge (1992). The analysis was performed by E. Gawalko and C. Jarrin at the *Grain Research Laboratory* (Winnipeg, MB).

4.2.4 *Methods of Analysis for Stored Chips*

Oil Extraction Procedures

Oils were extracted from the chips according to the method developed by Bligh and Dyer (1959) with modifications. Chips (8 - 9 g) were placed in a 100 mL beaker and crushed using a teflon rod. Chloroform:methanol (2:1) was added (50 mL) and the mixture was homogenized until no large pieces of chip remained. The liquid phase was added to a 250 mL separatory funnel using a funnel lined with #4 (15 cm diameter) filter paper. To extract further, more chloroform:methanol (2:1) was added (50 mL) to the remaining solid phase in

the beaker. The mixture was homogenized and all the contents were added to the separatory funnel. A final 20 mL of chloroform:methanol (2:1) was used to rinse the beaker of any remaining particles and the mixture was added to the separatory funnel. To allow time for the lipid material to adequately drain through the filter paper, the mixture stood for 30 minutes. Water was added (24 mL) and the separatory funnel was inverted several times to mix the crude extract. The emulsion stood overnight to allow time for separation. The lower layer was transferred into a 250 mL flask and the solvent was removed using an evaporator. To ensure all water had been removed, benzene was added (1 - 2 mL) to the extract. Evaporation was carried out until the weight of the extract did not change (approximately 20 - 25 minutes). Extracts were placed in 4 mL vials, flushed with nitrogen and stored at -25°C until analysis could be carried out (approximately 6 months).

Conjugated Dienes

Conjugated dienes were determined on oils extracted from the stored chips using AOCS method Ti 1a-64 (AOCS, 1990). Analysis was carried out in duplicate.

Polar Compounds

Total polar compounds (%) were measured on oils extracted from the stored chips using the Iatroscan TLC-FID (Iatron Laboratories, Tokyo, Japan) according to the method developed by Sebedio et al., (1987). The extracted oils were mixed with hexane (4% w:v) and spotted (0.4 μL) onto silica rods.

The rods were placed in a developing chamber for 55 minutes using a solvent mixture composed of dichloroethane (59 mL), chloroform (10 mL), acetone (1.4 mL), and acetic acid (0.4 mL). After removal from the chamber, the rods were placed in an oven (120°C) for five minutes before being run on the latroscan. The scan speed was 35 seconds/rod and the air and hydrogen volumes for the FID were 2.0 L/min. and 185 mL/min. respectively. The amount (percent) of triacylglycerols was determined using calibration curves. Percent total polars were calculated by subtracting the percent of triacylglycerols from 100%. Analysis was carried out in duplicate.

Sensory Evaluation

Odor evaluation of the stored potato chips was carried out using a trained panel. Ethical approval was granted by the Faculty of Human Ecology Ethics Committee before panelists were recruited by letters of invitation (Appendix D). Panelists were recruited from student and staff members in the Faculties of Human Ecology and Agricultural and Food Sciences. Twenty-two persons agreed to take part in the screening sessions (two days). Panelist selection was based on odor acuity, availability, and a desire to take part in a sensory evaluation project. To determine odor acuity, panelists completed six triangle tests. On screening day 1, panelists completed 3 triangle tests, evaluating each of the following potato chip sets:

- 0 and 4d chips fried partially hydrogenated canola oil
- 0 and 6d chips fried in low linolenic canola oil

→ 0 and 4d chips fried in SFO

On screening day 2, all evaluations were repeated. At each triangle test, the panelists were presented with three coded samples in which two of the samples were the same and one was different. The panelists' task was to determine which one of the three coded samples was different from the other two. Samples were labelled with 3-digit codes and the order of presentation for each panelist was randomized. Panelists carried out the evaluations in a sensory panel room equipped with individual computerized sensory booths and took a 15 second break between tests. *Compusense version 4.1* (Compusense Inc., Guelph, ON) a sensory evaluation software package, provided panelists with on-screen instructions, sample presentations and recorded their judgements. The criterion for selection was four correct tests out of six tests which represents a 66.6% success rate. This exceeded the *American Society for Testing Materials* (ASTM) suggested success rate of 60% for the selection of panelists. Of the 22 persons who completed the screening sessions, 12 achieved a success rate of 66.6% or greater. Of the 12 persons, one could not take part in training due to time constraints resulting in a final panel of 11 persons for training. Panelists who were not selected for training were notified by letter thanking them for their efforts.

Training

Prior to the start of training, the research team extensively evaluated the stored potato chips fried in the three oils. These sessions were held to identify

the predominant odors present in the samples throughout storage in order to accelerate the training process. During these sessions, it was found that chips fried in solin and SFO had fresh potato chip (FPC), stale, and rancid odors at the various storage intervals whereas chips fried in HSO had FPC, stale, and sour-cheesy odors. As a result, panelists were trained for the odor parameters present in chips fried in solin and SFO and then completed the testing on these chips. The panel was then trained for the odor parameters present in chips fried in HSO and then completed the testing on these chips.

Training sessions took place over a 6 week period with each session lasting approximately 30 minutes. The initial training session had four objectives: to introduce the panelists to one another and to the panel leader, to explain and demonstrate the evaluation technique, to become familiar with the reference samples, and to gain experience in evaluating chips. Once the evaluation technique was agreed upon by all panelists, the panel evaluated reference samples selected to illustrate FPC (potato chips fried in SFO and stored for 0d), stale (chips fried in low linolenic canola oil and stored for 12d), and rancid (chips fried in SFO and stored for 20d). The panel agreed that the three references were very distinct and that they were named appropriately. The panelists were then presented with 2 coded samples (chips fried in SFO and stored 0d and 16d) and were asked to match the odors found in the coded samples with those found in the reference samples. The panelists were able to successfully match the odor in the 0d coded sample with the FPC reference

and the odor in the 16d coded sample with the rancid reference.

At the next training session, panelists were introduced to the concept of scaling by giving them a short demonstration on the use of the 15 cm line scale. Separate line scales were used for the three attributes and the panel agreed on the following endpoint descriptors: 0 cm = *NONE*, 15 cm = *STRONG*. The panel also determined that the references for FPC, stale, and rancid should be placed at the 15 cm endpoints of the scales. The final ballot agreed upon by all panelists is presented in Figure 4.1.

Figure 4.1. Ballot used in sensory evaluation of potato chips

Method for Evaluation:

Cut the bag just below the seal, take three short sniffs. Fold the bag over and secure the bag with a paper clip.

Task:

Smell the FRESH POTATO CHIP, STALE, and RANCID references noting the presence and intensity of the odors. Wait 15 seconds between references. These references represent the right endpoints of the line scales. Evaluate each coded sample in the order listed below. Evaluate one sample for ALL THREE attributes BEFORE moving on to the next coded sample. Wait 15 seconds between samples. Place a vertical line at the point on the scale that represents the intensity of the attribute present in the sample.

SAMPLE:

Fresh Potato Chip		FPC
↓		↓
<i>None</i>		<i>Strong</i>
	Stale	
↓		↓
<i>None</i>		<i>Strong</i>
	Rancid	
↓		↓
<i>None</i>		<i>Strong</i>

During training, values from the scales were obtained by measuring in centimetres from the left (*NONE*) endpoint to the vertical line that had been placed on the scale. During test sessions, panelists recorded their evaluations directly on the computer screen with the use of a mouse and the software package automatically calculated the values.

In subsequent training sessions, panelists were presented with coded samples and were asked to rate the samples for their intensity of FPC, stale, and rancid odors in relation to the reference samples. As expected, panelists found the transitional samples (e.g. 4d, 8d, and 12d) to be the most difficult to evaluate since these samples were a complex mixture of all three odors. More training was required before panelists felt confident in their judgements of these samples. As training progressed, chips fried in solin oil were also presented to the panel. Panelists felt that the references were appropriate for these samples and after several practice sessions were confident in their judgements. During training, panelists were also given the same samples to evaluate on subsequent training days to ensure that they were consistent in their judgements.

The training sessions held for chips fried in HSO followed a similar pattern. The same FPC and stale references were used to evaluate chips fried in HSO. In addition, a sour cheesy reference (chips fried in HSO and stored 12d) was provided. The panel agreed to place all references at the 15 cm endpoint (*STRONG*) of the line scale. Panelists were presented with a range of

samples over the entire storage period in order to gain experience in the evaluation of chips fried in HSO.

Testing

Two test days with two sessions per day were required to complete the evaluation of chips fried in solin and SFO. On test day one, panelists evaluated chips fried in solin oil in the morning session and evaluated chips fried in SFO in the afternoon session. The evaluations were repeated on test day two. At each test session, chips from the six storage intervals were randomized so that each panelist received a different sample presentation order. The panelists evaluated three coded samples, took a five minute break and then evaluated the remaining three coded samples. Two test days with one session per day were required to complete the evaluation of chips fried in HSO. The same testing protocol was followed as for chips fried in solin and SFO.

Volatile Analysis

Volatile analysis was carried out using the method developed by Przybylski et al. (1993). The analysis on the stored potato chips was completed using a *Perkin-Elmer* gas chromatograph (*Perkin-Elmer Inc.*, Norwalk, CT) . A capillary column (60 m x 32 mm, DB-5) (*J&W*, Fulson, CA) was used with a DB-5 phase coating thickness of 1 μ m. The column temperature was programmed from 45°C, 85°C, 125°C, 235°C at rates 2, 3, 4, 5°C/min respectively. The temperature was held at lower and upper regions for 2 min and 10 min respectively. The injector temperature was set at 125°C while the

flame ionization detector (FID) was set at 250°C. Helium was used as the carrier gas. To carry out the analysis, 15 cm glass tubes were used. Each tube was packed with one - 2 cm glass wool plug that was placed 1.5 cm from the trap column end. Chips (2 bags) were crushed using a mortar and pestle and the appropriate amount of crushed chips was added to the glass tube. The amount of chips used for analysis was dependent on the interval being analyzed. The sample size was reduced for chips that had been stored for longer periods of time because of the large amount of volatiles present in these samples. Smaller sample sizes resulted in better peak separation and therefore better identification of volatile compounds. After the chip weight was noted, a second glass wool plug was placed in the glass tube to contain the chips. Dodecane (C_{12}) served as the the internal standard for the analysis and was injected (5 μ L, 187 ng of C_{12} in solution) into the trap column end of the glass tube. The trap column was cooled using liquid nitrogen and the samples were purged for 15 minutes using helium gas. Following purging, the trapped volatiles were separated and the total run time was 73 minutes. Reference samples containing hydrocarbons, saturated carbonyls, monounsaturated carbonyls, dienals, pyrazines, pentyl furan, and 1-octen-3-ol were used to identify peaks using relative retention times.

4.2.5

Statistical Analysis

Sensory Evaluation Data

Analysis of covariance (ANCOVA) was used to analyze the sensory data using the PROC MIXED procedure of *SAS* (*SAS Institute*, Cary, NC, 1992). Oil type and storage interval were selected as the predictor variables. The first step was the determination of appropriate statistical models for each of the four odor parameters. Analysis of the full models was done initially followed by the development of appropriate reduced models. Reduced models were tested for loss of information against full models and were also tested for any significant improvement over null models. The appropriate reduced models selected for all for all four sensory odor attributes are presented in Appendix F.

Fixed effects of oil type and storage interval were determined and can be found in Tables F.1. to F.4 in Appendix F. From the fixed effects tables, predictor equations were produced and 95% confidence intervals were determined on the differences in slopes. Sample calculations are presented in Appendix F.

Chemical and Volatile Data

ANCOVA was used to analyze the chemical and volatile results using the regression procedure of *Minitab version 8* (*Addison-Wesley Publishing Inc*, Reading, MA, 1992). Similar to the analysis of the sensory results, oil type and storage interval were used as the predictor variables. Fixed effects of oil type and storage interval were determined and can be found in Tables G.1. to

G.9. in Appendix G. Predictor equations were produced from the fixed effects tables and 95% confidence intervals were determined on the differences in slopes.

Pearson's correlation coefficients were calculated between the four sensory odor attributes and the chemical and GC volatile parameters using *Minitab*.

4.3

RESULTS

4.3.1

Fresh Oils

Tables 4.1 to 4.3 present results from the analysis of the fresh oils. The fatty acid compositions of solin and SFO were similar but solin oil had greater levels of linolenic (18:3) acid compared to sunflower oil (Table 4.1). Linoleic (18:2) was the predominant fatty acid in both oils followed by oleic (18:1), palmitic (16:0) and stearic (18:0) acids. Isomers comprised the largest percentage of fatty acids in HSO. These were likely isomers of linoleic and oleic acids but since accurate identification was not possible, these fatty acids were grouped as isomers. Following the isomer category, linoleic, palmitic, oleic and stearic acids comprised the majority of the fatty acid composition of HSO.

Table 4.1. Relative fatty acid composition (%) of fresh Oils

Fatty Acid	Solin	SFO	HSO
14:0	0.06	0.05	0.07
15:0	0.02	----	----
16:0	6.01	5.76	9.73
16:1	0.09	0.05	----
17:0	0.07	0.05	0.12
17:1	0.05	0.03	----
18:0	4.25	5.02	6.95
18:1	16.75	16.28	7.87
18:2	70.20	70.61	25.33
18:3	1.86	0.43	1.97
20:0	0.15	0.34	0.50
20:1	0.14	0.17	0.29
22:0	----	----	0.41
22:1	0.21	0.94	----
24:0	0.16	0.27	0.15
24:1	----	----	----
Isomers	----	----	46.62

All three oils were of good initial quality as indicated by low peroxide values and free fatty acids (Table 4.2). Fresh SFO contained greater amounts of iron compared to solin oil (Table 4.3) but the level was below the Codex Alimentarius Standards (1993) maximum level of 1.5 ppm. Neither oil contained significant amounts of copper or nickel. Metal analysis of fresh HSO was not performed.

Table 4.2. Peroxide values and free fatty acids determined for fresh oils

Chemical Indice	Solin	SFO	HSO
Peroxide value (meq/kg)	0.39	0	0
Free fatty acids (% as oleic)	0.1	0.1	0.1

Table 4.3 Metals in fresh solin and sunflower oils

Metal	Solin (ppm)	Sunflower (ppm)
Copper	<0.02	<0.02
Iron	<0.02	0.032
Nickel	<0.02	<0.02

4.3.2***Stored Potato Chips***

The data for the chemical, sensory and GC volatile analyses completed on the stored potato chips are presented in Figures 4.2 to 4.14. The data for all response parameters was analyzed for two separate time periods since there were two distinct periods of development for each response parameter. Time period I included 0, 4, 8d while time period II included 12, 16, and 20d. Since the data was analyzed as two time periods, a predictor equation was produced for each time period. Therefore, it is not possible to predict the response between 8 and 12d of storage and thus predictor equations were not used in the plotting of the figures, but were used for comparisons of slopes between the 3 oils.

Conjugated dienes in extracted oils from stored chips

Chips fried in SFO exhibited a large increase in conjugated dienes at day 4 of storage whereas chips fried in solin oil did not show a large increase in conjugated dienes until day 12 (Figure 4.2). Chips fried in HSO showed little change in conjugated dienes until day 16 of storage. Chips fried in SFO had a significantly ($p \leq 0.05$) greater rate of development of conjugated dienes in time period I (0, 4, 8d) compared to chips fried in solin and HSO (Table 4.4). For time period II (12, 16, 20d), chips fried in solin and SFO had significantly ($p \leq 0.05$) greater rates of development of conjugated dienes than chips fried in HSO.

Total polar compounds in extracted oils from stored chips

Chips fried in SFO increased in total polars at day 4 of storage, whereas chips fried in solin oil increased at day 12 (Figure 4.3). No change in total polars was observed for chips fried in HSO during storage. Chips fried in all three oils had similar rates of development of total polar compounds in time period I (Table 4.4). Chips fried in solin and SFO had significantly ($p \leq 0.05$) greater rates of development of polar compounds compared to chips fried in HSO during time period II.

