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**EFFECT OF OLEORESIN ROSEMARY AND TERTIARY BUTYL-
HYDROQUINONE ON THE DEVELOPMENT OF OXIDATIVE RAN-
CIDITY IN POTATO CHIPS FRIED IN CANOLA AND CORN OILS**

By

Kay Elizabeth Kresl

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ABSTRACT

EFFECT OF OLEORESIN ROSEMARY AND TERTIARY BUTYLHYDROQUINONE ON THE DEVELOPMENT OF OXIDATIVE RANCIDITY IN POTATO CHIPS FRIED IN CANOLA AND CORN OILS

By

Kay Elizabeth Kresl

The effects of oleoresin rosemary (OR) and tertiary butylhydroquinone (TBHQ) on the stability of oil in potato chips fried in canola and corn oils were investigated. Oxidation of the lipids was monitored by peroxide value, conjugated dienes, percent oil absorbed, and Agtron color change in the chips over a ten week storage study. The oil's resistance to breakdown caused by heating was monitored by the change in viscosity, Hunter L*a*b values, and sensory panel.

Canola oil exhibited consistently lower peroxide values, significantly lower conjugated diene values ($P < 0.01$), lower percent oil absorbed, and significantly lighter chips ($P < 0.05$), and a greater increase in viscosity with continual heating ($P < 0.01$) than corn oil .

TBHQ appeared to be a better antioxidant than OR when comparing the color and conjugated dienes. Sensory panelists preferred chips fried in fresh corn oil with TBHQ and the six hour old corn oil chips with rosemary.

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1993

In memory of the strongest, most inspirational woman I have ever known....

Caroline Elizabeth Baker Cassidy Dicus

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INTRODUCTION

The general trend among consumers today is toward a more health conscious lifestyle. Prevalent in this thinking is the need to decrease the overall consumption of fat and, in particular, reduce the intake of saturated fatty acids (SFA). According to Gould (1985), this demand for lower fat in the diet is an important consideration for the snack food industry because many of their products are fried and can be relatively high in fat. In addition, the frying medium can contain significant quantities of SFA. Therefore, use of an oil such as canola which is low in SFA could be a benefit in snack food processing. Other benefits canola oil has to offer are a bland flavor, longer frying life (LaBell, 1987), and a high smoke point (Pomeranz, 1987).

Prolonging the time before oxidative rancidity occurs in an oil which is used as a frying medium is another major concern in the snack food industry. In oils where rancidity is a problem, this change may occur in fried snack foods before the consumer receives the product (Dugan, 1976). The addition of substances which can retard oxidative rancidity and prolong shelf life can be a beneficial approach to solving this problem. There are a number of natural and synthetic antioxidants which work to prevent rancidity in oils, but consumers have expressed a preference for those which are classified as natural (Korczak et al., 1988). A natural choice used for

many years has been spices and herbs. As early as 1957, Chipault reported on the antioxidative activity of 32 spices in lard, discovering rosemary and sage to be powerful antioxidants which greatly extended stability. Many years later, Houlihan et al. (1985) reported that a number of compounds in rosemary to possess similar or greater antioxidative properties than butylated hydroxyanisole (BHA) which has been widely used in food products. The active compounds found in rosemary are carnosol, rosmanol, rosmaridiphenol, and rosmariquinone (Wu et al., 1982; Houlihan et al., 1984; and Houlihan et al., 1985).

The objectives of this research were as follows: a) to assess the suitability of canola oil as a frying medium for potato chips; b) to determine the effectiveness of oleoresin rosemary and TBHQ in retarding oxidative rancidity in potato chips when added directly to the frying oil; c) to determine if there was a perceivable difference in canola oil flavor over a continual oil heating period.

LITERATURE REVIEW

Fat and Oil Consumption in the United States

Min and Schweizer (1983) reported that 10 billion pounds of fats and oils were consumed each year in the United States, 15% of which are used for deep fat frying. Soybean and cottonseed dominate the oils used for frying in the United States, but canola oil accounts for 59% of Canada's vegetable oils consumed (LaBell, 1987). More recent statistics show canola oil consumption in the United States' has tripled over the last four years to approximately 300,000 metric tons in 1991 (Haumann, 1992). Canola oil, currently holding 10% of the United States' oil market (Haumann, 1992), has gained acceptance because it is recognized as having the lowest level of SFA of any vegetable oil and also contains relatively high levels of monounsaturated fatty acids. Procter and Gamble's recent change of their Puritan oil from a soybean-sunflower oil blend to canola oil has gained them a 3-4% share of the United States' oil market (Carr, 1991). Additionally, Mazola RightBlend, which is new to the market, is a combination of corn and canola oils (Haumann, 1992).

Frying Oil

In frying, the heat is transferred from a nonaqueous medium (oil) to an aqueous medium (food). The thermal energy is moved from the hot oil on the surface of the food to the inside of the

product by converting surface water to steam. In a starchy food, such as a potato, the outer surface becomes dehydrated and the water on the inside of the food is moved to the surface by mass transfer, gelatinizing the center. This continues until all the water is removed from the food even though the oil temperature is high (180°C) while the inside of the food is only 100°C. The heat transfer causes a breakdown in the oil by oxygen being absorbed at the oil-air interface. The more the oil breaks down, the more surfactants are formed, and the higher the contact between the food and oil. This causes an increase in the oil absorbed into the product as well as an increase in the fatty acids released by the oil. The frying oil remains mainly on the surface, not throughout the product (Keller et al., 1986).

Oil Nutrition

Dietary fats may be grouped into three fatty acid categories; monounsaturated fatty acids, polyunsaturated fatty acids, and saturated fatty acids. Definitions and examples of each category follow (USDA, 1979).

MONOUNSATURATED FATTY ACIDS (MUFA)

MUFA are fatty acids with one double bond, such as oleic acid (C18:1) and erucic acid (C22:1). MUFA cause the low-density-lipoprotein cholesterol (LDL), which tend to be deposited in the arterial walls, to be decreased without affecting the high-density-lipoprotein cholesterol (HDL) that functions as a remover of cholesterol build up in arterial walls (DuPont et al., 1990).

POLYUNSATURATED FATTY ACIDS (PUFA)

When two or more double bonds are present, the fatty acid is designated as PUFA. The most common examples of PUFA are linoleic acid (C18:2) and linolenic acid (C18:3). PUFA lower the LDL's, but also lower the HDL level (DuPont et al., 1990).

SATURATED FATTY ACIDS (SFA)

Fatty acids with no double bonds present, such as stearic acid (C18:0) and palmitic acid (C16:0), are said to be saturated. SFA cause an increase in LDL's (DuPont et al., 1990).

Comparison of Dietary Fats

According to current nutritional recommendations in the United States, the average diet should contain less SFA, intermediate levels of PUFA, and more MUFA (DuPont et al., 1990). Table 1 shows the composition of dietary fats currently being consumed (USDA, 1979). Conclusions drawn by DuPont et al. (1990) were that corn oil lowers cholesterol levels due to its high PUFA (mainly linoleic acid), decreasing both the HDL and LDL cholesterol levels. Canola oil lowers cholesterol levels also, but due to its high MUFA content (mainly oleic acid), the LDL cholesterol decreases without decreasing the HDL cholesterol level.

Canola Oil

The term "canola" originated in Canada and is used to identify cultivars of *Brassica napus* or *Brassica campestris* which are genetically low in both erucic acid and glucosinolates (Carr, 1991).

Table 1. Percent composition of dietary fats*.

<u>Dietary Fat</u>	<u>Percentage of the fatty acid</u>		
	<u>SFA</u>	<u>PUFA</u>	<u>MUFA</u>
CANOLA OIL	6	36	58
Safflower oil	9	78	13
Sunflower oil	11	69	20
CORN OIL	13	62	25
Olive oil	14	9	77
Soybean oil	15	61	24
Peanut oil	18	34	48
Cottonseed oil	27	54	19
Palm oil	51	10	39
Coconut oil	92	2	6
Beef tallow	52	4	44
Butterfat	66	4	30
Lard	41	12	47

*Adapted from Agricultural Handbook No. 8-4 and Human Nutrition Information Service, United States Department of Agriculture, Washington, DC., 1979.

"Canola oil" is processed from seed of canola cultivars which produce a low erucic acid edible oil which is also called low-erucic acid rapeseed (LEAR) or canola low acid (CLA). Erucic acid, in laboratory animals, has been shown to cause heart lesions, an increase in the fatty tissue around the heart (Carr, 1991), and was reported to have pathogenic potential in animal diets high in rapeseed oil (DuPont et al., 1989). A high glucosinolate content, another compound present in rapeseed, is undesirable because the decomposition of glucosinolates releases sulfur compounds which give unpleasant odors when heated and sulfur has been shown to enhance the development of thyroid disease (DuPont et al., 1989). Sulfur has also been suspected of catalyst poisoning. By decreasing the glucosinolates in the oil, it would be expected that the sulfur content would also be decreased and the oil would be more safe.

Due to the high erucic acid content, rapeseed oil was not approved as a food ingredient in the United States until LEAR oil was introduced in 1985. This product has subsequently been classified as a GRAS substance by the United States Department of Agriculture (McCurdy, 1990). Table 2 is a comparison of the differences in the compositions of canola and rapeseed oils (Eskin, 1987; Köseoglu and Lusas, 1990). Even though rapeseed oil is not used in the United States, Holms (1980) and Andres (1985) have reported on the extensive production and use of rapeseed and its oil in Europe, China, India, and Japan.

Table 2. Oil composition of canola and rapeseed oils*.

Oil composition	Canola	Rapeseed
Palmitic acid (16:0) (%)	4	4
Stearic acid (18:0) (%)	2	2
Oleic acid (18:1) (%)	55	34
Linoleic acid (18:2) (%)	26	17
Linolenic acid (18:3) (%)	10	7
14-Eicosenoic acid (20:1) (%)	2	9
Erucic acid (22:1) (%)	<1	26
Sulfur (ppm)	<17	25-40
Meal Glucosinolates (u mole/g)	<26.5	70-120

*Eskin, 1987; Köseoglu and Lusas, 1990.

Canola Oil Characteristics

Canola oil has clarity and a light texture which allows for smooth, easy blending with other vegetable oils. The small percentage of erucic acid content increases its shelf life (Eskin, 1987). In a study by Ory and St. Angelo (1975), peanut and soybean lipooxygenase activity was inhibited in the presence of erucic acid. Lipooxygenase causes rancid changes in the oilseeds by oxidizing the unsaturated fatty acids (Eskin, 1987) It is stable to heat and light and has a bland flavor allowing for use with a variety of products. Canola oil has a longer frying life than soybean oil (LaBell, 1987). LaBell showed canola oil could be used as a frying medium for 240

hours before one inch of foam formed on the oil surface while soybean oil exhibited this foaming characteristic after 168 hours of use. This is probably due to canola oil having less PUFA (36%) than soybean oil (61%) (Table 1). It is known that the more double bonds, the more unstable the oil is to degradation.

Canola oil has a smoke point of 242°C which means the oil is fairly stable at frying temperatures and less oil is absorbed in the product (Pomeranz, 1987). Although the canola oil smoke point is somewhat lower than that of soybean oil, few sensory differences were apparent during the frying of french fries with oils of varying ages (Andres, 1985).

In measuring the oxidative stability of canola oil, peroxide value has been reported to be a consistently chosen method. Rossell (1989) reports a lower peroxide value for canola oil than corn, cottonseed, olive, peanut, safflower, soybean, and sunflower oils. A freshly refined fat was shown by Rossell (1989) to have a peroxide value of 1 milliequivalent of peroxide/kg of sample or less while a stored fat could exhibit a peroxide value up to 10 milliequivalent of peroxide/kg sample before off-flavors develop. Due to the different percentages of various unsaturated fatty acids, different vegetable oils break down at different rates. Hamilton (1989) explains that oleic acid is oxidized 100 times slower than linolenic acid and 64 times slower than linoleic acid. With the high oleic acid content in canola oil, a prolonged oxidation period is expected when compared to an oil high in linolenic acid. In another study, deMan et al. (1987) used an active oxygen test to determine that canola oil was more

stable than corn, sunflower, soybean, and butterfat, and less stable than olive, peanut, and lard.

Canola Oil Uses

HYDROGENATION

Due to the number of double bonds, the PUFA are more susceptible to heat degradation than SFA and MUFA . The PUFA have two or more double bonds which are separated by a single methylene group. When one double bond is eliminated, this is called hydrogenation, which increases the stability of the oil (Prior et al., 1991). Oil oxidation is affected by traces of heavy metals in the oils (Benjelloun et al., 1991). As the saturation in the oil increases, the more resistant the oil is to oxidative breakdown. The oils which contain high amounts of SFA are less fluid at room temperatures and tend to leave a "greasy" film on the cooled fried product. Oils with high amounts of PUFA, such as corn oil, are more fluid at room temperatures and are more prone to oxidation. They are generally not very stable to frying and yield products with increased off-flavors and off-colors. Oils high in MUFA, such as canola oil, remain fluid at room temperature and are highly stable to oxygen and heat. Repeated long heating times (Perkins and van Akkersen, 1965; Leszkiewicz and Kasperek, 1988), extreme temperatures, and aeration (Kilgore and Windham, 1973) may rapidly decrease the nutrient value and digestibility of the oil. When canola oil is hydrogenated, hard, brittle beta-crystals are formed and over time an undesirable grainy texture develops (DuPont et al., 1989). Vaisey-

Genser and Ylimaki (1989) pointed out that selectively hydrogenating canola oil ensures the saturation of the linolenic acid and firmness is achieved. Selective hydrogenation is the process of hydrogenating the oil with low concentrations of hydrogen on the surface of the metal catalyst using a high temperature and low pressure, causing the hydrogenation of specific fatty acids. With the three bonds, linolenic acid tends to be hydrogenated first, followed by linoleic acid and then oleic acid. To obtain a solid, smooth, hydrogenated product, mono- and diglycerides may be added to canola oil for the production of margarine and shortenings similar to other all purpose products.

WINTERIZATION

With its natural winterization, which means the oil is unsaturated and no other high-melting glycerides are present, the canola oil remains liquid at refrigerator temperature (Andres, 1985), unlike many other oils.

FRYING MEDIUM

Many types of media are used for frying foods. Animal fat was originally used for frying but now vegetable oils are more likely to be used. As pointed out by Jacobson (1991), the frying medium should develop a flavor that enhances the product, and animal fats impart flavors which are well liked by most people. However, animal fats have undesirably higher levels of saturated fatty acids, which have been reported to cause an increase in LDL cholesterol. This has caused a number of restaurants to change to vegetable oils for their

deep fat frying needs (Ha and Lindsay, 1991). The majority of snack foods have previously been fried in corn, palm, soybean, peanut, or sunflower oil. Many of these oils are produced in the United States and are readily available at a low cost to the industry. Now that the consumer has more of a choice in their snack food selections, they have shown that they want to purchase products with healthier oils. This is also true in the consumers choice of restaurants. In Canada, 610 McDonald's restaurants replaced their corn oil with canola oil, allowing the restaurant to say their product contains less SFA. Corn oil has a higher amount of SFA (13%) and PUFA (62%) than canola oil with 6% SFA and 36% PUFA. As previously stated, SFA increase the LDL cholesterol and PUFA decreases the LDL and HDL cholesterol. Another difference is in the MUFA content; canola oil contains 58% MUFA and corn oil contains 25% MUFA. The MUFA decrease the LDL cholesterol without affecting the HDL cholesterol (USDA, 1979). This change in oil gave the restaurants half a day more frying use due to the canola oils superior heat stability (Carr, 1991).