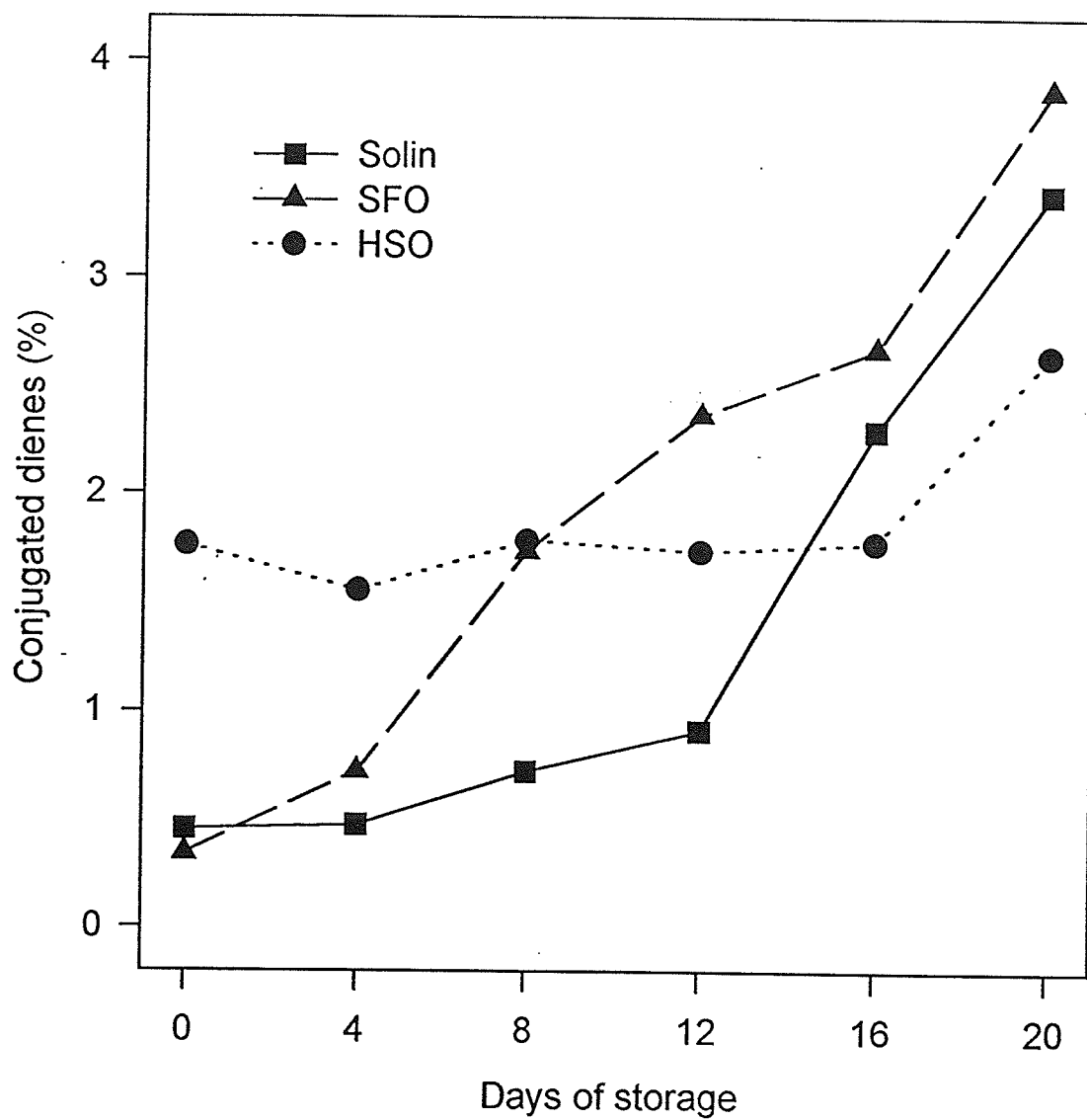


Figure 4.2. Conjugated dienes in extracted oils from stored potato chips

Table 4.4. Summary of equations and confidence intervals for conjugated dienes and polar compounds in stored potato chips

Parameter (time period)	Oil	Equations ¹	Confidence interval (C.I. ²) (95%)
Conjugated dienes(%) (I)	Solin	$0.42 + 0.04(\text{INT})$	SFO vs Solin (0.14,0.34)
	SFO	$0.14 + 0.28(\text{INT})$	Solin vs HSO (-0.06,0.14)
	HSO	$1.69 + 0.00(\text{INT})$	SFO vs HSO (0.18,0.38)
Conjugated dienes(%) (II)	Solin	$-2.74 + 0.36(\text{INT})$	SFO vs Solin (-0.20,0)
	SFO	$-1.40 + 0.26(\text{INT})$	Solin vs HSO (0.15,0.35)
	HSO	$0.23 + 0.11(\text{INT})$	SFO vs HSO (0.05,0.25)
Polar compounds(%) (I)	Solin	$3.3 - 0.01(\text{INT})$	SFO vs Solin (-0.25,1.73)
	SFO	$0 + 0.73(\text{INT})$	Solin vs HSO (-1.05,0.93)
	HSO	$0.9 + 0.05(\text{INT})$	SFO vs HSO (-0.31,1.67)
Polar compounds(%) (II)	Solin	$-25.57 + 2.46(\text{INT})$	SFO vs Solin (-0.89,1.09)
	SFO	$-14.57 + 2.56(\text{INT})$	Solin vs HSO (1.41,3.39)
	HSO	$0.63 + 0.06(\text{INT})$	SFO vs HSO (1.51,3.49)

¹ INT = storage interval

² significant ($\alpha = 0.05$) difference in slope if zero is not included in C.I.

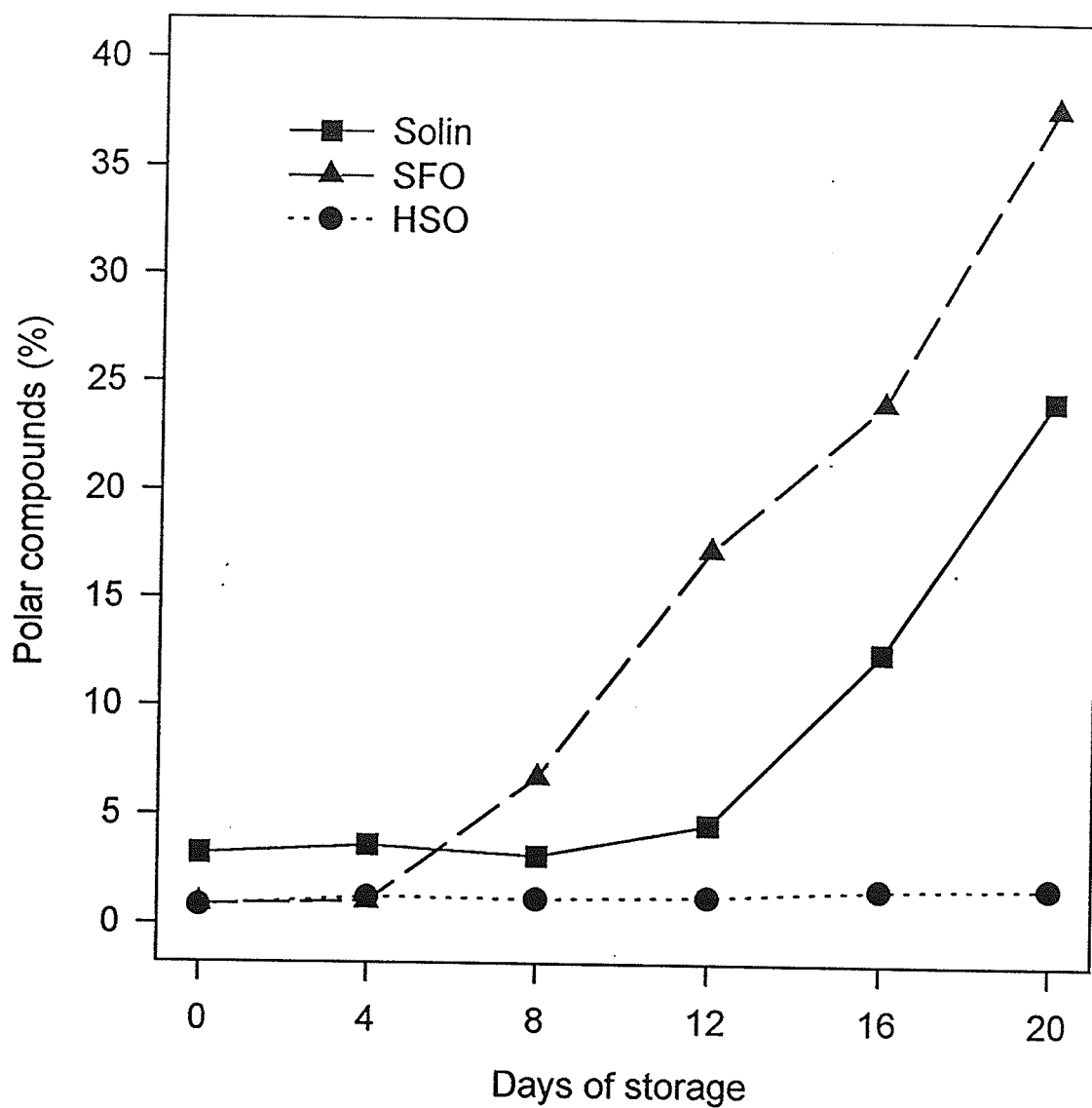


Figure 4.3. Polar compounds in extracted oils from stored potato chips

Sensory evaluation

As storage progressed, chips fried in all three oils showed a decrease in FPC odor intensities (Figure 4.4). Chips fried in SFO exhibited a significantly ($p \leq 0.05$) greater rate of decrease in FPC odor compared to chips fried in solin and HSO during time period I (Table 4.5). Chips fried in all three oils had similar rates of decrease in FPC odor during time period II.

Chips fried in SFO had the highest intensity of stale odor at day 4 of storage which proceeded to decrease throughout the remainder of storage (Figure 4.5). This same trend occurred for chips fried in solin oil but stale odor peaked at day 12 of storage. Chips fried in HSO gradually increased in stale odor throughout storage. Chips fried in solin and SFO exhibited similar rates of development of stale odor during time period I, and were significantly ($p \leq 0.05$) greater than chips fried in HSO (Table 4.5). Chips fried in solin and SFO exhibited significantly ($p \leq 0.05$) greater rates of decrease in stale odor intensity than chips fried in HSO during time period II. Chips fried in solin oil also showed a significantly ($p \leq 0.05$) greater rate of decrease in stale odor compared to chips fried in SFO during time period II.

Chips fried in SFO showed a rapid increase in rancid odor at day 4 of storage, whereas chips fried in solin oil did not show this increase until storage day 8 (Figure 4.6). Chips fried in SFO had a significantly ($p \leq 0.05$) greater rate of development of rancid odor through time period I compared to solin oil but this trend was reversed during time period II (Table 4.5).

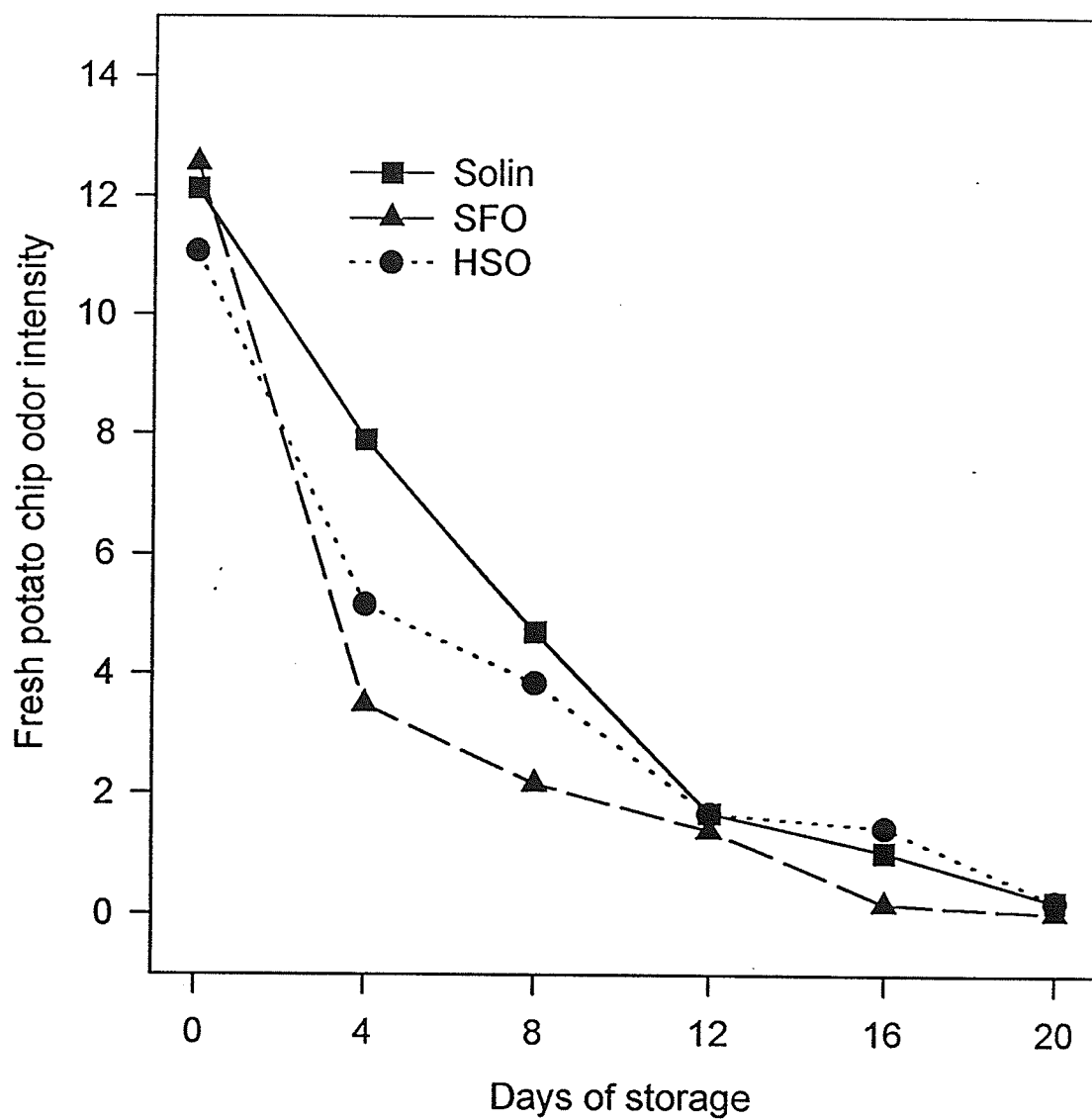


Figure 4.4. Fresh potato chip odor scores in stored potato chips

Table 4.5. Summary of equations and confidence intervals for FPC, stale, rancid, and sour-cheesy odor attributes in stored potato chips

Parameter (time period)	Oil	Equations ¹	Confidence interval (C.I. ²) (95%)
Fresh potato chip odor intensity (I)	Solin	11.94-0.93(INT)	SFO vs Solin (-0.63,-0.11)
	SFO	11.25-1.30(INT)	Solin vs HSO (-0.29,0.23)
	HSO	10.30-0.90(INT)	SFO vs HSO (-0.66,-0.14)
Fresh potato chip odor intensity (II)	Solin	3.90-0.18(INT)	SFO vs Solin (-0.25,0.27)
	SFO	3.23-0.17(INT)	Solin vs HSO (-0.26,0.26)
	HSO	4.0-0.18(INT)	SFO vs HSO (-0.25,0.27)
Stale odor intensity (I)	Solin	1.60 + 0.70(INT)	SFO vs Solin (-0.30,0.32)
	SFO	2.14 + 0.71(INT)	Solin vs HSO (0.03,0.65)
	HSO	0.93 + 0.36(INT)	SFO vs HSO (0.04,0.66)
Stale odor intensity (II)	Solin	19.56-0.91(INT)	SFO vs Solin (0.41,1.03)
	SFO	5.60-0.19(INT)	Solin vs HSO (-1.58,-0.96)
	HSO	-1.06 + 0.36(INT)	SFO vs HSO (-0.86,-0.24)
Rancid odor intensity (I)	Solin	0.03 + 0.01(INT)	SFO vs Solin (0.29,0.83)
	SFO	-0.56 + 0.57(INT)	
Rancid odor intensity (II)	Solin	-9.08 + 1.01(INT)	SFO vs Solin (-0.78,-0.24)
	SFO	2.01 + 0.50(INT)	
Sour-cheesy odor intensity(I)	HSO	2.09 + 0.52(INT)	
Sour-cheesy odor intensity(II)	HSO	9.48-0.33(INT)	

¹ INT = storage interval

² significant ($\alpha = 0.05$) difference in slope if zero is not included in C.I.