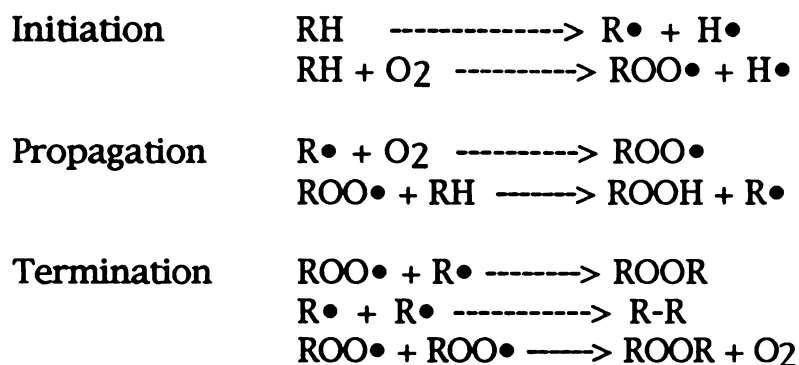
Optimal conditions for frying will increase the frying life of the oil, reduce oil pick-up by the food, increase efficiencies in the cleanup, conserve energy, and decrease the operating costs according to Blumenthal (1991).

Lipid Oxidation

Lipid susceptibility and rate of oxidation of fatty acids vary with the presence of activating agents such as heat, oxygen, steam, alkaline conditions, degree of unsaturation, and light exposure (Nawar, 1985). For example, in fried snack foods, lipid oxidation

usually occurs before the consumer receives the product (Dugan, 1976). The oxidation is caused by light exposure and degree of unsaturation of the frying oil.

The free-radical attack is the classical mechanism for oxidation in an unsaturated lipid. The various steps in the free-radical chain mechanism for lipid oxidation follows:

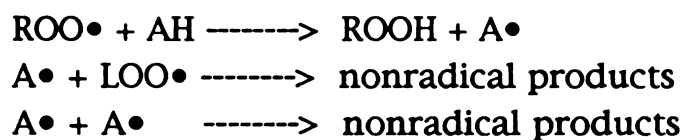


RH is any unsaturated fatty acid, R• is a lipid free radical, and ROO• is a lipid peroxy radical. In the initiation step the unsaturated fatty acid loses the hydrogen radical in the presence of trace metals, light, or heat. This results in the formation of a lipid free radical. The free radical combines with oxygen to form a lipid peroxy radical in the propagation step. The initiation also occurs when the unsaturated fatty acid combines with oxygen, forming a lipid peroxy radical and a hydrogen atom. Next the peroxy radical combines with another unsaturated fatty acid forming a hydroperoxide. The hydroperoxides are the primary products formed. And finally in the termination step, new radicals are formed which react with oxygen and continue to react or new radicals react with another radical and are terminated. This may also occur with double bonds to form a

diradical. These are the secondary products of the reaction. These products include alcohols, ketones and aldehydes.

Antioxidants

Lipid oxidation may be prevented or slowed by antioxidants which retard the oils deterioration due to oxidation. The process of autoxidation occurs when a lipid peroxy radical in the propagation step is in the presence of an antioxidant (AH). The hydrogen atom



from the antioxidant combines with the peroxy radical to form a hydroperoxide. The stable radical (A•) can be too unreactive or may form nonradical products. This stops or slows the chain reaction thus extending the induction period of antioxidation, resulting in an increased shelf life of the product. Most vegetable oils contain naturally occurring antioxidants called tocopherols, but at low concentrations. Oils with little or no tocopherols need antioxidants to prevent oxidative deterioration from occurring so readily. Antioxidants cannot reverse lipid oxidation, but may be able to slow the onset if added before oxidation begins. When antioxidants are combined with sequestering or chelating agents, the metal ions which promote the initial stages of oxidation are temporarily inactivated (Dziezak, 1986).

Types of Antioxidants

There are two types of antioxidants: free radical scavengers and free radical production preventors. The free radical scavengers donate hydrogen ions to a radical. Examples of scavengers would be butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), and tertiary butylhydroquinone (TBHQ). Free radical production preventors inhibit the oxidation by chelating trace metals which may occur in, or be added to, foods. The Food and Drug Administration (FDA) has set regulations that allow the addition of synthetic antioxidants to be no more than 0.02% of the weight of the oil or fat, one reason being due to the toxicity. An advantage to natural antioxidants according to Löliger (1989) is there is no known concern for toxicity which may exist with synthetic antioxidants. The natural antioxidants may have toxic levels, but, they have not been tested to determine what these levels are.

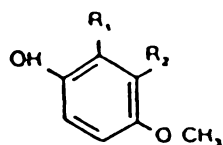
Ideal Antioxidants

The ideal antioxidant, according to Coppen (1989), meets the following criteria. The antioxidant must be safe to use, effective at low concentrations, and not contribute any odor, flavor, or color to the product. Ease of incorporation of the antioxidant into the oil must be considered, along with the amount of time the antioxidant will remain effective. Also, the conditions under which the antioxidant reacts must be known and situations which render the material inactive must be available. As with any additive, the antioxidant must be as inexpensive as possible.

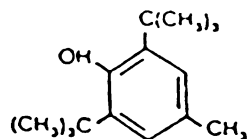
Synthetic Antioxidants

In the recent past, BHA, BHT, TBHQ, and ascorbyl palmitate (AP) have been the major antioxidants used in food products. The main differences among synthetic antioxidants, as shown in Figure 1, are the types and position of the substituent groups affixed to the benzene ring nucleus of the compound, with the exclusion of ascorbyl palmitate. When two or more of these compounds are combined, synergism occurs. This causes an increase in the antioxidant effects of reducing and retarding lipid oxidation in foods. An example of the synergistic effect was observed in a study where the interval before lipid oxidation occurred in fried foods was extended when a TBHQ/citric acid blend in propylene glycol was added directly to the frying oil (Lörliger, 1989). However, the synergistic effect may not always be true. A BHA/BHT blend did not effect the stability of canola oil in studies carried out by McMullen et al. (1991). But, with accelerated storage, ascorbyl palmitate retarded oxidative rancidity in canola oil.

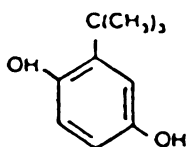
Generally BHA is considered to be more effective in animal fats, with excellent carry-through properties, but it also has been shown to have the capability of protecting the flavor and color of essential oils (Dziezak, 1986). BHA was shown to prolong the storage stability of salad dressings (Warner et al., 1986). In other studies, Hawrysh et al. (1990) found that BHA and BHT showed little retardation of oxidative rancidity while TBHQ was an effective antioxidant for canola oil. Tokarska et al. (1986) also found BHA and BHT to be inadequate in improving the storage stability of canola oil at the



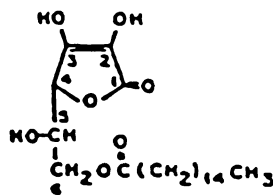
Butylated hydroxyanisole



Butylated hydroxytoluene



Tertiary butylhydroquinone



Ascorbyl Palmitate

Figure 1. Synthetic antioxidant structures.

maximum level permitted (200 ppm) while TBHQ was successful in retarding the oxidation at a level of 100 ppm.

According to Coppen (1989), TBHQ is a very effective antioxidant in unsaturated vegetable oils. It is stable at high temperatures with carry-through properties similar to BHA in fried foods while being less effective than BHA in baked goods. TBHQ is the best antioxidant for retarding lipid oxidation in frying oils because it is being more effective with highly unsaturated oils (Dziezak, 1986).

Natural Antioxidants

The commercial use of chemically synthetic antioxidants is strictly controlled, and increasing consumer awareness of food additives and safety has prompted increased interest in the use of natural antioxidants. Løvaas (1991) expressed the need for finding a new antioxidant of high potency, low toxicity, and good solubility properties in aqueous and organic phases. Also there is an interest in natural substances to replace the synthetic antioxidants (Korczak et al., 1988). Even though "natural antioxidant" has not yet been defined, there are a number of natural products which have exhibited antioxidative activity. Most vegetable oils contain tocopherols which act as natural antioxidants. The problem is not enough tocopherol occurs naturally in the oil to cause a significant change in lipid oxidation (Löliker, 1989). Others have found ascorbic acid and citric acid, when combined with other antioxidants to increase the protection of the oil (Haumann, 1990).

People have commonly used spices and herbs to prevent oxidation in meat products and Chipault (1957) reported on the antioxidative activity of 32 spices in lard. The antioxidative effects of spices were also indicated by Korczak et al. (1988) in precooked meats. Despite their favorable activity, one of the problems with most natural antioxidants is the flavors they impart to the products. A natural antioxidant should have a desired solubility in the fat substance, with no toxicological effects. The natural antioxidant must be cost effective with no carry-through properties. Rosemary extract is an antioxidant which fits this description.

Rosemary

For a number of years, rosemary (*Rosmarinus officinalis*) has been used as an antioxidant in the spice form (Lölinger, 1989). Chang et al. (1977) reports the spice may be used as a bland natural antioxidant when the rosemary leaves are alcohol extracted followed by vacuum steam distillation. Vacuum distillation eliminates the flavors and odors which may interfere with the final product. Chang's study showed rosemary extract to be as effective as Tenox VI (a blend of BHA/BHT/propylene glycol/citric acid) in vegetable oil and lard at a 0.02% level. Previous studies have indicated the rosemary extract may have specific compounds responsible for the majority of the antioxidative activity (Brieskorn et al., 1964; Wu et al., 1982; Inatani et al., 1983; Lölinger, 1983; Nakatani and Inatani, 1984; Houlihan et al., 1984; Houlihan et al., 1985).

COMPOSITION AND STRUCTURE OF ROSEMARY EXTRACT

The raw extract of *Rosmarinus officinalis* has been identified by reversed phase high performance liquid chromatography with an ultraviolet detector as having at least 45 compounds. Due to the instability of many of the components in the pure form, only about half have been identified (Lölinger, 1989). The presumed antioxidative effect of rosemary was based on carnosol (Figure 2) according to Brieskorn et al. (1964). Years later, Wu et al. (1982) again identified carnosol as a main antioxidative component of rosemary, demonstrating its effectiveness in prime steam lard to be comparable to that of rosemary antioxidant and BHT (Table 3).

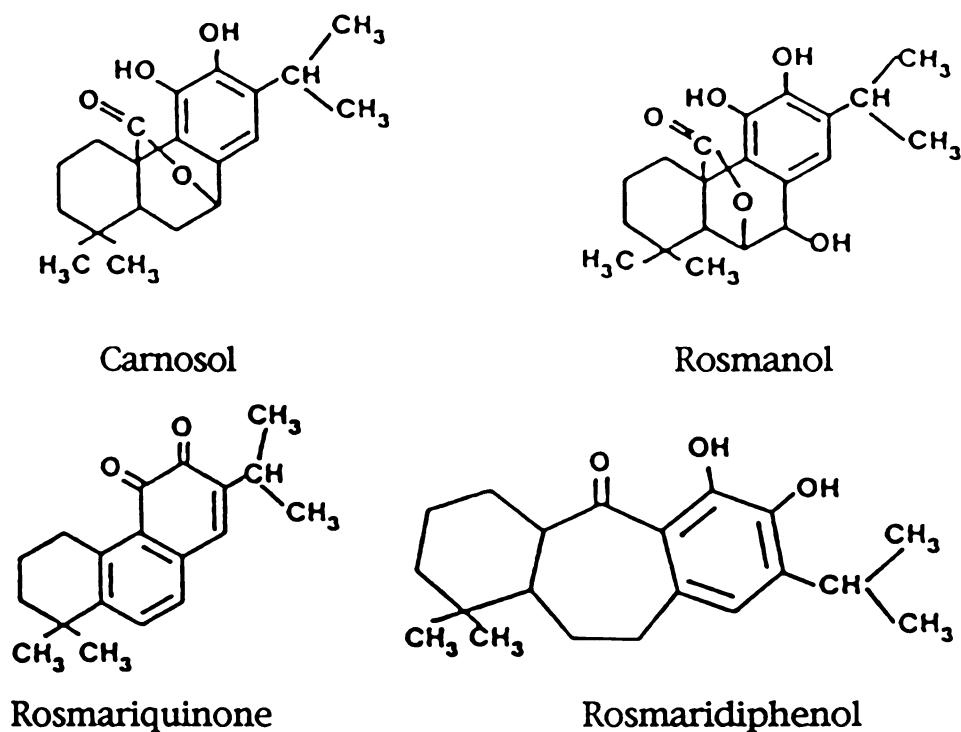


Figure 2. Natural compounds from rosemary extract.

Table 3. Antioxidant activities of carnosol and rosemary¹.

Additive (0.02%)	Peroxide value (meq/kg)				
	Prime steam lard stored for weeks at 60°C				
	0	2	3	4	5
Control, no additive	0.2	5.0	9.0	84.7	193.6
BHT	0.2	1.3	2.3	3.0	3.9
Carnosol	0.2	2.8	3.0	3.5	6.8
RA ²	0.2	1.0	1.3	2.0	2.6

¹Adapted from Wu et al., 1982.

²Rosemary antioxidant.

Carnosol was also shown to exhibit antioxidative properties greater than BHA, BHT, and alpha tocopherols (synthetic tocopherol) at 0.02% in lard using the active oxygen method (AOM). At 0.01%, carnosol was found to be a more effective antioxidant than BHA at 0.02%. Inatani et al. (1983) also discovered rosmanol in this study and defined it as another compound from rosemary leaves. At a 0.02% level, rosmanol had better antioxidant properties than BHA or BHT in lard when the AOM method of measurement was used. In a later study by the same research group (Nakatani and Inatani, 1984), two derivatives of rosmanol were isolated and named epirosmanol (ER) and isorosmanol (IR). Both of these compounds, as well as rosmanol, were about four times more active than BHA and BHT in lard. At 0.005%, ER and IR were stronger antioxidants than both BHA and BHT at the 0.02% level. Meanwhile, two other compounds were isolated from *Rosmarinus officinalis* by Houlihan et al. Rosmaridiphenol (RD) (1984) and rosmariquinone (RM) (1985) (Figure 2) were both superior to BHA. Table 4 shows RD is approaching the effectiveness of BHT, with RM being slightly inferior to that of BHT at a 0.02% level.