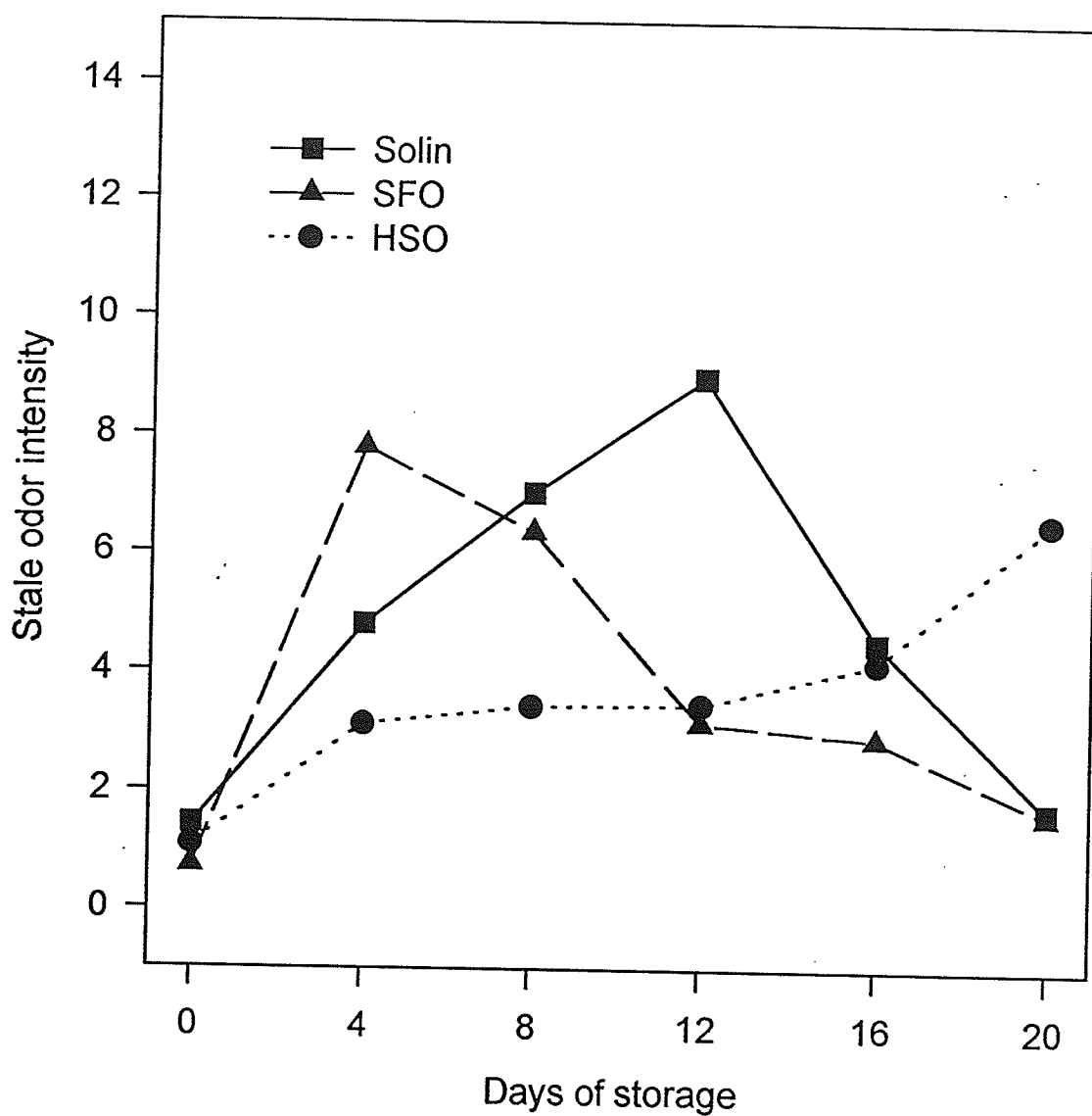


Figure 4.5. Stale odor scores in stored potato chips

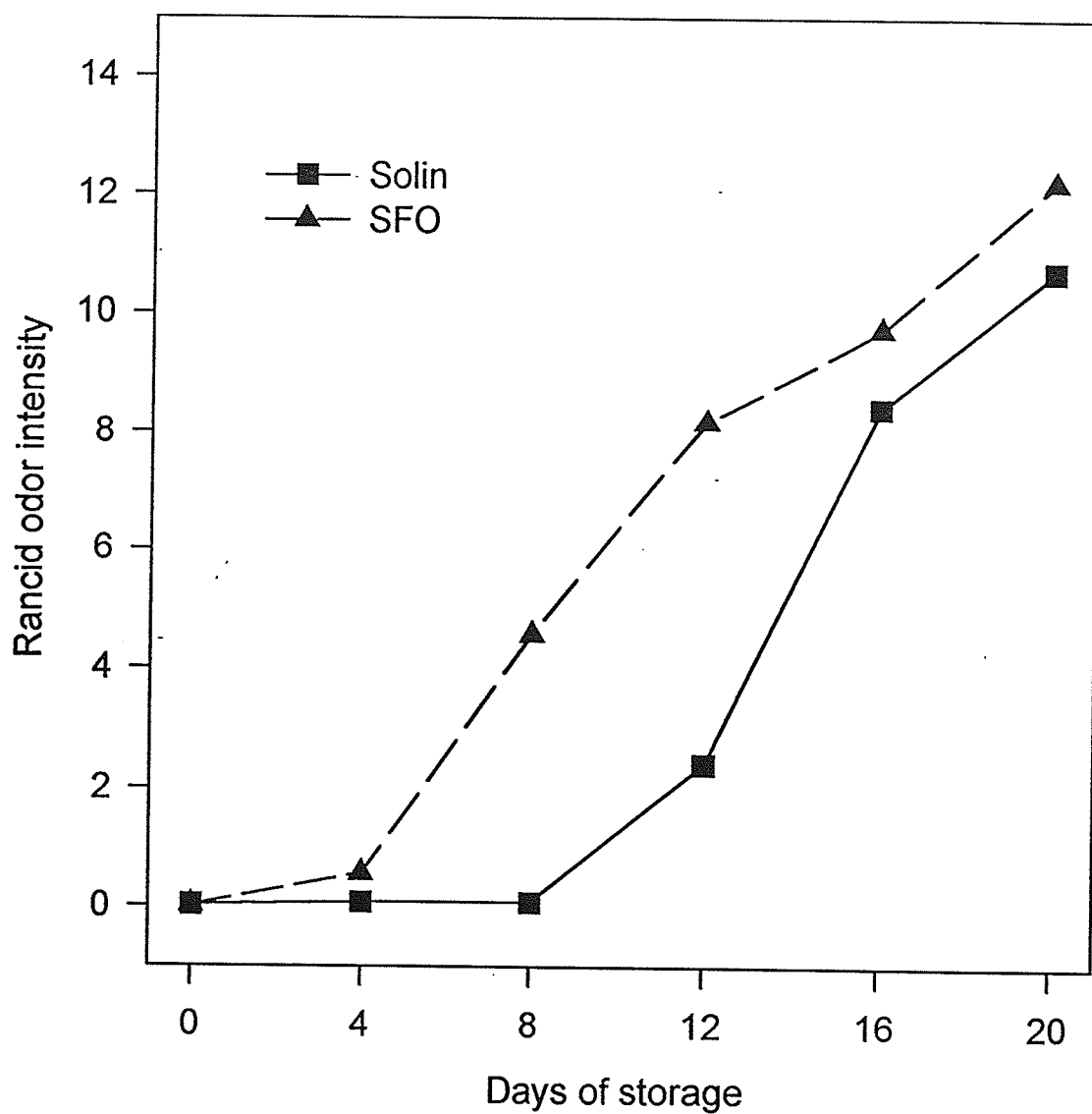


Figure 4.6. Rancid odor scores in stored potato chips

Chips fried in HSO had the most intense sour-cheesy odor at storage day 4 and the least intense sour-cheesy odor at day 0 (Figure 4.7). This odor gradually decreased throughout the remainder of storage.

In summary, chips fried in all three oils exhibited different odor characteristics throughout the storage period. The odor transition for chips fried in HSO was different than for chips fried in solin and SFO. Chips fried in solin and SFO had high initial FPC odor intensities which decreased rapidly with storage. This was followed by a subsequent increase in stale odor which gave way to an intense rancid odor. Chips fried in HSO had a high initial FPC odor which decreased rapidly with storage. At day 4, the chips had an intense sour-cheesy odor but this was followed by a subsequent increase in stale odor throughout the remainder of storage.

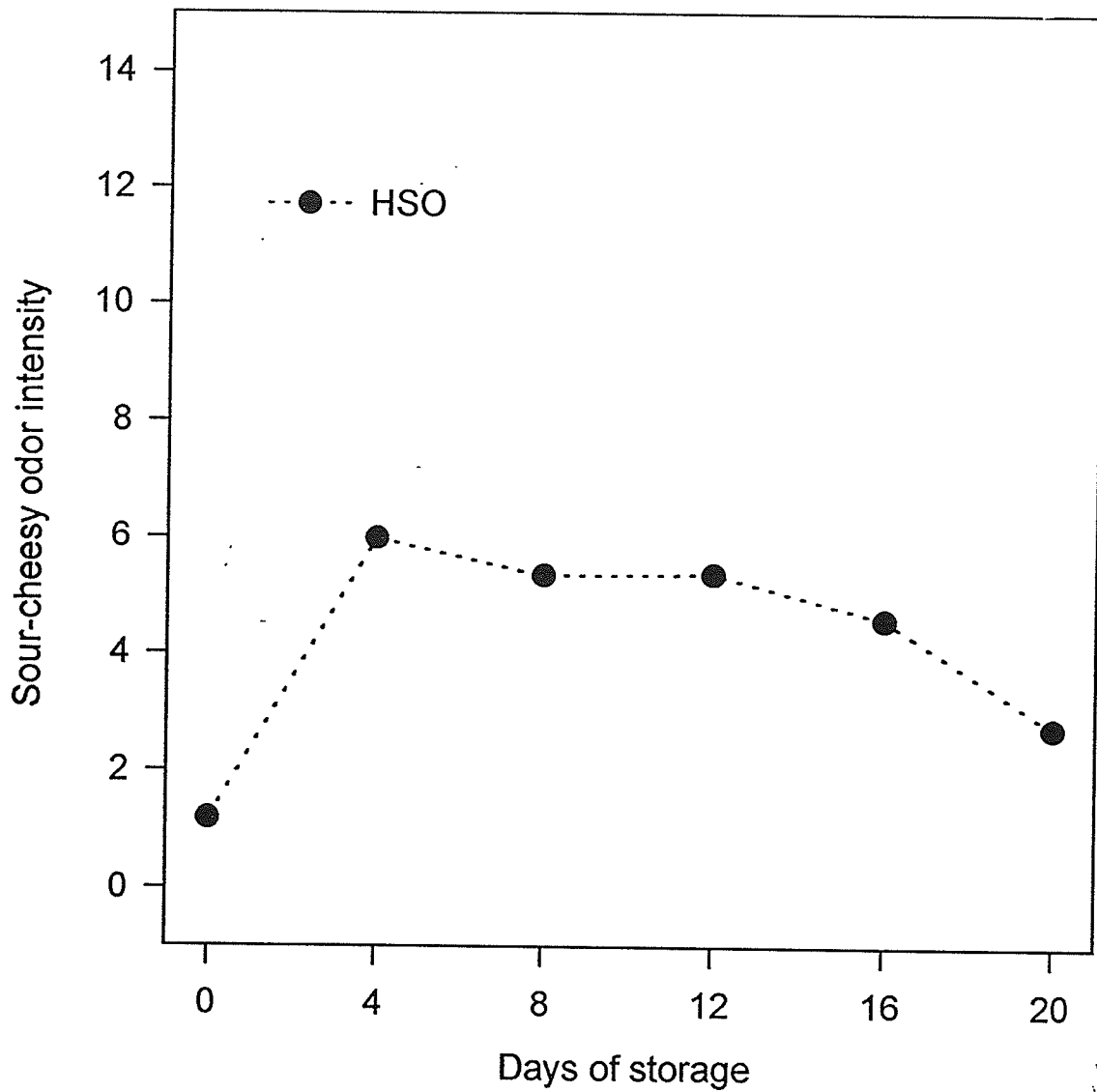


Figure 4.7. Sour-cheesy odor in stored potato chips

Volatile Analysis

Chips fried in solin and SFO increased rapidly in total volatiles (Figure 4.8), hydrocarbons (Figure 4.9), dienals (Figure 4.10), monounsaturated carbonyls (Figure 4.11), saturated carbonyls (Figure 4.12), other volatiles (Figure 4.13) and unknown volatiles (Figure 4.14) at day 12 of storage. No changes in total volatiles and volatile sub-classes were observed for chips fried in HSO throughout storage. Chips fried in all three oils had similar rates of development of total volatiles and all volatile subclasses in time period I (Tables 4.6 - 4.8). In time period II, chips fried in SFO had significantly ($p \leq 0.05$) greater rates of development of total volatiles and all volatile subclasses compared to chips fried in solin and HSO. Chips fried in solin oil also had significantly ($p \leq 0.05$) greater rates of development of total volatiles, dienals, saturated carbonyls, other volatiles, and unknown volatiles in time period II compared to chips fried in HSO.