ANTIOXIDANT EFFECT OF ROSEMARY EXTRACT IN FOOD PRODUCTS

Rosemary has been shown by Barbut et al. (1985) to be comparable to BHA/BHT/citric acid blend in retarding rancidity in certain meat products. Rosemary and sage improved the flavor stability of oil and fried foods (Faria, 1982) and were shown to be more effective than Tenox VI when added at 0.02% concentrations to

Table 4. Antioxidative activity of rosmaridiphenol and rosmariquinone¹.

Additive (0.02%) ²	Peroxide value (meq/kg)			
	Prime steam lard stored for days at 60°C			
	7	14	21	28
Control, no additive	4.70	10.08	29.93	119.67
BHT	1.26	1.86	2.71	3.37
BHA	2.72	6.54	12.10	17.01
RD	1.57	2.30	3.10	4.09
RM	3.28	3.81	4.52	5.10

¹Adapted from Houlihan et al. 1984, 1985.

²BHT=Butylated hydroxytoluene; BHA=Butylated hydroxyanisole; RD=Rosmaridiphenol; RM=Rosmariquinone.

vegetable oils (Houlihan et al., 1985). Rosemary, as an antioxidant, was found to be effective in retarding oxidative changes in products such as precooked meat products (Korczak et al., 1988; Lai et al., 1991; Stoick et al., 1991), lard (Chipault, 1957), chicken fat (Bracco et al., 1981), vegetable oil (Chang et al., 1977), and the emulsions of monoglycerides (Lölinger, 1989). Gray et al. (1988) discussed the use of rosemary in lard and potato flakes. When added to prime steam lard held at 98°C, rosemary and sage both were shown to be effective antioxidants. Rosemary exhibited even better antioxidative activity than BHT or BHA when used in lard at a 2% level. Rosemary extract was shown to stabilize potato flakes during storage yielding organoleptic results similar to BHA/BHT standards (Lölinger, 1989). MacNeil et al. (1973) concluded rosemary spice extracts and BHA

maintain lower thiobarbituric acid (TBA) values (a measurement of the lipid oxidation) and tend to decrease the bacterial count. It was reported by Wu et al. (1982) that rosemary exhibited similar antioxidant effectiveness as BHT at a level of 2% in lard and was 4 times more active than BHA and BHT when rosemary was used at 0.005% versus 0.02% concentrations of BHA and BHT (Inatani et al., 1983). Rosemary, in lard, exhibited superior antioxidative properties when compared to BHA (Houlihan et al., 1984). Chipault et al. (1952) stated that some antioxidants may be destroyed or inactivated during baking. Both BHT and BHA are quite volatile and are easily decomposed at high temperatures (Chang et al., 1977), but rosemary has been shown to have good heat stability so it might be much better suited for use in products which will be cooked at high temperatures.

Upon decomposition of a vegetable oil, reversion flavors which are grassy or hay-like may form. Rosemary has been shown to retard these reversion flavors. In the past, one negative characteristic of rosemary as an antioxidant pointed out by Löliker (1989) is the green color of the powder. Currently there are white colored rosemary antioxidants on the market.

Rosemary would appear to be a good antioxidant for canola oil because rosemary as an antioxidant retards linoleic degradation and protects the oil from oxygen (Bracco et al., 1981). Since canola oil is high in linoleic acid, the match should be beneficial. The rosemary oleoresin at high concentrations was almost as effective as BHT in maintaining the beta carotene levels (Berset et al., 1989) in canola oil.

MATERIALS AND METHODS

Experimental Design

The experiment was designed to evaluate the suitability of canola oil as a frying medium for potato chips. Also included in this study, was the effect of oleoresin rosemary (OR) on the resistance of the oil to oxidation during the frying process. In the storage study, oxidative changes in the oil extracted from the potato chips over a ten week storage period was measured. The frying study monitored the effects of frying on the oil quality over continuous six hour oil heating period with chips being fried at three hour intervals.

The following treatments were used:

1. Canola oil- no antioxidant
2. Canola oil- 0.02% TBHQ
3. Canola oil- 0.5% OR
4. Canola oil- 0.2% OR*
5. Corn oil- no antioxidant
6. Corn oil- 0.02% TBHQ
7. Corn oil- 0.5% OR
8. Corn oil- 0.2% OR*

*Omitted from the continual frying study.

Two replications were carried out for all experiments.

Ingredients

Russet Burbank potatoes (80 count) were purchased from Irsherwood and Sons Farm in Plover, Wisconsin for the storage study. For this study we chose tubers with a low specific gravity (1.073) to allow for maximum oil absorption in the chips. This was necessary in order to collect enough oil for the analytical methods. The tubers were stored at $8.9^{\circ}\text{C} \pm 1^{\circ}\text{C}$ with high humidity until two days before chipping when they were moved to $23.9^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

Another cultivar was required for the frying study, due to the requirement for a sensory panel as a means of evaluation, where the chips should contain an amount of oil similar to commercial chips. Snowden tubers with a specific gravity of 1.098 from Larry Young and Sons in Montcalm County, Michigan were used for this study. Tubers were stored as described above.

The oils used were Puritan canola oil (Crisco, Procter and Gamble, Cincinnati, OH) and Mazola corn oil (Best Foods, CPC International Inc., Englewood Cliffs, NJ). Corn oil was chosen as a comparison due to the inexpensiveness and availability of the oil

Incorporated into these oils were 0.2% and 0.5% oleoresin rosemary (OR) (Herbalox™ Seasoning, O Type) supplied by Kalsec, Inc. (Kalamazoo, MI) and 0.02% TBHQ (Tenox TBHQ) supplied by Eastman Chemical Products, Inc. (Kingsport, TN). The percentage of the antioxidants added to the oils were based on the total weight of the oil added to the fryer. The amounts of antioxidants incorporated was based on previous studies with canola oil and both TBHQ and OR. A study by Calvo (1992) utilized canola oil as the frying medium with 0.02% TBHQ and 0.05% OR. The OR proved to be one of the least

effective antioxidants and TBHQ the best. Therefore, OR incorporated at a higher level may have proven to be a better antioxidant. In meats, OR has been incorporated at 0.1% and appeared to be closer to the antioxidative properties of TBHQ (Lai et al., 1991; Stoick et al., 1991).

Potato Chip Process

Tubers were washed in cold water and the skins scrubbed. After washing, the tubers were immediately sliced using the Eagle Tool and Machine Co. slicer (Chicago, IL) with the blade set to cut 0.0625 inch slices. The slices, prepared using a method by Tangel et al. (1977), were cut into a gallon container of water with a temperature of $18.3^{\circ}\text{C} \pm 1^{\circ}\text{C}$, then transferred to a 5 gallon bucket of running tap water. In each bucket, no more than 10 sliced tubers were collected. Slices were drained using a strainer then placed between sheets of paper to dry. After the slices were dry, they were immediately placed in the 184.8°C fryer.

The Hotpoint fryer, manufactured by General Electric (Chicago, IL), washed and dried between sample treatments, was filled with a known amount of oil. The weighed antioxidants were added to the oils at 32.2°C and stirred into the oil with a wooden spatula until fully incorporated. The temperature was monitored continually with a fryer thermometer remaining in the oil the entire time of heating. After the fryer reached 184.8°C , 140 grams of sliced potatoes were added, dropping the oil temperature to $173.7^{\circ}\text{C} \pm 2^{\circ}\text{C}$ as described by Gould, 1984b. The chips were fried in a stainless steel fry basket for two minutes, with stirring after the first minute. The stirring was

done using a new wooden spatula for each treatment. Chips were stirred to separate the slices and to turn the chips allowing even cooking. After cooking, the basket of chips was removed from the oil and gently shaken for 30 seconds. The fresh chips were drained on brown paper towels for two minutes, then transferred to a larger sheet of brown paper. More than one batch of chips was required for each treatment so after an entire treatment of chips was prepared, it was mixed and placed in labeled, one gallon zip lock bags (1.75mil thick) (Gorden Food Services, Grand Rapids, MI). The bags, containing 170 grams of chips were sealed and stored in cardboard boxes. The chips, intended for taste panel analysis, were all prepared at one time and stored until needed for the panel.

The boxes of bagged chips were placed in two controlled temperature storage areas for the storage study. The temperatures, checked every other day, were set at $23.9^{\circ}\text{C} \pm 1^{\circ}\text{C}$ (T_1) and $32.2^{\circ}\text{C} \pm 1^{\circ}\text{C}$ (T_2). In replication 1, the temperature of storage cubicle for T_1 was not consistent, so the samples were subsequently moved to a different cubicle set at the proper temperature. However, for the first 2 weeks of storage, the T_1 samples were exposed to a temperature of approximately $29.0\text{-}35.0^{\circ}\text{C}$.

Oils for the frying studies were stored at room temperature until used. For these studies, the various oils were heated to 184.8°C , then 140 grams of potato slices were fried every three hours for a total heating time of six hours. The color and viscosity of each oil was measured at the beginning of the study, after three hours of heating, six hours of heating, and after the final chip batch was fried.

The chips, intended for taste panel analysis, were stored at room temperature in sample bags as described in the storage study. The time span between taste panels was no more than two weeks.

Method of Analysis

All chemical reagents and solvents utilized in this study were analytical grade. All methods of analysis were done in duplicate.

Specific Gravity

Specific gravity was determined by the Potato Chip/Snack Food Association method (1976). Eight pounds of potatoes were placed in a basket and a potato hydrometer was used to measure the specific gravity of the tubers under water. Good quality chipping potatoes should have a specific gravity of 1.080 or more. Tubers with a specific gravity of less than 1.070 generally produce poor quality chips (Talbert and Smith, 1987) which have a greater percentage of oil (38.0%) than chips made from higher specific gravity potatoes (i.e., 1.080= 36.1% oil).

Chip Moisture Content

Moisture content of chips was measured weekly in the storage study using a Cenco moisture balance. The balance was calibrated before each use by the Potato Chip/Snack Food Association method 5.2.B1 (1976). The balance temperature was 43.3°C.

Soxtec Lipid Extraction Method

The Soxtec method used for this experiment was adapted from an application note (67/83) in the Soxtec manual, the Analytical American Cereal Chemists (AACC) method 02-01A (1991), and the American Oil Chemist's Society (AOCS) Official method 14.084 (1984). Petroleum ether (40-60°C) was used for the solvent and the Soxtec system HT6, made by Tecator (Högånas, Sweden) was used for the extraction unit.

The samples were prepared for analysis by blending the chips in a Waring commercial blender until the particles were all equal size. Samples were loaded into thimbles. The Soxtec manual explains that meat products and samples with a high moisture content need to be dried before extracting. Since the chip moisture content was low, the drying step was eliminated. Forty milliliters of petroleum ether were added to each extraction cup and the samples were boiled for 15 minutes then rinsed for 30 minutes. The solvent recovery step took 15 minutes. The cups were then dried at 100°C for 30 minutes and cooled in a desiccator. The percentage of oil was calculated according to the following formula:

$$\% \text{ Oil} = \frac{(W_3 - W_2)}{W_1} \times 100$$

W_1 = Original Sample Weight

W_2 = Pre-extraction Weight of Extraction Cup

W_3 = Post-extraction Weight of Extraction Cup

Peroxide Value

The amount of peroxide present in proportion to the amount of iodine converted from potassium iodide is reported as a peroxide value. Titration of sodium thiosulfate is used to quantitate the amount of iodine released (Dziezak, 1986). The oil extracted from the potato chips via the Soxtec procedure was measured for the peroxide value using the AOCS Official method Cd 8-53 (1981). The peroxide value was calculated using the following equation:

$$\text{Peroxide value (meq/kg)} = \frac{(S)(N)(1000)}{\text{weight of sample}}$$

S = Titration of Sample

N = Normality of sodium thiosulfate solution

The peroxide value was measured until the moisture content of the chips reached 3% which is considered unsalable (Kaghan, 1969). The peroxide values were taken at the tenth week of the study to allow for a final measurement of the chips.

Agtron Colorimeter

The color of the potato chips was measured using the Agtron E-10 colorimeter (Fillper Magnuson, Reno, NV) which is the standard used by the snack food industry. Using the manufacturers suggestion, the black (M-00) disc was used to establish meter zero and the white (M-97) disc used to standardize at 90. Chips were measured after frying and every five weeks thereafter. The Agtron color evaluation

is as follows: Agtron color > 60 = Excellent; 56-60 = Acceptable; 50-55 = Marginal.

Conjugated Diene Value

The ultraviolet absorption of the lipid extracts at 234 nm were determined with the LKB Biochrom Ultrospec II UV spectrophotometer. Suitable dilutions of "spectrograde" hexane were used (Sinha, 1977) to determine the conjugated diene content.

Hunter Colorimeter

To evaluate the color change in the oil over the six hour frying period, the HunterLab DP-9000 with a D25 L optical sensor (Hunter Assoc. Lab Inc., Reston, VA) was used in the reflectance mode with a specimen viewing area 95 mm in diameter. The specimen was illuminated from all sides. With this colorimeter, the chromaticity was calculated as CIE (1976) $L^*a^*b^*$ where L^* corresponds to lightness, a^* to red/green chromaticity, and b^* to yellow/blue chromaticity.

Brookfield Viscometer

Viscosity increases as the oil degrades. And as an oil degrades, flammable ketones and ethers form. Carbon to carbon links form with heating causing the carbon chains to increase in size, increasing the molecular weight of the polymers. An increase in the polymers means an increase in the viscosity. Corn oil, due to its higher PUFA and SFA content, would be less viscous at room temperature than

canola oil. The Brookfield viscometer was used to measure the variation of the viscosity of the oils as the oil broke down during the frying period. The RV model (Brookfield Engineering Laboratories, Inc., Stoughton, MS) was used according to the Brookfield viscometer manufacturers directions. The #1 spindle was used at 5 rpm. The viscosity was reported in centipoise (cP) and was calculated using the following equation:

$$\text{cP} = \text{factor} \times \text{reading}$$

Sensory Evaluation

Potato chips were evaluated for their degree of rancidity and the panelists' degree of liking of the chips by a 23 member untrained consumer sensory panel. The panel was conducted within 72 hours of the treatments initial and final frying times. Individual booths were used to allow for privacy.

Chips were served at room temperature, portioned (10 grams each) and served in one ounce white paper cups. The sensory evaluation ballots used by the panelists are shown in Appendix A.

For the first evaluation, a multiple comparison test as described by Larmond (1977) was used to examine the effects of frying. Fresh potato chips were labeled "R" for reference as a known fresh sample. The reference samples were fried in an equal mixture of corn and canola oils. Coded samples were then evaluated in comparison to the reference (Robertson et al., 1978).

The second evaluation was a hedonic scale (Larmond, 1977). The purpose for this scale was to observe the degree of like or dislike

between chips fried in fresh oil as compared to chips from used oil which contained break down products.

Statistical Analysis

The experiments were designed as a split plot model blocked by replication. The whole plot was the combination of the oil types and antioxidant levels while the split plot was a mix of the temperature and time of analysis. Means, standard errors, sum of square, mean square error, Tukey's test, and correlation coefficient of data from all tests were calculated using the Super ANOVA (Abacus Concepts, Inc., Berkeley, CA, 1989) program. Interactions of main effects and correlation between sensory scores and results from chemical analyses were interpreted according to Gill (1978).