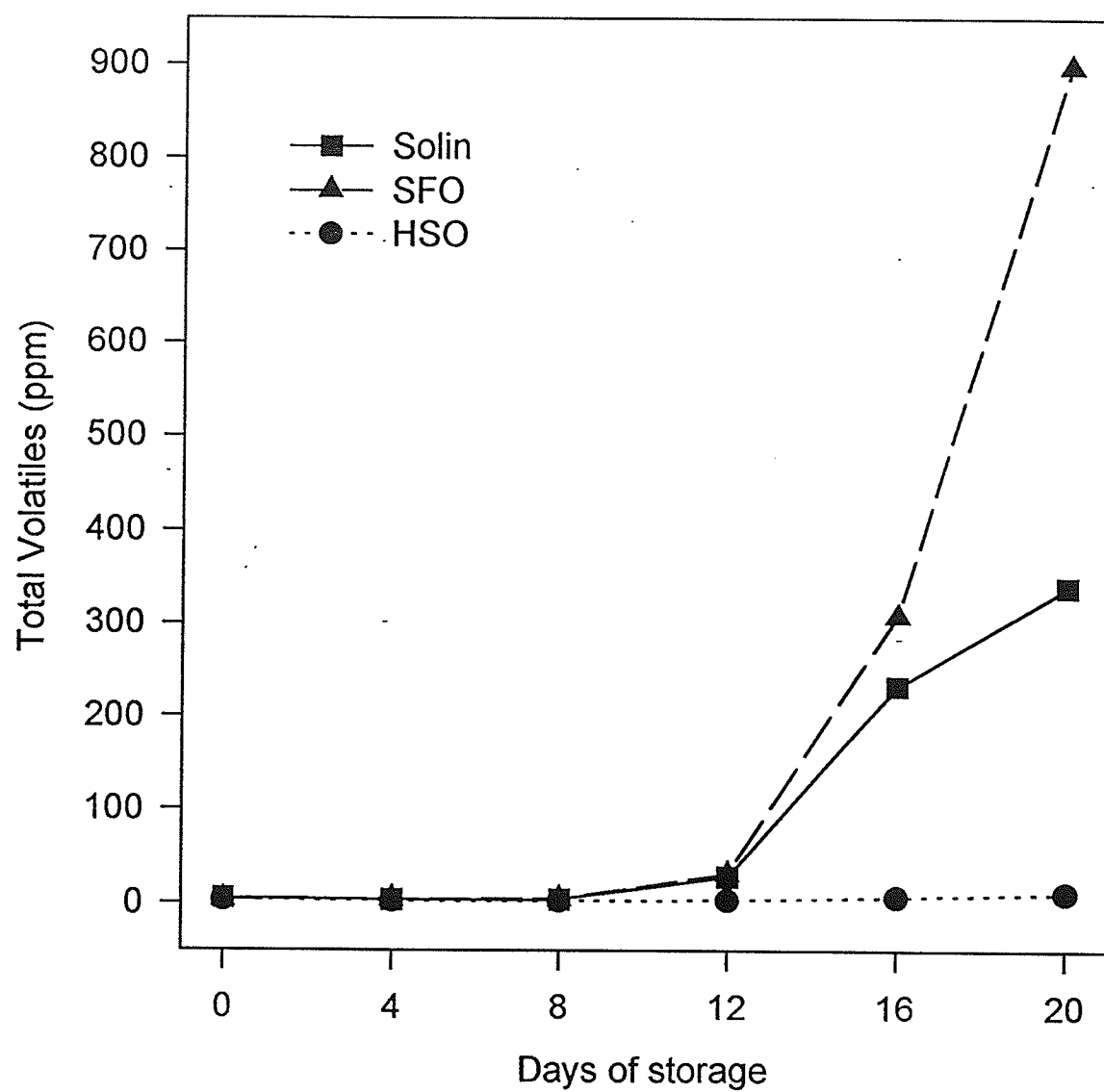


Figure 4.8. Total volatiles in stored in potato chips

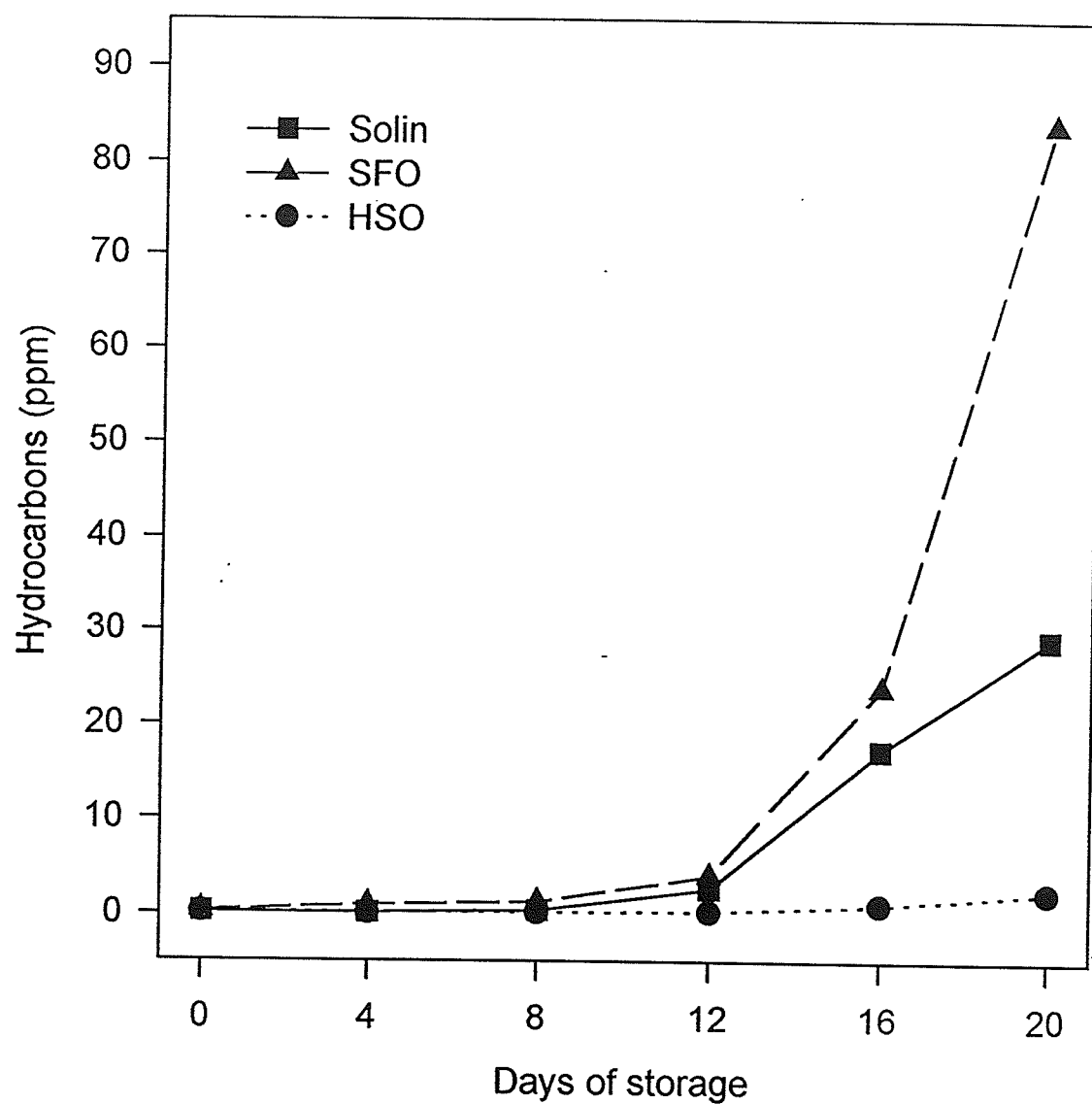


Figure 4.9. Hydrocarbons in stored potato chips

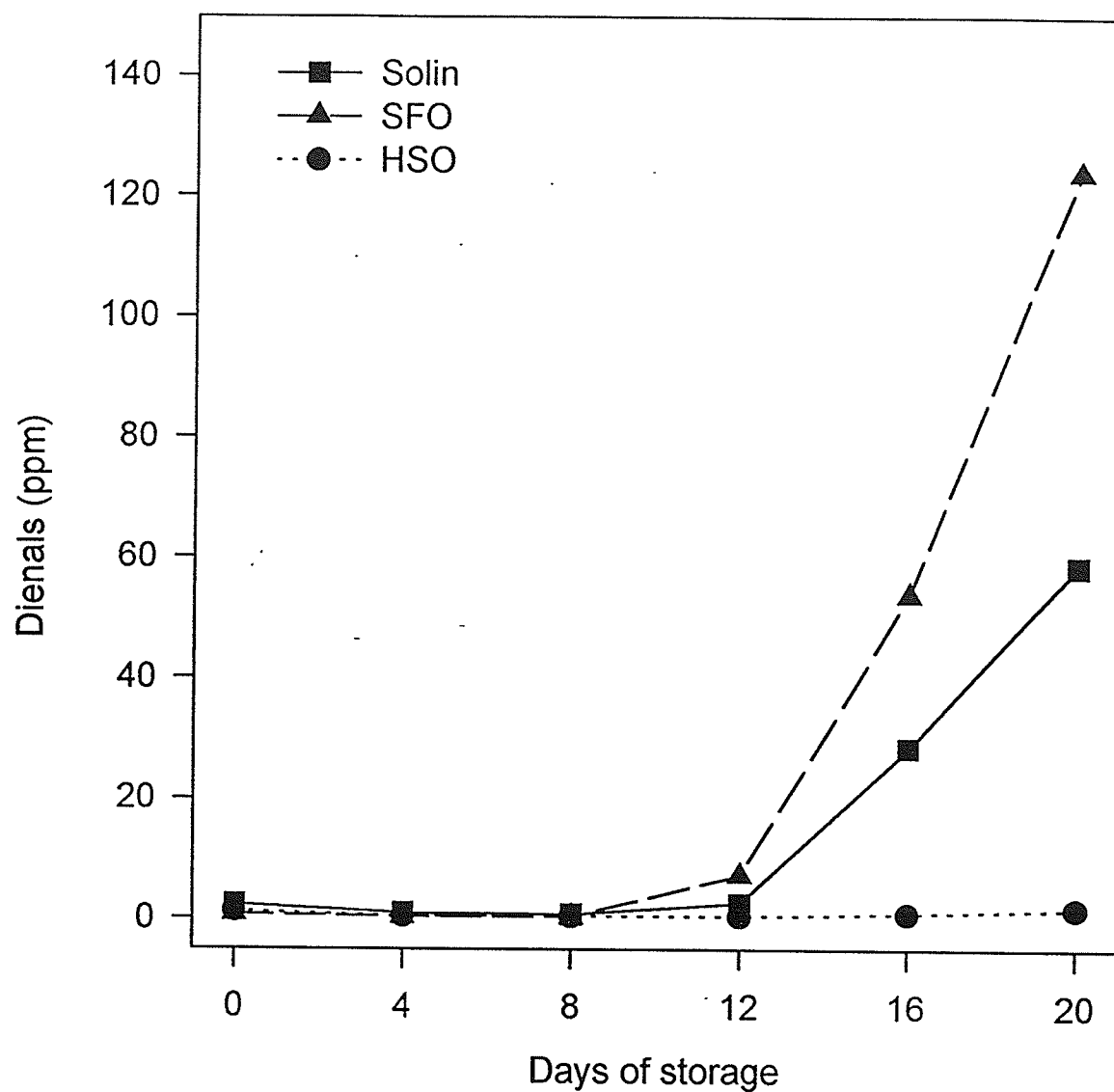


Figure 4.10. Dienals in stored potato chips

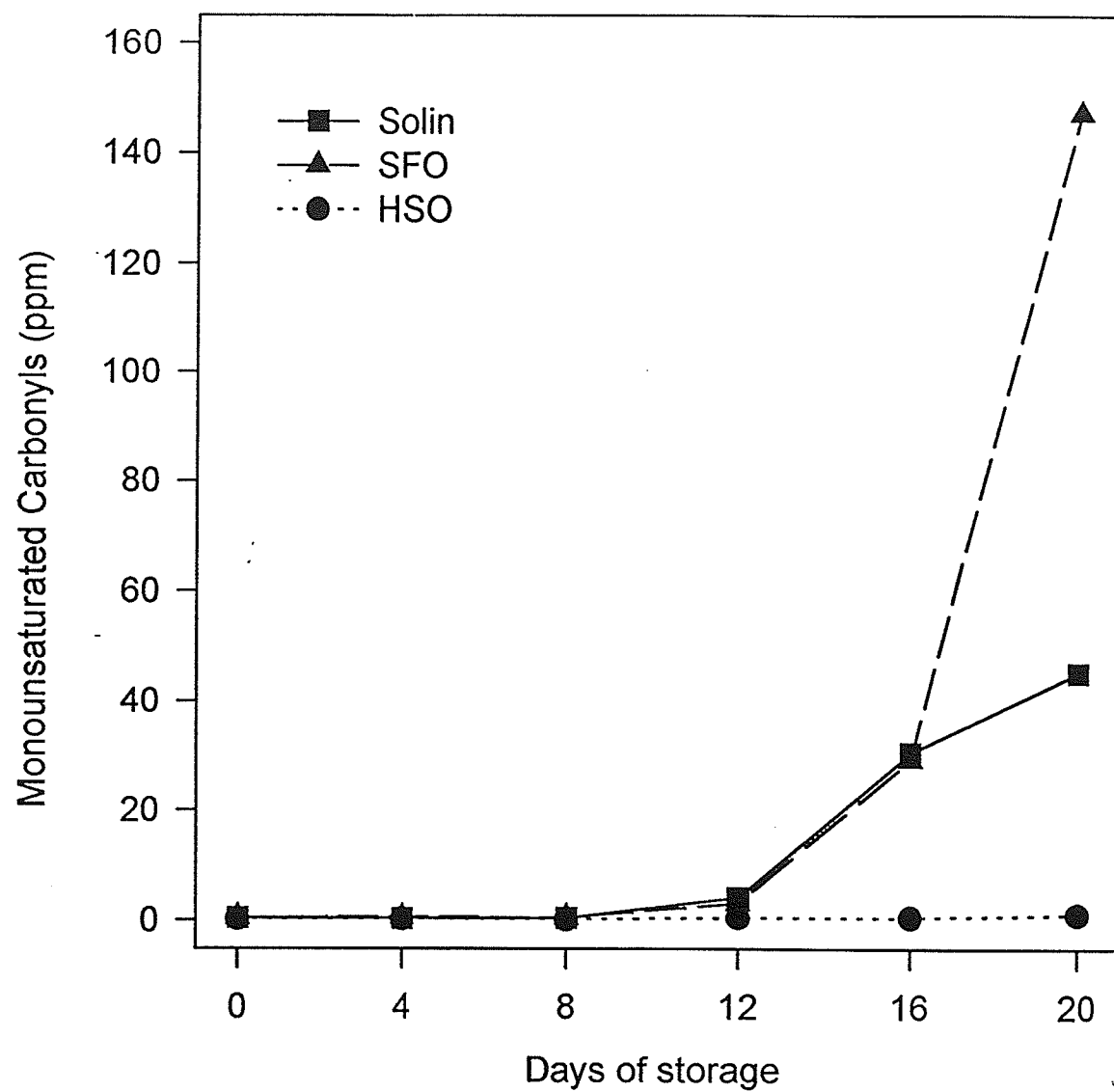


Figure 4.11. Monounsaturated carbonyls in stored potato chips

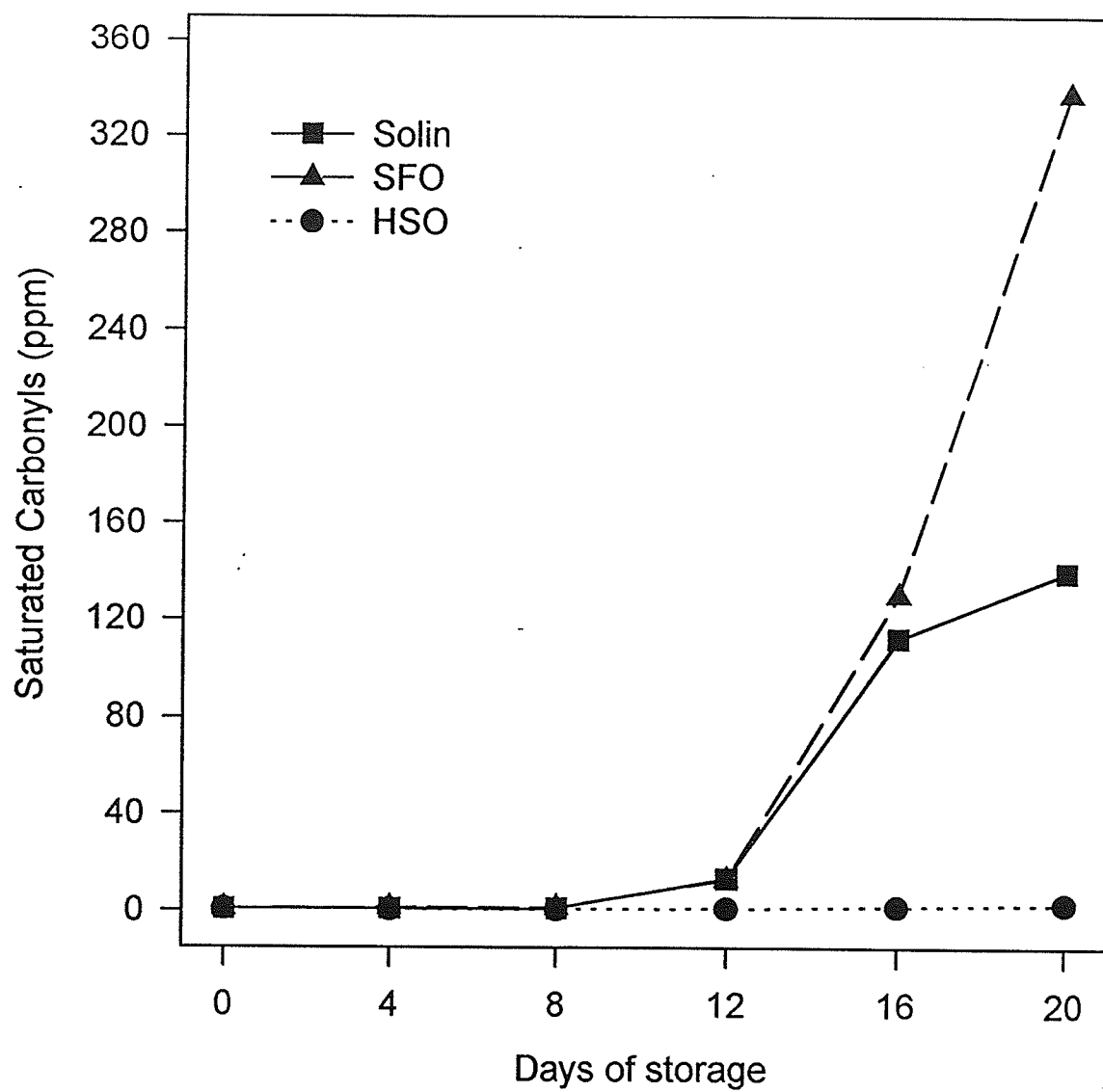


Figure 4.12. Saturated carbonyls in stored potato chips

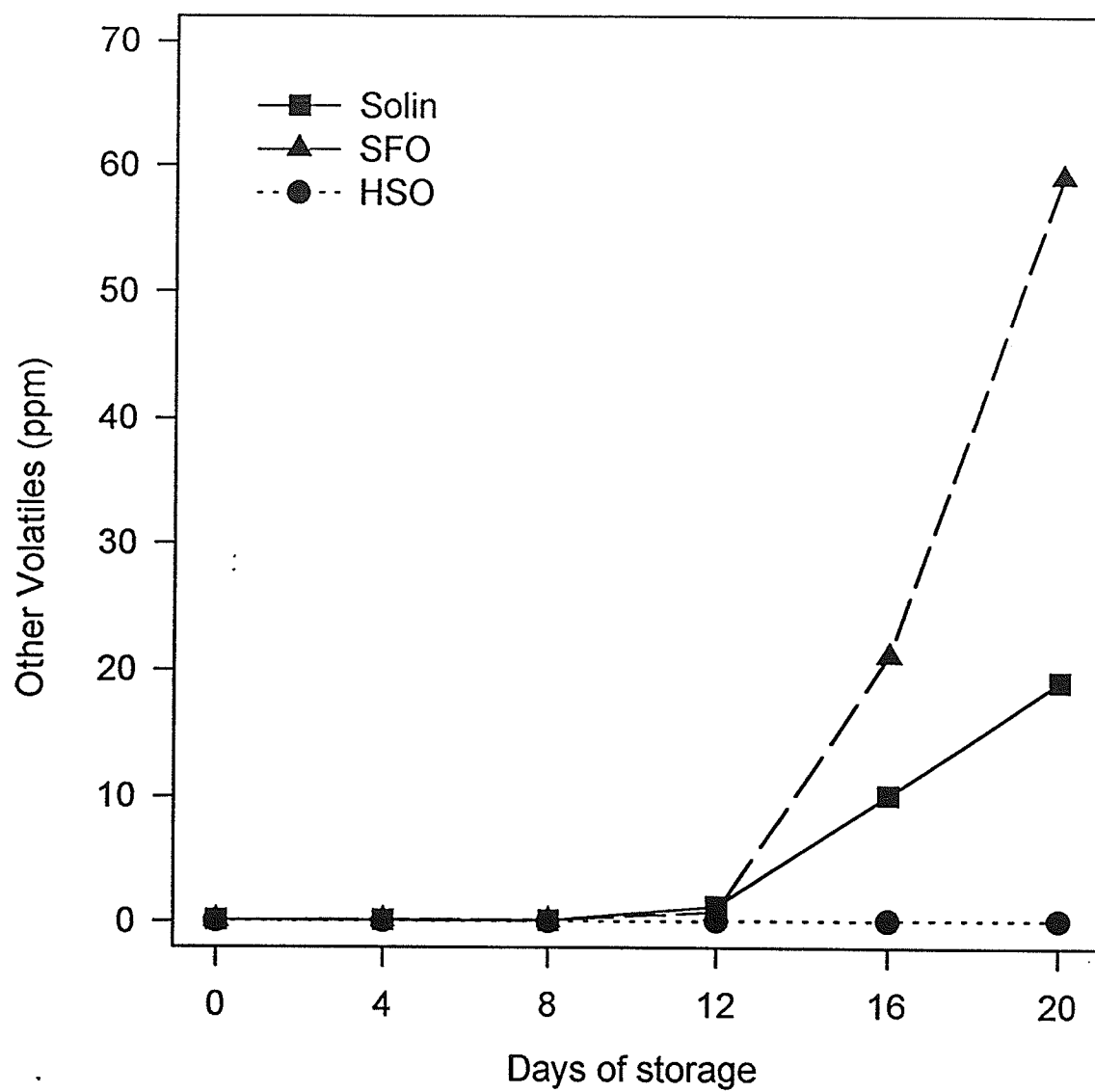


Figure 4.13. Other volatiles in stored potato chips

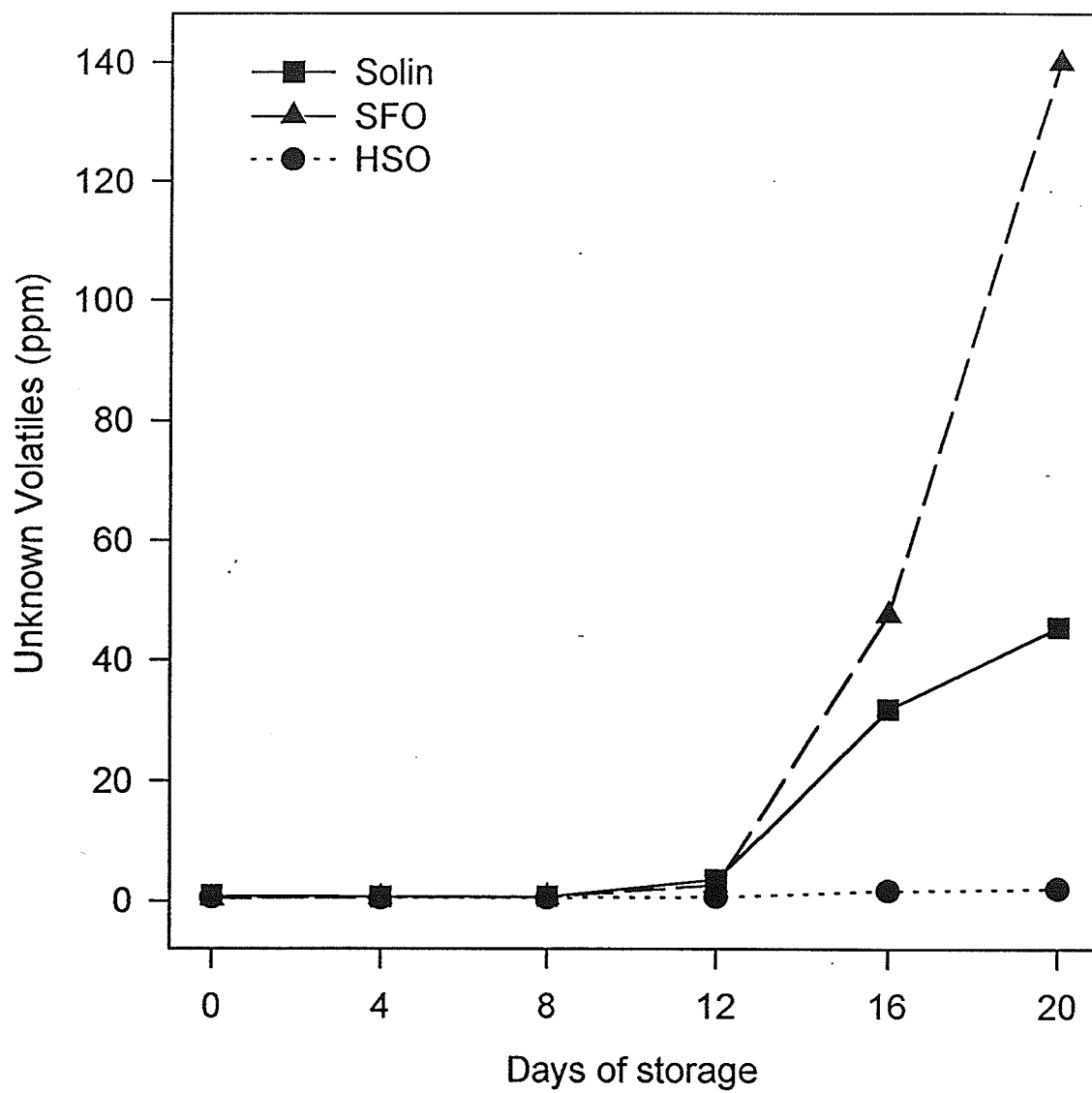


Figure 4.14. Unknown volatiles in stored potato chips

Table 4.6. Summary of equations and confidence intervals for total volatiles, hydrocarbons and dienals in stored potato chips

Parameter (time period)	Oil	Equations ¹	Confidence interval (C.I. ²) (95%)
Total Volatiles (I)	Solin	5.0-0.14(INT)	SFO vs Solin (-33.0,33.6)
	SFO	3.0+0.16(INT)	Solin vs HSO (-33.3,33.3)
	HSO	3.0-0.14(INT)	SFO vs HSO (-33.0,33.6)
Total Volatiles (II)	Solin	-423+38.91(INT)	SFO vs Solin (35.7,102.3)
	SFO	-1322+107.91(INT)	Solin vs HSO (4.7,71.3)
	HSO	-8+0.91(INT)	SFO vs HSO (73.7,140.3)
Hydrocarbons (I)	Solin	0.2+0.02(INT)	SFO vs Solin (-4.00,4.22)
	SFO	0.2+0.13(INT)	Solin vs HSO (-4.09,4.13)
	HSO	0.2-0.0(INT)	SFO vs HSO (-3.98,4.24)
Hydrocarbons (II)	Solin	-36.5+3.31(INT)	SFO vs Solin (2.56,10.78)
	SFO	-122.9+9.98(INT)	Solin vs HSO (-1.06,7.16)
	HSO	-2.9+0.26(INT)	SFO vs HSO (5.61,13.83)
Dienals (I)	Solin	2.2-0.20(INT)	SFO vs Solin (-2.73,3.03)
	SFO	1.1-0.05(INT)	Solin vs HSO (-2.98,2.78)
	HSO	-1.5-0.10(INT)	SFO vs HSO (-2.83,2.93)
Dienals (II)	Solin	-85.9+7.33(INT)	SFO vs Solin (5.76,11.51)
	SFO	-188.5+15.96(INT)	Solin vs HSO (4.30,10.05)
	HSO	-1.5+0.16(INT)	SFO vs HSO (12.93,18.68)

¹ INT = storage interval

² significant ($\alpha = 0.05$) difference in slope if zero is not included in C.I.

Table 4.7. Summary of equations and confidence intervals for monounsaturated carbonyls, saturated carbonyls and other volatile compounds in stored potato chips

Parameter (time period)	Oil	Equations ¹	Confidence interval (C.I. ²) (95%)
Monounsatur. Carbonyls (I)	Solin	0.4-0.0(INT)	SFO vs Solin (-9.43,9.43)
	SFO	1.3+0-0(INT)	Solin vs HSO (-9.42,9.44)
	HSO	0.3-0.01(INT)	SFO vs HSO (-9.42,9.44)
Monounsatur. Carbonyls (II)	Solin	-55.4+5.13(INT)	Solin vs SFO (3.42,22.28)
	SFO	-227.6+17.98(INT)	Solin vs HSO (-4.38,14.48)
	HSO	-0.6+0.08(INT)	SFO vs HSO (8.47,27.33)
Saturated Carbonyls (I)	Solin	0.7+0.03(INT)	SFO vs Solin (-11.67,11.77)
	SFO	0.7+0.08(INT)	Solin vs HSO (-11.68,11.76)
	HSO	0.7-0.01(INT)	SFO vs HSO (-11.63,11.81)
Saturated Carbonyls (II)	Solin	-163.8+15.83(INT)	SFO vs Solin (12.98,36.42)
	SFO	-488.8+40.53(INT)	Solin vs HSO (3.88,27.32)
	HSO	-1.8+0.23(INT)	SFO vs HSO (28.58,52.02)
Other volatiles (I)	Solin	0.16+0.0(INT)	SFO vs Solin (-1.78,1.80)
	SFO	0.06+0.01(INT)	Solin vs HSO (-1.79,1.79)
	HSO	0.06+0.0(INT)	SFO vs HSO (-1.78,1.80)
Other volatiles (II)	Solin	-25.55+2.23(INT)	SFO vs Solin (3.27,6.85)
	SFO	-89.65+7.29(INT)	Solin vs HSO (0.34,3.92)
	HSO	-0.05+0.01(INT)	SFO vs HSO (5.49,9.07)

¹ INT = storage interval

² significant ($\alpha = 0.05$) difference in slope if zero is not included in C.I.

Table 4.8. Summary of equations and confidence intervals for unknown compounds stored potato chips

Parameter (time period)	Oil	Equations ¹	Confidence interval (C.I. ²) (95%)
Unknown volatile compounds (I)	Solin	0.9-0.03(INT)	SFO vs Solin (-4.56,4.70)
	SFO	0.6+0.04(INT)	Solin vs HSO (-4.64,4.62)
	HSO	0.6-0.02(INT)	SFO vs HSO (-4.57,4.69)
Unknown volatile compounds (II)	Solin	-51.3+4.89(INT)	SFO vs Solin (6.26,15.52)
	SFO	-193.4+15.78(INT)	Solin vs HSO (0.08,9.34)
	HSO	-1.4+0.18(INT)	SFO vs HSO (10.97,20.23)

¹ INT = storage interval

² significant ($\alpha = 0.05$) difference in slope if zero is not included in C.I.

Table 4.9 presents the amount of methylpyrazine, 2-,5-dimethylpyrazine and 3-ethyl,2-methylpyrazine and total pyrazines found in stored chips. Pyrazines are formed during the frying of potato chips and contribute to the fried potato flavor (Buttery et al., 1971). In general, levels of individual and total pyrazines decreased throughout storage for chips fried in solin and SFO. No clear trend was found for chips fried in HSO.

Table 4.9. Pyrazines in stored potato chips

Oil treatment/days of chip storage		Methyl Pyrazine (ppm)	2-,5-Dimethyl Pyrazine (ppm)	3-Ethyl, 2-Methyl Pyrazine (ppm)	Total Pyrazines (ppm)
<i>Solin oil</i>	0d	0.09	0.21	0.09	0.39
	4d	0.08	0.19	0.09	0.36
	8d	0.07	0.08	0.08	0.23
	12d	0.05	0.07	0.08	0.20
	16d	----	----	----	----
	20d	----	----	----	----
<i>SFO</i>	0d	0.14	0.34	0.15	0.63
	4d	0.05	0.11	0.07	0.23
	8d	0.05	0.13	0.06	0.24
	12d	0.03	0.15	0.04	0.22
	16d	----	----	----	----
	20d	----	----	----	----
<i>HSO</i>	0d	0.08	0.32	0.10	0.50
	4d	0.04	0.09	0.05	0.18
	8d	0.06	0.17	0.08	0.31
	12d	0.12	0.32	0.13	0.57
	16d	0.09	0.21	0.08	0.38
	20d	----	0.11	0.06	0.17

Selected GC chromatograms (Figures 4.15 to 4.18) are presented to provide information on the specific volatiles that are formed in stored potato chips. The major volatiles present in chips fried in solin oil and stored for 0d included: 2,4-decadienal, hexanal, nonanal, 2-heptenal, pentane,