RESULTS AND DISCUSSIONS

STORAGE STUDY

Effect of Oil Type

Potato chips were used for the evaluation of the suitability of canola and corn oil frying mediums. The means for testing the differences in these two oils were the percent oil absorbed, peroxide value, amount of conjugated dienes, and chip color. All analysis of variance tables are found in Appendix B. There were no statistical differences between the two oils with regard to percent oil absorbed or peroxide value although corn oil had consistently higher peroxide values than canola oil (Figure 3 and Table 5). Figure 3 compares the peroxide values for different treatments at different weeks of storage of the potato chips. The control, TBHQ, and 0.2% OR levels for corn oil over storage time were higher than the values found in chips made from canola oil, except for the TBHQ for one week of storage in corn oil being lower than in canola oil. The 0.5% OR was opposite, with corn oil having lower peroxide values than canola oil. The general trend of corn oil being higher than canola oil for peroxide values is also shown in Table 5. Snyder et al. (1985) found this same trend when he compared canola oil to seven other vegetable oils in an 8 and 16 day storage study at 60°C. In their study, canola oil

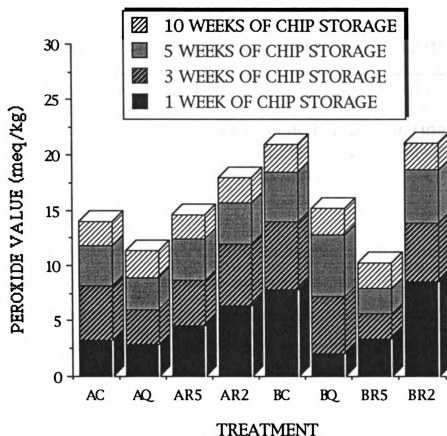


Figure 3. Effects of control (C), oleoresin rosemary at 0.2% (R2) and 0.5% (R5), and tertiary butylhydroquinone (Q) on peroxide values of the canola (A) and corn (B) oils extracted from potato chips after 1, 3, 5, and 10 weeks of storage*.

*Due to no statistical significant differences among replication or temperatures, these values represent an average of two replications and two temperatures (23.9°C and 32.2°C).

Table 5. Mean values of the effect of oil type on potato chip quality as measured by peroxide value, conjugated dienes, percent oil absorbed, and Agtron colorimeter over a ten week storage time^{1,2}.

Oil Type	PV	CD	% Oil	AGTRON
Canola Oil	3.79 ^a	0.097 ^a	41.6 ^a	45.0 ^b
Corn Oil	4.41 ^a	0.118 ^b	42.0 ^a	44.1 ^a

¹PV=Peroxide value(meq/kg); CD=Conjugated dienes; %Oil=Percent oil present in chips.

²Within an effect, values in the same row not bearing the same letter are highly significantly different ($P < 0.01$, conjugated dienes) and significantly different ($P < 0.05$, Agtron).

exhibited a lower peroxide value than corn, olive, cottonseed, peanut, safflower, soybean or sunflower oil. This was thought to be due to canola oil's high monounsaturated fatty acid content (LaBell, 1987) that would be more stable to light and heat than oils high in polyunsaturated fatty acids such as corn oil.

Highly significant differences ($P < 0.01$) were observed in the conjugated diene values between oils (Table 5). It is known that polyunsaturated fatty acids, such as linoleic acid and linolenic acid, are more prone to oxidation than monounsaturated fatty acids and saturated fatty acids because of the greater number of double bonds. When linoleic acid and linolenic acid are oxidized, they form hydroperoxides, where the double bonds become conjugated. The measurement of these hydroperoxides is reported as conjugated

dienes. Since canola oil contains 36% polyunsaturated fatty acids and corn oil contains 62% polyunsaturated fatty acids, it would be reasonable to expect that the conjugated diene content of canola would be lower than corn oil (USDA, 1979). This has been shown in previous work by Tautorus and McCurdy (1990) who compared canola, corn, soybean, linseed, and sunflower oils. The corn and soybean oils stored at 28°C exhibited a higher rate of conjugated diene accumulation but at 55°C the difference was not apparent.

Agtron values were also significantly different ($P < 0.05$) between chips fried in the canola versus corn oil (table 5). Chips fried in canola were lighter in color, possibly due to the phospholipid content of the two oils. Even though phospholipid content was not measured in this study Prior et al. (1991), found that higher phospholipid contents, as in corn oil, may result in discoloration of oil during prolonged heating. Although oil color is not usually considered a major factor in chip color, it may contribute to lighter or darker chips under certain circumstances.

Evaluation of Oil Content in Potato Chips

The oil content of the potato chips was measured weekly using the Soxtec extractor although oil content, as expected, remained constant during storage. duPlessis et al. (1981) showed no change in oil content of potato chips fried in peanut and cottonseed oils stored over a 12 week period. Their chips remained in the typical potato chip percent oil range of 30-40% (Mottur, 1989), where our chips reached the high end of the range (41.8%). The higher oil content

may be due to the low specific gravity of the raw Russet Burbank tubers. Gould (1984a) reports the oil content of finished potato chips may be decreased by using tubers high in specific gravity. Another reason may be due to some difficulty in controlling the oil temperature in the small fryer, which could make the set frying time too long or too short depending on temperature.

Generally, chips stored at 23.9°C exhibited a significantly ($P < 0.01$) higher oil content (42.0%) than those stored at 32.2°C (41.5%). No explanation was found for these results, but, on a practical basis the differences in oil content are very slight.

Effect of Specific Gravity

Specific gravity is a measure of the dry matter content of potatoes which plays a major role in oil uptake and percent yield of chips (Talbert and Smith, 1987). In general, the higher the specific gravity of tubers, the greater the yield and the lower the oil uptake in finished chips. The potatoes used in the storage study had a fairly low specific gravity (1.073) which gave low chip yield and high oil content (Table 6). The frying study used potatoes with a specific gravity of 1.098 which is fairly high and gave good chip yield with low oil content (Table 6).

It is important to keep in mind that tubers low in specific gravity may be used to produce potato chips due to their availability. Matz (1984) suggests using these tubers, keeping in mind the following: reducing sugar content should be around 0.2% to yield the desired golden brown chip color, store tubers at 20.6-30.0°C to

minimize sugar accumulation, chemical or physical treatments may improve potatoes yielding dark chips, thinner slices, lower moisture in tuber slice or placing slices in hot water before frying.

Table 6. Specific gravity, chip yield, and percent oil found in three representative samples of the tubers used for the storage and frying studies^{1,2}.

Sample	Specific Gravity		Chip Yield		Percent Oil	
	Storage Study	Frying Study	Storage Study	Frying Study	Storage Study	Frying Study
1	1.074	1.098	26.75	35.60	41.6	35.8
2	1.072	1.097	26.30	32.70	41.8	34.9
3	1.073	1.097	27.35	34.00	41.9	35.1
Mean	1.073	1.097	26.80	34.10	41.8	35.3

¹Samples are not the exact same product for specific gravity, chip yield, and percent oil, they are 3 representative samples of the entire potato lot.

²Chip yield= pounds of chips yield for 100 pounds of tubers.

Effect of Storage on Potato Chips

Potato chip storage is an important area for the snack food industry. The average shelf life of a bag of potato chips, without the use of inert gas, according to Gould (1985) is 8-10 weeks. Matz (1984) reported 4-6 weeks shelf life without any vacuum packaging, freezing, or other special treatments, including the addition of antioxidants. In the storage study, a higher than average chip storage

temperature (32.2°C) allowed the maximum moisture content to be reached much more quickly than it would under normal storage conditions.