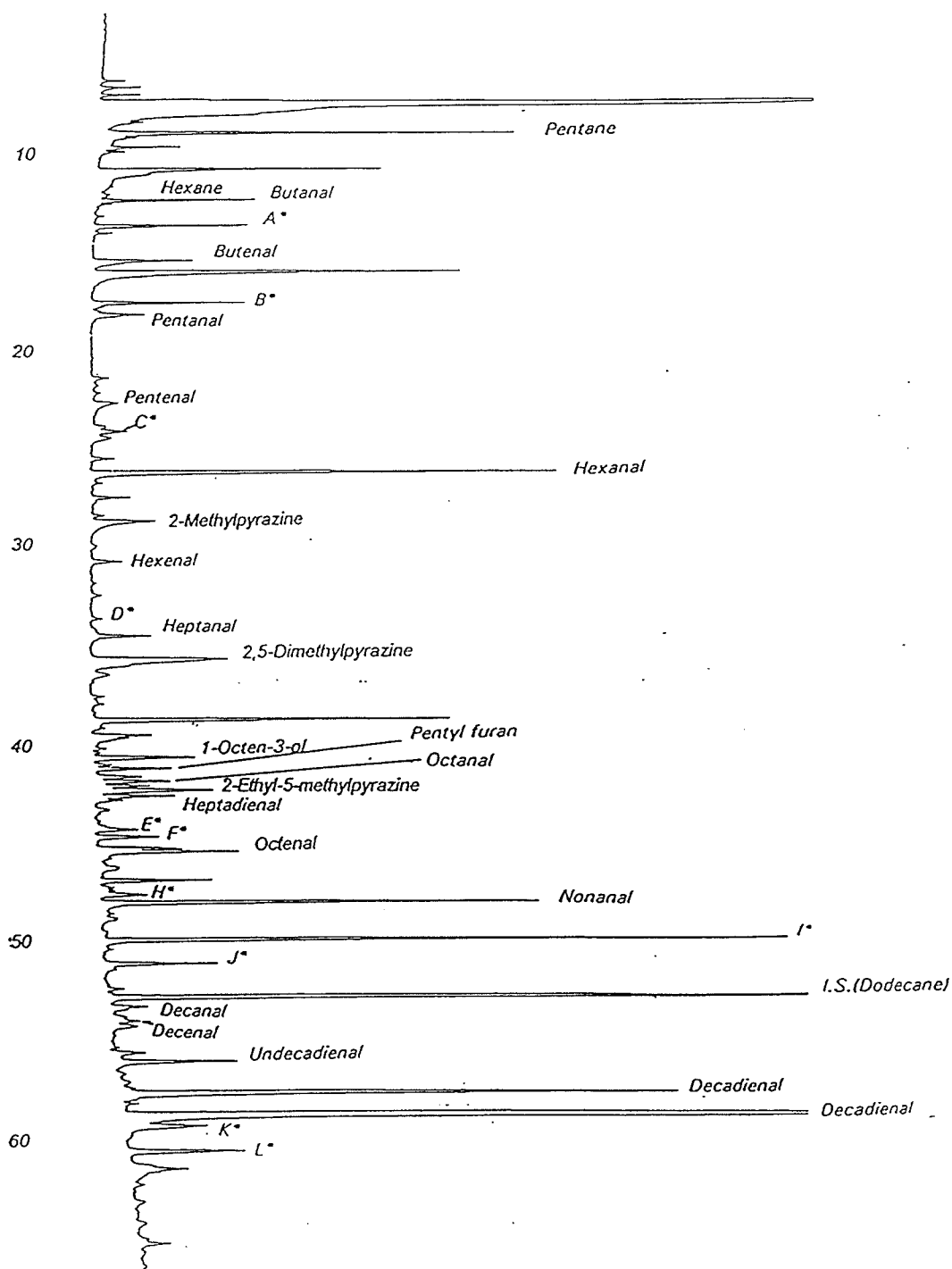


Figure 4.15. Volatile compounds in fresh (0d) potato chips¹ fried in solin oil

¹Sample size = 250 mg

* indicates unknown volatile

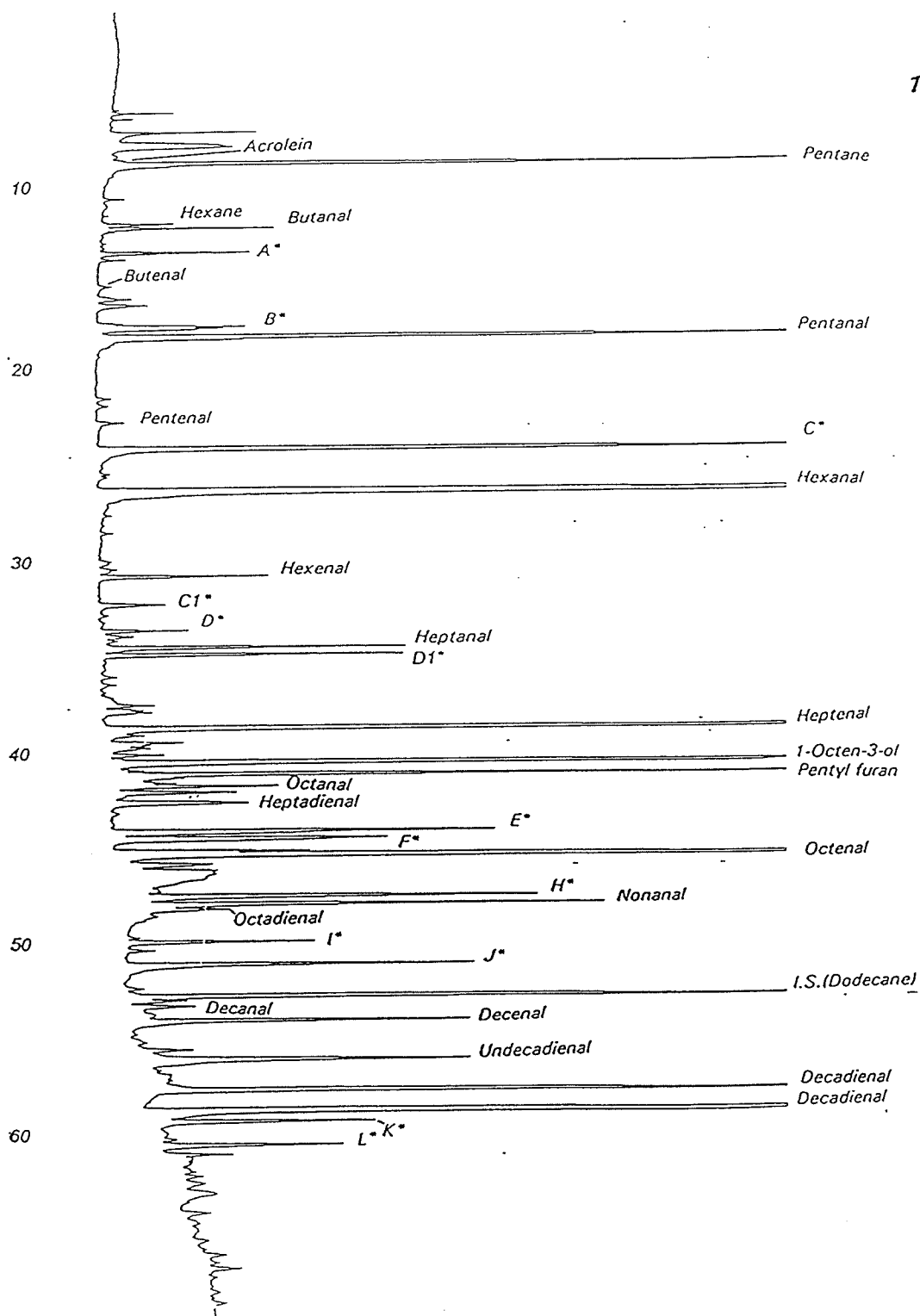


Figure 4.16. Volatile compounds in stored (20d) potato chips¹ fried in solin oil

¹Sample size = 15.3 mg

* indicates unknown volatile

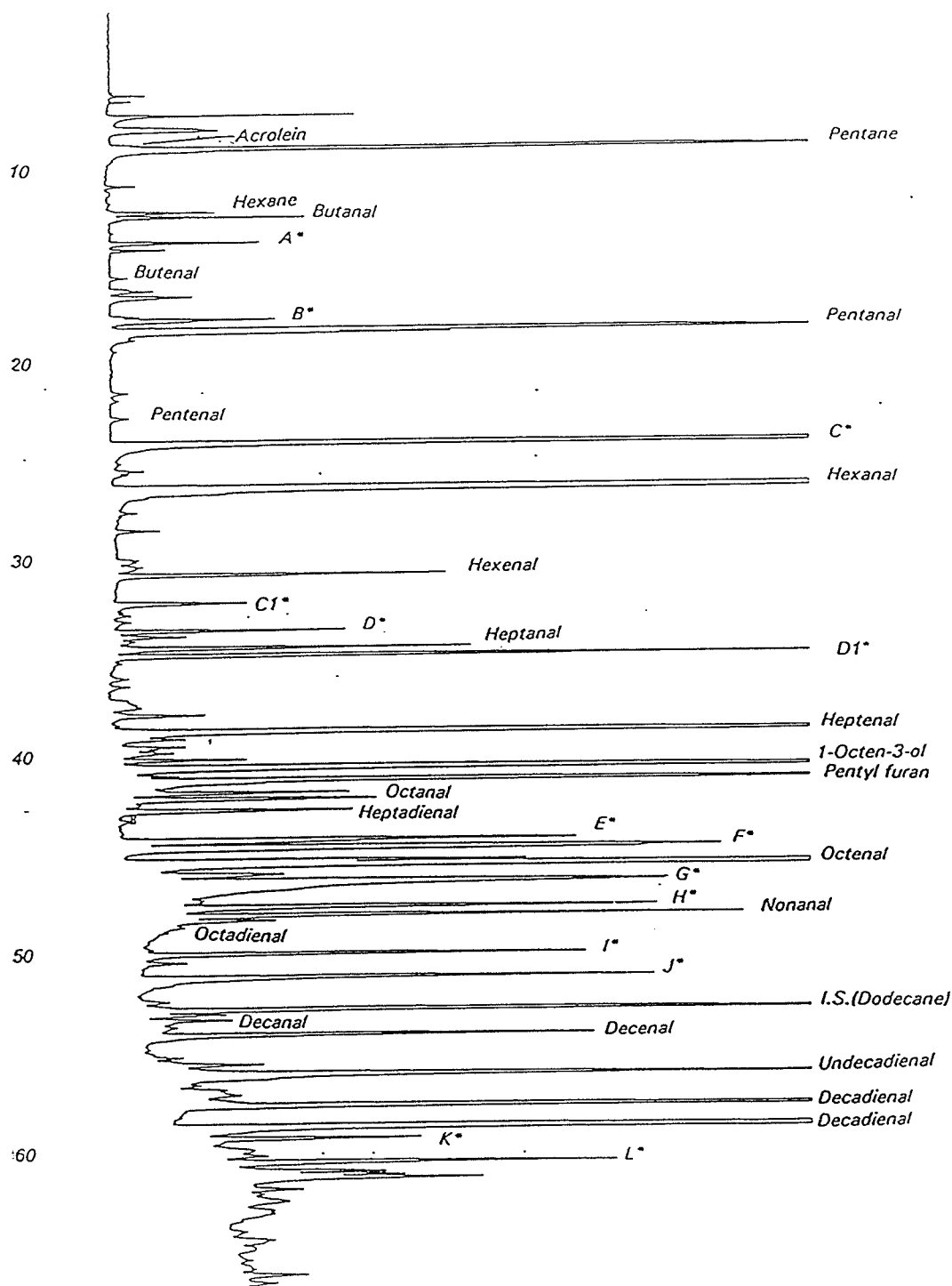


Figure 4.17. Volatile compounds in stored (20d) potato chips¹ fried in SFO

¹Sample size = 9.7 mg

* indicates unknown volatile

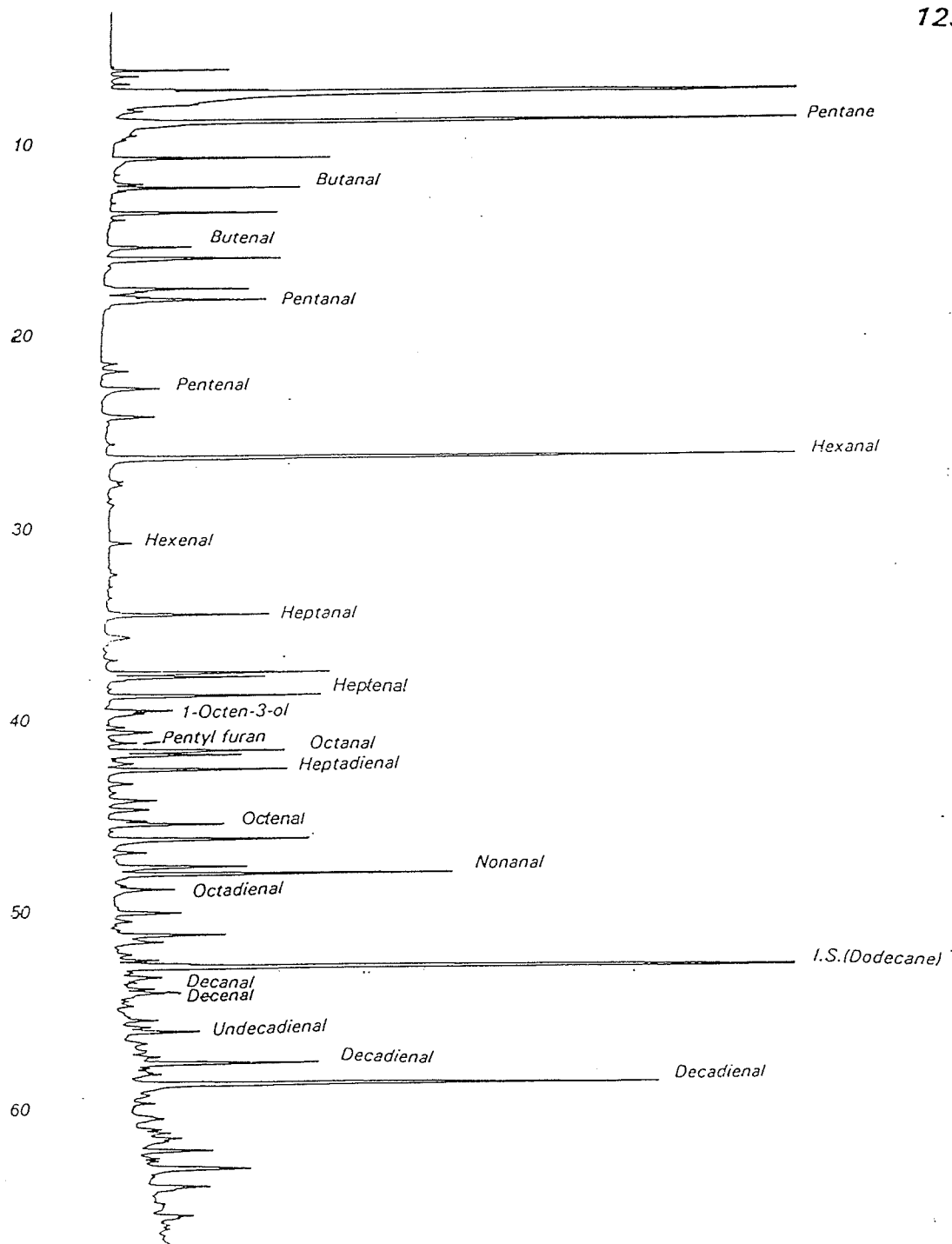


Figure 4.18. Volatile compounds in stored (20d) potato chips¹
fried in HSO

¹Sample size = 98.6 mg

* indicates unknown volatile

undecadienal, and 2-,5-dimethylpyrazine (Figure 4.15). In chips fried in solin and SFO and stored 20d, the major volatiles included: hexanal, 2,4-decadienal, pentane, octenal, 2-heptenal, 1-octen-3-ol and pentyl furan (Figures 4.16 and 4.17) while in chips fried in HSO and stored 20d, the major volatiles included: pentane, 2,4-decadienal, hexanal, nonanal, 2-heptenal, heptanal, and pentanal (Figure 4.18).

Correlation coefficients between the four sensory odor attributes and the chemical and volatile parameters are presented in Table 4.10. Rancid odor exhibited strong correlations with all chemical and volatile parameters especially with conjugated dienes (0.95) and total polars (0.94). A strong correlation was also found between sour-cheesy odor and dienals (0.84).

Table 4.10. Correlation coefficients between sensory odor attributes and chemical and volatile parameters

Indice	FPC odor	Stale odor	Rancid odor	Sour-cheesy odor
Conjugated Dienes	-0.69	-0.23	0.95	-0.47
Total Polars	-0.50	-0.31	0.94	-0.20
Total Volatiles	-0.41	-0.32	0.79	-0.42
Hydrocarbons	-0.41	-0.30	0.76	-0.34
Dienals	-0.42	-0.34	0.81	0.84
Monounsatur. Carbonyls	-0.37	-0.30	0.72	-0.37
Saturated Carbonyls	-0.43	-0.31	0.81	-0.31
Other Volatiles	-0.39	-0.32	0.75	-0.27
Unknown Volatiles	-0.40	-0.31	0.77	-0.31

4.4

DISCUSSION

Chips fried in SFO showed an increase in conjugated dienes and total polars early in storage compared to chips fried in solin oil. Chips fried in SFO also exhibited a significantly greater rate of increase in conjugated dienes during time period I. Chips fried in solin and SFO had similar rates of development of conjugated dienes for time period II which were significantly greater than chips fried in HSO. Chips fried in all three oils had similar rates of development of total polars for time period I whereas for time period II, chips fried in solin and SFO had significantly greater rates of development compared to chips fried in HSO.

Fresh (0d) potato chips from all three oils had an intense FPC odor but this decreased rapidly with storage. Two distinct odor transition patterns occurred with the storage. Chips fried in solin and SFO showed an increase and then a decrease in stale odor during the early to intermediate storage intervals (e.g. 4, 8, 12d). Stale odor has been defined as the initial stage of oxidation (Warner, 1995). This was followed by the development of an intense rancid odor during the intermediate to later storage intervals (12, 16 and 20d). Similar to chips fried in solin and SFO, chips fried in HSO developed stale odors at early storage intervals (0, 4, 8d) but this continued to increase throughout storage. Chips fried in HSO also exhibited a sour-cheesy odor at 4d of storage which gradually decreased as storage continued. A sour-cheesy odor is characteristic of hydrogenated fats (K. Warner, personal communication,

1996). Although chips fried in solin and SFO followed a similar odor transition pattern throughout storage, differences were evident between the two oils. FPC odor in chips fried in SFO decreased at a significantly greater rate compared to chips fried in solin oil. Chips fried in SFO exhibited an intense stale odor at storage day 4, whereas for chips fried in solin oil, the most intense stale odor was found at day 12 of storage. Chips fried in SFO increased rapidly in rancid odor at day 4 while chips fried in solin oil did not show this increase until day 8. Chips fried in SFO showed a significantly greater rate of development in rancid odor compared to chips fried in solin for time period I but this trend was reversed for time period II.

Chips fried in SFO exhibited greater rates of development of total volatiles and all volatile sub-classes during time period II compared to chips fried in solin oil. Chips fried in HSO showed little change in total volatiles and all volatile sub-classes over the entire storage period. The level of total pyrazines was highest in fresh (Od) chips fried in solin and SFO which decreased with increasing storage time. No clear trend was evident for chips fried in HSO.

Of the four sensory attributes measured, only rancid odor showed strong correlations with all chemical and GC volatile indices.

Little work has been published on the storage stability of potato chips fried in SFO and no work has been published on the storage stability of potato chips fried in solin oil making comparisons of this work with previous research

difficult.

Robertson and Morrison (1978) reported that chips fried in SFO had a high initial fresh odor which decreased rapidly with storage and was not evident by 28 days of storage at 31°C. At 42 days of storage, chips fried in SFO had an intense stale odor and by 70 days of storage the chips had an intense rancid odor. Thus, the odor transition pattern found by Robertson and Morrison (1978) for chips fried in SFO is similar to the pattern found in this study. Evans and Shaw (1968) reported that chips fried in sunflower oil were rancid at 14 days of storage at 60°C compared to 12 days found in this study.

In contrast to the study by Hawrysh (1995), chips fried in HSO in this study did not maintain most of their original characteristic odor during storage. However, similar to Hawrysh's study, chips fried in HSO did not develop painty or rancid odors during storage.

In this study, the induction period for hydrocarbons (predominantly pentane) in chips fried in SFO was at storage day 12 similar to the 13 or 14 day period reported by Evans and Shaw (1968) for chips stored at 60°C. Hawrysh (1995) reported that chips fried in partially hydrogenated soybean oil showed little change in total volatiles, pentane and 2,4-decadienals over the 16 days of storage similar to the results found in this study.

4.5

CONCLUSIONS

Potato chips fried in SFO were the least stable to changes during accelerated heat storage as measured by sensory, chemical and GC methods. Potato chips fried in solin and SFO exhibited similar odor transition patterns during storage. However, potato chips fried in SFO had a significantly greater rate of decrease in FPC odor and significantly greater rate of increase in rancid odor for time period I compared to chips fried in solin oil. In addition, chips fried in SFO had greater rates of development of conjugated dienes during time period I and had significantly greater rates of development of total volatiles and all volatile subclasses during time period II compared to chips fried in solin oil. Since the fatty acid compositions of the solin and SFO were similar and the two oils were of good initial quality, the differences in stability must be attributed to other factors such as tocopherols. Although tocopherols were not measured in the oils used, it is possible that similar tocopherol compositions would be found as for the fresh oils used in the storage stability studies (Chapter 3). Gamma-tocopherol was the predominant tocopherol found in solin oil whereas α -tocopherol was the predominant tocopherol present in sunflower oil. This difference in tocopherol type may account for differences observed in the storage stabilities of potato chips fried in solin and sunflower oils.

Potato chips fried in HSO were stable to the development of conjugated dienes, polar compounds and GC flavor volatiles throughout accelerated heat storage. These results are not surprising since hydrogenated frying oils are

known for their stability and are used extensively by the potato chip industry. Although chips fried in HSO had a high initial FPC odor, they also had an underlying sour-cheesy odor which was considered to be unpleasant by the panel.

*Chapter 5***CONCLUSIONS AND RECOMMENDATIONS****5.1****CONCLUSIONS****Stored oils**

Fresh solin oil was described as having a bland odor with a slight vegetable/cereal/grassy odor. Fresh sunflower oil was described as having a buttery/sweet odor. Solin oil showed greater stability to peroxide development during accelerated heat storage compared to sunflower oil however, solin oil exhibited greater painty odor development throughout storage. Both oils showed similar development of GC flavor volatiles. Solin oil showed greater stability to the development of peroxides and GC flavor volatiles during accelerated light storage compared to sunflower oil. Neither oil developed an intense painty odor during the period used. It is possible that other odor attributes may have masked the painty odor which may have lead to the lower painty odor scores. In addition, a longer storage time may have been required for greater painty odor development in the light stored oils.

The findings of this study demonstrate the importance of measuring stability by more than one method. Methods which measure primary oxidation products e.g. peroxide value may not be reliable indicators of the development of secondary oxidation products which are the sources of off-odor/flavor development in oils. Evidence of this can be seen in the accelerated heat storage results where solin oil showed greater stability to peroxide development

but was less stable to painty odor development.

Stored potato chips

Potato chips fried in sunflower oil were the least stable to accelerated heat storage as compared to chips fried in solin and HSO. Although chips fried in solin and sunflower oils demonstrated similar patterns of change in sensory odor attributes, conjugated dienes and total polars, chips fried in sunflower oil generally showed greater rates of development of these parameters during time period I. Furthermore, chips fried in sunflower oil showed greater development of GC flavor volatiles compared to chips fried in solin oil during time period II.

Chips fried in hydrogenated soybean oil exhibited the greatest stability to the development of conjugated dienes, total polars, and GC flavor volatiles. However, these chips also had an underlying sour-cheesy odor which panelists perceived as unpleasant and suggests that this odor would influence consumer acceptability of chips fried in hydrogenated soybean oil.

Solin and sunflower oils had similar fatty acid compositions. Linoleic acid was the major fatty acid in both oils but solin oil contained slightly more linolenic acid compared to sunflower oil. Since the fatty acid composition of the two oils was similar, the differences observed in storage stability (oils and potato chips) are somewhat unexpected suggesting that fatty acid composition alone cannot fully predict storage stability. Other factors such as tocopherols and possibly triacylglycerol structure may have influenced the storage stability of the oils. Gamma - tocopherol was the predominant tocopherol found in fresh

solin oil, whereas in sunflower oil, α - tocopherol was the predominant form. Gamma - tocopherol has been shown to have greater antioxidant activity in oils which may explain why solin oil and potato chips fried in solin oil exhibited greater stability to accelerated storage compared to sunflower oil. The position of fatty acids on the triacylglycerol molecule has also been shown to influence the storage stability of oils. Although, the triacylglycerol structure of the oils used in this study are not known it is possible that differences in triacylglycerol structure may exist and that these differences may have influenced the storage stability of the two oils.

Considerable effort was made in this study to ensure that the storage protocol used did not influence the results. Positioning of the jars containing the oils and the bags of potato chips in the storage cabinet was randomized minimizing positional effects of the cabinet. The chemical, sensory and GC methods of analyses were optimized before any test samples were analyzed thereby decreasing the operator effect. The sensory panel was extensively and adequately trained to ensure that the data was valid and reliable.

A possible limitation of this study was that solin oil was pilot plant processed while sunflower oil was commercially processed. Even though evaluations of the fresh solin oil indicated that it was of good initial quality, it is difficult to predict whether commercially processed solin oil would yield the same results as the pilot plant processed solin oil. In addition, measurements of tocopherols throughout the storage of oils and potato chips may have

presented a more complete picture of tocopherol changes during storage and may have been useful in explaining the differences in storage stability for chips between solin and sunflower oils.

5.2

RECOMMENDATIONS

The fatty acid composition of sunflower oil varies tremendously with climate. Sunflower oil from seeds grown in the southern U.S. has a lower linoleic acid content and higher oleic acid content compared to sunflower oil from seeds grown in the northern U.S. and Canada (Robertson, 1972). Currently, research is underway to develop varieties of solin that produce oils with consistent fatty acid compositions regardless of climate conditions and therefore would be advantageous for the food industry (Haumann, 1990).

Further research is needed with solin oil from commercial processors which would make comparisons with other commercially processed oils more valid. Since solin and sunflower oils did not develop an intense painty odor after 8 days of light storage, future studies on accelerated light storage using a similar light intensity (4360 lux) should incorporate a longer storage time of at least 16 days in duration. Varieties of solin oil are currently being developed with higher saturated fatty acid contents, similar to those of cottonseed oil. These varieties will need to be examined for their frying performance. From this study, it is evident that there are other factors in addition to fatty acid composition that influence the storage stability of edible oils and the storage stability of potato chips. Measurement of minor components such as

tocopherols and chlorophylls is recommended in order to provide information on the role these compounds play on storage stability. In addition, the influence of triacylglycerol structure on storage stability should be further examined and the role of sterols in the oxidation of edible oils needs to be investigated.

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APPENDIX A

Faculty of Human Ecology Ethics Approval

UNIVERSITY OF MANITOBA

FACULTY OF HUMAN ECOLOGY

APPROVAL FOR RESEARCH PROPOSAL INVOLVING HUMAN SUBJECTS

This is to certify that Dr. L. Malcolmson, of the Faculty of Human Ecology, submitted a proposal for a research project entitled:

Evaluation of Vegetable Oils Stored Under Accelerated Storage Conditions

The Faculty of Human Ecology Ethics Review Committee is satisfied that the appropriate ethical criteria for research involving human subjects have been met.

Members of the Committee:

<u>Name</u>	<u>Position</u>	<u>Department</u>
J. Bond	Professor	Family Studies
W. Pelton	Associate Professor	Clothing and Textiles
G. P. Sevenhuysen	Associate Professor	Foods and Nutrition

Date: March 7, 1995

Rosemary Mills
Committee Chair

APPENDIX A (Cont'd)

Letter of Invitation

THE UNIVERSITY OF MANITOBA

FACULTY OF HUMAN ECOLOGY
DEPARTMENT OF FOODS AND NUTRITIONHuman Ecology Building
Winnipeg, Manitoba
Canada R3T 2N2(204) 474-9555
(204) 275-5299 FAX*GEORGE WESTON LIMITED SENSORY AND FOOD RESEARCH CENTRE*

March 13, 1995

Dear:

As part of my thesis research in the Department of Foods and Nutrition in the Faculty of Human Ecology, I am planning to use a trained sensory panel to study the odor attributes of stored vegetable oils. I invite you to participate in this project.

Your task upon successful completion of three screening sessions will be to examine the odor of a series of oil samples. There will be approximately 10, 30 minute training sessions where you will learn how to assess the odor attributes of oils as well as the method for recording these evaluations. The actual experiment will require 8 sessions of about 15 minutes each. Scheduling of sessions will be dependent on the availability of participants. For your efforts, you will receive a \$20 gift certificate redeemable at *Applebee's Neighborhood Grill and Bar* upon completion of all training and test sessions.

The training and testing will take place during the weeks of March 27 - April 28, 1995 in the George Weston Limited Sensory and Food Research Laboratory, Room 400 of the Human Ecology Building.

If you would like to be a part of this research work, please sign the consent form, and return it to me (Room 402 Human Ecology Building) with your timetable and a completed questionnaire by March 17, 1995. Once confirmations are received, I will contact you to arrange times for the screening sessions which will take place March 21 - 23. If you have any questions, please feel free to contact me at 474-6874.

I hope that you will be able to assist us with this project.

Sincerely,

Don Kibiuk, Graduate Student

cc. L. Malcolmson
R. Przybylski

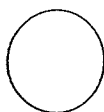
APPENDIX B

Scaling Exercise

USE OF LINE SCALES

Name _____ Date _____

Estimate the proportion of the circle that is shaded and place a vertical mark across the line scale to indicate that amount.



none _____ all



none _____ all



none _____ all



none _____ all



none _____ all



none _____ all



none _____ all



none _____ all

APPENDIX C

Statistical Analysis of Sensory Evaluation Data for Accelerated Heat and Accelerated Light Stored Oils

Full models containing all random variables was the first step in the analysis of the sensory data. The full models for both heat and light stored oils included the following variables:

- 1) Replication
- 2) Panelist
- 3) Replication x Panelist
- 4) Replication x Oil
- 5) Panelist x Oil
- 6) Replication x Panelist x Oil
- 7) Storage Interval x Replication
- 8) Storage Interval x Panelist
- 9) Storage Interval x Replication x Panelist
- 10) Storage Interval x Panelist x Oil

Reduced models were then obtained by removing one variable at a time. The reduced models were tested against the full model for loss of information using the Likelihood Ratio Test (LRT). The appropriate reduced model had no loss of information compared to the full model but was an improvement over the null model.

For heat stored oils, the reduced model containing only 'Panelist' produced a p-value of 0.9999 for the LRT indicating that the reduced model exhibited no loss of information. In addition, when the reduced model was compared to the null model, the LRT resulted in a p-value of 0.0001 indicating an improvement over the null model. Thus, this reduced model was the most appropriate model in explaining the source of the variability in the heat stored

data. The fixed effects of oil type ('Oil'), adjusted storage interval ('INT') and 'Oil x INT' on $\text{Ln}(\text{painty odor score} + 0.5)$ are presented in Table C.1.

Table C.1. Fixed effects of interval, oil, and oil x interval on painty odor scores¹ of heat stored oil

Parameter	Estimate	Std. Error	DDF	T	Pr>T
Intercept	0.24457	0.12734	338	1.92	0.0556 ²
Oil	-0.29980	0.13670	338	-2.19	0.0290 ³
INT	0.10054	0.01198	338	8.39	0.0000 ⁴
Oil x INT	0.03446	0.01694	338	2.03	0.0427 ⁵

¹ painty odor score = $\text{Ln}(\text{painty odor score} + 0.5)$

² non-significant non-zero intercept

³ significant difference in painty odor at day 0 between the oils

⁴ significant non-zero slope i.e. as storage increases painty odor increases

⁵ significant difference in the rate of painty odor development between oils

After examining the analysis, it was decided that comparing the two oils in terms of their respective rates of change would provide the most meaningful information. To achieve this comparison, equations were produced for each oil using the output from Table C.1. The equations were calculated in the following manner:

Equation of the line:

$$\begin{aligned}
 &= \text{Intercept} + \text{'Oil'} + \text{'INT'} + \text{'Oil x INT'} \\
 &= 0.25 + (-0.30\text{'Oil'}) + 0.10\text{'INT'} + 0.04\text{'Oil x INT'}
 \end{aligned}$$

Solving for Solin Oil where 'Oil' = 1:

$$\begin{aligned}
 &= 0.25 - 0.30 + 0.10\text{'INT'} + 0.04\text{'INT'} \\
 &= -0.05 + 0.14\text{'INT'}
 \end{aligned}$$

Solving for Sunflower Oil where 'Oil' = 0

$$= 0.25 + 0.10\text{'INT'}$$

Differences in slopes between the two oils were tested for significance using a t-test and 95% confidence intervals on the difference in slopes were also calculated. This gave greater information on the magnitude of the difference in slopes in terms of actual indice units. The 95% confidence interval calculation for the difference in the rate of painty odor development was as follows:

Confidence Interval Formula:

$$D \pm t_{\alpha/2, \infty} \times \text{Std. Error of 'Oil x INT'}$$

where:

D = difference in slopes

$\alpha = 0.05$

From Table A.1:

$$D = 0.04 \pm 1.96 \times 0.017 \\ (0.01, 0.07)$$

Reversing the Ln (painty odor score + 0.5) transformation:

$$(e^{0.01}) - 0.5 = 0.51 \text{ painty odor score units}$$

$$(e^{0.07}) - 0.5 = 0.57 \text{ painty odor score units}$$

$$(0.51, 0.57)$$

Since zero is not included in the calculated confidence interval, the slopes are considered to be significantly ($p < 0.05$) different.

The identical procedure was used for the analysis of the light stored oils. The reduced model containing 'Panelist' and 'INT x Panelist x Oil' was considered the most appropriate model. The LRT test indicated very little loss of information ($p\text{-value} = 0.8143$) when the reduced model was compared to

the full model. When the reduced model was compared to the null model, the LRT test resulted in a p-value < 0.0001 which indicated an improvement of the reduced model over the null model. The fixed effects of oil type ('Oil'), storage interval ('INT') and 'Oil x INT' on painty odor score are presented in Table C.2.

Table C.2. Fixed effects of interval, oil, and oil x interval on painty odor scores of light stored oil

Parameter	Estimate	Std. Error	DDF	T	Pr>T
Intercept	2.26304	0.39886	274	5.67	0.0000 ¹
Oil	0.22928	0.30991	274	0.74	0.5996 ²
INT	0.13517	0.13460	274	1.00	0.3161 ³
Oil x INT	0.14787	0.19035	274	0.78	0.4379 ⁴

¹ significant non-zero intercept

² no significant difference in painty odor at day 0 between the oils

³ no significant non-zero slope i.e. as storage increases painty odor does not significantly increase

⁴ no significant difference in the rate of painty odor development between oils

APPENDIX D

Statistical Analysis of Chemical and GC Volatile Data for Accelerated Heat and Accelerated Light Stored Oils

The fixed effects of oil type ('Oil'), storage interval ('INT') and 'Oil x INT' for the chemical and GC volatile results for both heat and light storage are presented in Tables D.1 to D.14.

Table D.1 Fixed effects of interval, oil, and oil x interval on the peroxide values of heat stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	-5.45	1.99	-2.73	0.02
Oil	4.62	2.82	1.64	0.13
INT	3.15	0.25	12.76	0.00
Oil x INT	1.20	0.35	3.42	0.01

Table D.2 Fixed effects of interval, oil, and oil x interval on the total volatiles of heat stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	156.99	57.55	2.73	0.02
Oil	19.75	81.39	0.24	0.81
INT	72.20	7.13	10.12	0.00
Oil x INT	0.01	10.09	0.00	1.00

Table D.3 Fixed effects of interval, oil, and oil x interval on the hydrocarbons of heat stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	-11.28	20.68	-0.55	0.60
Oil	24.02	29.24	0.82	0.43
INT	21.28	2.56	8.31	0.00
Oil x INT	3.54	3.62	0.98	0.35

Table D.4 Fixed effects of interval, oil, and oil x interval on the dienals of heat stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	3.18	24.09	0.13	0.90
Oil	9.43	34.06	0.28	0.79
INT	18.01	2.99	6.04	0.00
Oil x INT	3.67	4.22	0.87	0.40

Table D.5 Fixed effects of interval, oil, and oil x interval on the monounsaturated carbonyls of heat stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	8.07	14.84	0.54	0.60
Oil	25.04	20.98	1.19	0.26
INT	17.49	1.84	9.51	0.00
Oil x INT	-6.97	2.60	-2.68	0.02

Table D.6 Fixed effects of interval, oil, and oil x interval on the saturated carbonyls of heat stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	158.57	16.60	9.55	0.00*
Oil	-42.98	23.47	-1.83	0.09
INT	9.38	2.06	4.56	0.00*
Oil x INT	1.69	2.91	0.58	0.57

Table D.7 Fixed effects of interval, oil, and oil x interval on the other volatiles of heat stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	-1.53	5.64	-0.27	0.79
Oil	4.23	7.98	0.53	0.61
INT	6.04	0.70	8.63	0.00
Oil x INT	-1.92	0.99	-1.94	0.08

Table D.8 Fixed effects of interval, oil, and oil x interval on the peroxide values of light stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	1.00	4.49	0.22	0.83
Oil	8.74	6.35	1.38	0.20
INT	4.54	1.04	4.36	0.01
Oil x INT	3.05	1.47	2.07	0.07

Table D.9 Fixed effects of interval, oil, and oil x interval on the total volatiles of light stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	269.40	140.00	1.92	0.08
Oil	-204.10	198.00	-1.03	0.33
INT	122.57	32.48	3.77	0.00
Oil x INT	129.15	45.94	2.81	0.02

Table D.10 Fixed effects of interval, oil, and oil x interval on the hydrocarbons of light stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	13.02	44.78	0.29	0.78
Oil	-22.26	63.34	-0.35	0.73
INT	29.95	10.39	2.88	0.02
Oil x INT	49.31	14.70	3.36	0.01

Table D.11 Fixed effects of interval, oil, and oil x interval on the dienals of light stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	23.23	26.19	0.89	0.40
Oil	-9.01	37.04	-0.24	0.81
INT	25.42	6.08	4.18	0.00
Oil x INT	31.11	8.60	3.62	0.01

Table D.12 Fixed effects of interval, oil, and oil x interval on the monounsaturated carbonyls of light stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	61.32	24.21	2.53	0.03
Oil	-53.47	34.23	-1.56	0.15
INT	21.40	5.62	3.81	0.00
Oil x INT	19.74	7.94	2.49	0.03

Table D.13 Fixed effects of interval, oil, and oil x interval on the saturated carbonyls of light stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	158.23	51.44	3.08	0.01
Oil	-97.77	72.75	-1.34	0.21
INT	39.72	11.94	3.33	0.01
Oil x INT	19.22	16.88	1.14	0.28

Table D.14 Fixed effects of interval, oil, and oil x interval on other volatiles of light stored oil

Parameter	Estimate	Std. Error	T	Pr>T
Intercept	13.62	10.15	1.34	0.21
Oil	-21.59	14.36	-1.50	0.16
INT	6.07	2.36	2.58	0.03
Oil x INT	9.76	3.33	2.93	0.02

APPENDIX E

Faculty of Human Ecology Ethics Approval

THE UNIVERSITY OF MANITOBA

INTER-DEPARTMENTAL CORRESPONDENCE

DATE: November 20, 1995

TO: Dr. Linda Malcolmson

FROM: G. P. Sevenhuysen, Chair Ethics Review Committee

RE: Ethics Review:

1. Sensory evaluation of potato chips stored under accelerated heat conditions.
2. Sensory evaluation of modified canola oils stored under heat and light conditions.
3. Sensory evaluation of milled stored flaxseed and flaxseed bread.

The Ethics Committee has reviewed the proposed research procedures you submitted. The procedures meet ethical guidelines. The Committee approves the proposed research procedures.

APPENDIX E (Cont'd)

Letter of Invitation

THE UNIVERSITY OF MANITOBA

FACULTY OF HUMAN ECOLOGY
DEPARTMENT OF FOODS AND NUTRITIONHuman Ecology Building
Winnipeg, Manitoba
Canada R3T 2N2(204) 474-9555
(204) 275-5299 FAX

GEORGE WESTON LIMITED SENSORY AND FOOD RESEARCH CENTRE

02 November 1995

Dear

As part of our ongoing research on the storage and frying stability of fats and oils we invite you to participate in a study to examine the odor properties of potato chips.

Your task will be to attend two screening sessions which will assess your suitability for discriminating differences in potato chip odors. From this screening, 8 to 12 panelists will be selected to participate in the training sessions designed to teach you about specific odor attributes and how to scale their intensities. Once the training is completed the test sessions will be conducted in the computerized sensory facility.

How much time would you be committing to the project? Approximately 30 training sessions and 14 test sessions will be required. Sessions will take about 30 minutes each. Scheduling of sessions will depend on the availability of participants.

Panelists will receive a \$50 gift certificate redeemable at the University of Manitoba Bookstore upon completion of all required sessions. A limited number of other gift certificate options are available.

If you would like to be a part of this research work, please read and sign the consent form, and return it to Donna (Room 400 F Human Ecology Building) or Don (Room 402) with your timetable and completed questionnaire by November 8. We will contact those of you agreeing to participate to arrange times for the screening sessions. If you have any questions, please contact Donna at 474-8071 or Don at 474-6874.

We hope that you will be able to assist us with this project.

Sincerely,

Donna Ryland

Don Kibiuk

cc. L. Malcolmson
R. Przybylski

APPENDIX F

Statistical Analysis of Sensory Evaluation Data of Stored Potato Chips

The analysis of the full models (all random variables) was the first step in determining the sources of the variability in the results. The full models for all four sensory response parameters included the following variables:

- 1) Replication
- 2) Panelist
- 3) Replication x Panelist
- 4) Replication x Oil
- 5) Panelist x Oil
- 6) Replication x Panelist x Oil
- 7) Storage Interval x Replication
- 8) Storage Interval x Panelist
- 9) Storage Interval x Replication x Panelist
- 10) Storage Interval x Panelist x Oil

To produce the appropriate reduced models, one variable at a time was removed from the analysis and the subsequent reduced model was tested against the full model for loss of information using the Likelihood Ratio Test (LRT). The optimum reduced model would have no loss of information as compared to the full model but would be an improvement over the null model (pooled variance only).

For FPC, stale and sour-cheesy odors, the null model was the most appropriate model in each case i.e. there was no clear advantage to adding any other variance terms other than the residual (Armstrong, personal comm., 1996). When the null models were tested against the full models, the LRT produced the following p-values: FPC (0.9659), stale (0.9984), and sour-cheesy (0.9321). These p-values indicated that the null models exhibited no

loss of information when compared to the full models. As a result, the null models were the most appropriate models in explaining the variability in the results for FPC, stale and sour-cheesy odors. For rancid odor, 'Storage interval x Panelist' was the parameter chosen for the reduced model. The LRT test indicated very little information loss ($p\text{-value} = 0.9999$) when reduced model was compared to the full model. When the reduced model was compared to the null model, the LRT test resulted in a $p\text{-value} < 0.0064$ which indicated an improvement of the reduced model over the null model. As a result, the reduced model was the most appropriate model in explaining the source of the variability in the results for rancid odor.

The fixed effects of 'Intvl1', 'Dummy1', 'Intvl2', 'I', 'J', 'I x Dummy1', 'J x Dummy1', 'Intvl1 x I', 'Intvl1 x J', 'Intvl2 x I', and 'Intvl2 x J' from FPC, stale, rancid, and sour-cheesy odor scores are presented in the following tables (Tables F.1., F.2., F.3., F.4. respectively).

Table F.1. Fixed effects from FPC odor scores of stored chips

Parameter	Estimate	Std. Error
Intercept	4.00000	2.12997
Intvl1	-0.90313	0.13043
Dummy1	6.29583	2.23393
Intvl2	-0.18125	0.13043
I	-0.10606	2.94298
J	-0.77272	2.94298
Dummy1 x I	1.75152	3.08662
Dummy1 x J	1.73068	3.08662
Intvl1 x I	-0.02443	0.18022
Intvl1 x J	-0.39517	0.18022
Intvl2 x I	-0.00199	0.18022
Intvl2 x J	0.01222	0.18022

Using the output from Table F.1 as an example, the equations were calculated as follows:

STORAGE PERIOD I (0, 4, 8d; 'Dummy1' = 1):

FPC = Intercept + 'Intvl1' + 'Dummy1' + 'Intvl2' + 'I' + 'J' + 'I x Dummy1' + 'J x Dummy1' + 'Intvl1 x I' + 'Intvl1 x J' + 'Intvl2 x I' + 'Intvl2 x J'

Solving for Solin Oil where 'I' = 1; 'J' = 0:

FPC = 4.00000 - (0.90313'Intvl1') + 6.29583 - 0.10606 + 1.75152 - (0.02443'Intvl1')

FPC = 11.94 - 0.93'Intvl1'

Solving for Sunflower Oil where 'I' = 0; 'J' = 1:

$$\begin{aligned} \text{FPC} &= 4.00000 - (0.90313' \text{Intvl1}') + 6.29583 - 0.77272 + 1.73068 - \\ &\quad (0.39517' \text{Intvl1}') \\ \text{FPC} &= 11.25 - 1.30' \text{Intvl1}' \end{aligned}$$

Solving for HSO where 'I' = 0; 'J' = 0:

$$\begin{aligned} \text{FPC} &= 4.00000 - (0.90313' \text{Intvl1}') + 6.29583 \\ \text{FPC} &= 10.30 - 0.90' \text{Intvl1}' \end{aligned}$$

STORAGE PERIOD II (12, 16, 20d; 'Dummy1' = 0):

$$\begin{aligned} \text{FPC} &= \text{Intercept} + ' \text{Intvl1}' + ' \text{Dummy1}' + ' \text{Intvl2}' + 'I' + 'J' + \\ &\quad 'I \times \text{Dummy1}' + 'J \times \text{Dummy1}' + ' \text{Intvl1} \times I' + ' \text{Intvl1} \times J' + ' \text{Intvl2} \times I' + \\ &\quad ' \text{Intvl2} \times J' \end{aligned}$$

Solving for Solin Oil where 'I' = 1; 'J' = 0:

$$\begin{aligned} \text{FPC} &= 4.00000 - (0.18125' \text{Intvl2}') - 0.10606 - (0.00199' \text{Intvl2}') \\ \text{FPC} &= 3.90 - 0.18' \text{Intvl1}' \end{aligned}$$

Solving for Sunflower Oil where 'I' = 0; 'J' = 1:

$$\begin{aligned} \text{FPC} &= 4.00000 - (0.18125' \text{Intvl2}') - 0.77272 - (0.01222' \text{Intvl2}') \\ \text{FPC} &= 3.23 - 0.17' \text{Intvl2}' \end{aligned}$$

Solving for HSO where 'I' = 0; 'J' = 0:

$$\text{FPC} = 4.00000 - 0.18125' \text{Intvl2}'$$

From the equations, slope differences between oils in the same time period were tested for significance using confidence intervals on the difference in slopes. The following is an example of the 95% confidence interval calculation for the difference in the rate of decrease in FPC for time period I (0, 4, 8d):

Confidence Interval Formula:

$$D \pm t_{\alpha/2; \infty} \times \text{Std. Error of Intvl} \times \text{Indicator (Oil)}$$

where:

D = difference in slopes

$\alpha = 0.05$

From the equations and Table F.1:

D (SFO - solin) = -0.37

D (solin - HSO) = -0.03

D (SFO -HSO) = -0.40

Std. Error = 0.18022

$t_{\alpha/2; \infty} = 1.96$

SFO vs solin -0.37 $\pm$ 0.35 or (-0.63,-0.11)

solin vs HSO -0.03 $\pm$ 0.35 or (-0.29,0.23)

SFO vs HSO -0.40 $\pm$ 0.35 or (-0.66,-0.14)

If zero is included in the interval, the slopes are not significantly ($p < 0.05$) different and if zero is not included in the interval, the opposite is true. In the above example, for time period I chips fried in SFO decreased in FPC odor at significantly ($p < 0.05$) greater rate than chips fried in solin or HSO. Equations and confidence intervals for all parameters were calculated in the same manner.

Table F.2. Fixed effects from stale odor scores of stored chips

Parameter	Estimate	Std. Error
Intercept	-1.06250	2.54967
Intvl1	0.35781	0.15614
Dummy1	1.98958	2.67412
Intvl2	0.35625	0.15614
I	20.62689	3.52288
J	6.66099	3.52288
Dummy1 x I	-19.94602	3.69482
Dummy1 x J	-5.44602	3.69482
Intvl1 x I	0.34247	0.21573
Intvl1 x J	0.34815	0.21573
Intvl2 x I	-1.26250	0.21573
Intvl2 x J	-0.54659	0.21573

Table F.3.Fixed effects from rancid odor scores of stored chips

Parameter	Estimate	Std. Error
Intercept	2.01136	2.15306
Intvl1	0.56960	0.13573
Dummy1	-2.57765	2.25815
Intvl2	0.50142	0.13461
I	-11.09470	3.04489
Dummy1 x I	11.69129	3.19350
Intvl1 x I	-0.56392	0.18646
Intvl2 x I	0.51136	0.18646

Note:only chips fried in solin and SFO were evaluated for rancid odor therefore variable 'J' was not required

Table F.4.Fixed effects from SC odor scores of chips stored at 60°C

Parameter	Estimate	Std. Error
Intercept	4.00000	2.12997
Intvl1	-0.90313	0.13043
Dummy1	6.29583	2.23393
Intvl2	-0.18125	0.13043

Note:only chips fried in HSO were evaluated for sour-cheesy (SC) odor therefore variables 'I' and 'J' were not required

APPENDIX G
Statistical Analysis of Chemical and GC Data of Stored Potato Chips

The fixed effects of 'Intvl1', 'Dummy1', 'Intvl2', 'I', 'J', 'I x Dummy1', 'J x Dummy1', 'Intvl1 x I', 'Intvl1 x J', 'Intvl2 x I', and 'Intvl2 x J' from chemical and GC results are presented in tables G.1.→ G.9.

Table G.1. Fixed effects from CDA in extracted oils from stored chips

Parameter	Estimate	Std. Error
Intercept	0.227	0.782
Intvl1	0.003	0.048
Dummy1	1.460	0.820
Intvl2	0.114	0.048
I	-2.973	1.106
J	-1.633	1.106
Dummy1 x I	1.698	1.160
Dummy1 x J	0.077	1.160
Intvl1 x I	0.031	0.068
Intvl1 x J	0.250	0.068
Intvl2 x I	0.195	0.068
Intvl2 x J	0.145	0.068

Table G.2. Fixed effects from percent polars in extracted oils from stored chips

Parameter	Estimate	Std. Error
Intercept	0.630	4.652
Intvl1	0.045	0.285
Dummy1	0.273	4.879
Intvl2	0.060	0.285
I	-26.177	6.579
J	-15.217	6.579
Dummy1 x I	28.635	6.901
Dummy1 x J	14.285	6.901
Intvl1 x I	-0.054	0.403
Intvl1 x J	0.686	0.403
Intvl2 x I	2.399	0.403
Intvl2 x J	2.501	0.403

Table G.3. Fixed effects from total volatiles in stored chips

Parameter	Estimate	Std. Error
Intercept	-8.10	157.10
Intvl1	-0.14	9.62
Dummy1	11.10	164.80
Intvl2	0.91	9.62
I	-415.20	222.20
J	-1313.60	222.20
Dummy1 x I	416.70	233.10
Dummy1 x J	1313.80	233.10
Intvl1 x I	-0.03	13.61
Intvl1 x J	-0.30	13.61
Intvl2 x I	38.02	13.61
Intvl2 x J	107.47	13.61

Table G.4. Fixed effects from hydrocarbons in stored chips

Parameter	Estimate	Std. Error
Intercept	-2.91	19.41
Intvl1	-0.00	1.19
Dummy1	3.06	20.35
Intvl2	0.26	1.19
I	-33.59	27.44
J	-119.59	27.44
Dummy1 x I	33.60	28.78
Dummy1 x J	119.71	28.78
Intvl1 x I	0.02	1.68
Intvl1 x J	0.13	1.68
Intvl2 x I	3.05	1.68
Intvl2 x J	9.73	1.68

Table G.5. Fixed effects from dienals in stored chips

Parameter	Estimate	Std. Error
Intercept	-1.47	13.57
Intvl1	-0.10	0.83
Dummy1	2.57	14.23
Intvl2	0.16	0.83
I	-84.45	19.19
J	-187.28	19.19
Dummy1 x I	85.50	20.12
Dummy1 x J	186.88	20.12
Intvl1 x I	-0.10	1.18
Intvl1 x J	0.05	1.18
Intvl2 x I	7.17	1.18
Intvl2 x J	15.80	1.18

Table G.6. Fixed effects from monounsaturated carbonyls in stored chips

Parameter	Estimate	Std. Error
Intercept	-0.61	44.50
Intvl1	-0.01	2.73
Dummy1	0.94	46.67
Intvl2	0.08	2.73
I	-54.82	62.93
J	-227.48	62.93
Dummy1 x I	54.93	66.00
Dummy1 x J	227.70	66.00
Intvl1 x I	0.01	3.85
Intvl1 x J	0.01	3.85
Intvl2 x I	5.05	3.85
Intvl2 x J	17.91	3.85

Table G.7. Fixed effects from saturated carbonyls in stored chips

Parameter	Estimate	Std. Error
Intercept	-1.76	55.31
Intvl1	-0.01	3.39
Dummy1	2.50	58.01
Intvl2	0.23	3.39
I	-162.38	78.21
J	-486.78	78.21
Dummy1 x I	162.41	82.03
Dummy1 x J	486.90	82.03
Intvl1 x I	0.04	4.79
Intvl1 x J	0.09	4.79
Intvl2 x I	15.56	4.79
Intvl2 x J	40.31	4.79

Table G.8. Fixed effects from other volatiles in stored chips

Parameter	Estimate	Std. Error
Intercept	-0.05	8.45
Intvl1	0.00	0.52
Dummy1	0.11	8.87
Intvl2	0.01	0.52
I	-25.50	11.95
J	-89.60	11.95
Dummy1 x I	25.55	12.54
Dummy1 x J	89.65	12.54
Intvl1 x I	0.00	0.73
Intvl1 x J	0.01	0.73
Intvl2 x I	2.22	0.73
Intvl2 x J	7.28	0.73

Table G.9. Fixed effects from unknown volatiles in stored chips

Parameter	Estimate	Std. Error
Intercept	-1.39	21.86
Intvl1	-0.02	1.34
Dummy1	2.00	22.92
Intvl2	0.18	1.34
I	-51.30	30.91
J	-192.17	30.91
Dummy1 x I	51.56	32.42
Dummy1 x J	192.01	32.42
Intvl1 x I	-0.01	1.89
Intvl1 x J	0.04	1.89
Intvl2 x I	4.71	1.89
Intvl2 x J	15.57	1.89