Effect of Moisture Content

According to Kaghan (1969) the salability of potato chips depends upon their moisture content. If a chip exceeds 3% moisture, it is unacceptable to the consumer (Kaghan, 1969; Matz, 1984). Gould (1984a) suggests frying to a final moisture content of 1.75-2.0% to allow for maximum shelf life. In this study, the chips were fried to a final moisture content of 1.8-1.95%. During storage, the chips gained moisture and upon reaching a moisture content of 3%, the peroxide values were no longer taken until the final week of the study. For 32.2°C, the potato chips for both replications reached a 3% moisture level after 5 weeks, the 23.9°C chips did not reach this level until 7 weeks. These are similar results to Matz's (1984) prediction of 4-6 week shelf life of untreated potato chips.

Effect of Storage Temperature

The potato chips were stored at 23.9°C and 32.2°C in temperature controlled cubicles. These temperatures were chosen because most consumers store their potato chips at room temperature (23.9°C) or in a slightly warmer area (32.2°C). The results for chip color, conjugated dienes, and peroxide values show no statistical difference between the two temperatures (Appendix B). This may be due to such small range in the temperatures. The differences may have been more obvious if 25°C and 35°C were

used, as Covey and Wan (1991) did in their research. They found that soybean oil had a lower peroxide value (2.5 meq/kg or less) for samples stored at 25°C than those stored at 35°C (15 meq/kg).

Effect of Storage on the Color of Potato Chips

The color of the potato chips was measured at 0, 5, and 10 weeks of storage, using an Agtron colorimeter. No differences were noted between the storage temperatures and the time of chip storage, but highly significant differences ($P < 0.01$) were observed between replications. Replication 1 had a mean Agtron value of 44.4 which was lower than replication 2 at 44.8. Even though there are significant differences, the difference are very small. For the Agtron value of measurement, a difference of 0.4 would generally be unnoticeable to the human eye. A reason for the small color difference may be due to the difficulty in controlling the oil temperature in the small fryer as mentioned previously. As recorded in Table 7, the colors do not fall within the acceptable Agtron chip color range described in the materials and methods section of this paper. Since the tubers had a low specific gravity, leading to a low percent solids content, a higher sugar content is likely in the chips (Talbert and Smith, 1987).

Table 7 also shows the variation of the color values due to the treatments (oil type combined with antioxidants). The mean treatment Agtron values represent the combination of the two replications as well as a combination of the two storage temperatures. There are significant differences between the treatments at a 95% confidence level (Table 7). When the

antioxidants alone are compared, they are highly significantly different ($P < 0.001$) as shown in Appendix B.

Table 7. Average Agtron values for two replications of chips stored for ten weeks^{1,2}.

Treatment	Replication	Weeks of Chip Storage			Average
		0	5	10	
Canola oil-Control	1	43.8	44.2	43.5	44.5 ^c
	2	45.6	45.2	44.8	
Canola oil-TBHQ	1	47.1	47.4	48.1	47.6 ^e
	2	48.0	47.3	47.9	
Canola oil-OR 0.5%	1	44.4	44.2	44.1	43.6 ^{bc}
	2	43.0	42.3	43.8	
Canola oil-OR 0.2%	1	43.7	43.5	44.0	44.1 ^c
	2	44.0	45.3	44.1	
Corn oil-Control	1	46.7	46.5	47.0	46.3 ^{de}
	2	46.1	45.8	45.7	
Corn oil-TBHQ	1	46.1	45.5	46.3	46.1 ^d
	2	46.5	46.3	45.8	
Corn oil-OR 0.5%	1	40.9	40.7	41.3	41.4 ^a
	2	41.6	42.3	41.8	
Corn oil-OR 0.2%	1	42.2	42.0	42.0	42.6 ^{ab}
	2	42.6	43.1	43.4	

¹TBHQ=Tertiary butylhydroquinone; OR=Oleoresin rosemary

²All values represent an average of two storage temperatures (23.9°C and 32.2°C).

³All numbers bearing the same letter do not differ significantly at $P < 0.05$.

Effect of Antioxidants on Potato Chip Rancidity

The rate of oxidation may be decreased, according to Landers (1981), by the addition of antioxidants, a decrease in the storage temperature or by packaging the product under nitrogen or vacuum packing. Antioxidants function by lengthening the induction period through the interruption of the free radical chain reaction of oxidation. For the storage study, differences were expected to appear between antioxidant treatments. The control and 0.2% OR exhibited the least amount of antioxidative activity in most incidences as measured by peroxide value. For the conjugated dienes, the 0.5% OR treatment was the least responsive. Based on the results of a study completed by Calvo (1992), it was expected that TBHQ would be a more effective antioxidant than OR and this was the case in most instances. In Calvo's study, she observed OR at a 0.05% level in both canola and palm oils to be the least effective antioxidant when compared to BHA/BHT, TBHQ, TBHQ/citric acid blend, tocopherols, and an OR/tocopherol blend. Based on these results obtained by Calvo, 0.5% and 0.2% OR were used for the storage study.

Peroxide Value

The differences in the peroxide values between the antioxidant treatments are shown in Figure 3. The control, TBHQ, and 0.2% OR levels for corn oil over storage time were higher than the values found in chips made from canola oil, except for the TBHQ for one week of storage in corn oil being lower than in canola oil. The 0.5% OR was opposite with corn oil having lower peroxide values

than canola oil. Again, in Calvo's study (1992), she observed 0.05% OR to be the least effective antioxidant over time. Similar results were shown in a study conducted by Lai et al. (1991) where OR was shown to have no beneficial effects on the oxidative rancidity in chicken nuggets under refrigerated storage. When combined with sodium tripolyphosphate (STPP), 0.1% OR was better at retarding oxidative rancidity as was TBHQ, when combined with STPP. The STPP/TBHQ blend prolonged development of oxidative changes of the chicken nuggets and maintained fairly consistent thiobarbituric acid (TBA) values over storage times. Rosemary increased in TBA values when used alone, but its combination with STPP resulted in more consistently lower values. The 0.1% OR/STPP was significantly different ($P < 0.05$) than the 0.05% OR and the control.

Conjugated Dienes

Highly significant differences ($P < 0.001$) were observed between replications. A study done by duPlessis et al. (1981) shows A_{232} determination to be a very sensitive means to measure oil stability in stored chips and on cottonseed and peanut oils which were fried continuously for 80+ hours. But in the storage study, highly significant differences ($P < 0.01$) were observed between oil types.

Figures 4 and 5 show there are highly significant differences ($P < 0.01$) in the conjugated dienes values for the antioxidants when observed over time. Overall, the canola oil with TBHQ exhibited fewer double bonds than all the other treatments and the 0.5% OR in corn oil showed the most. In the first four weeks, the treatments with

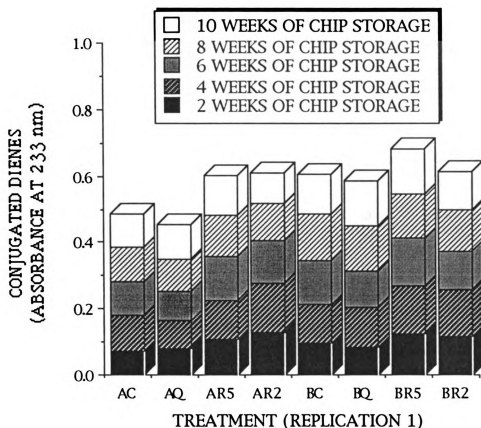


Figure 4. Effects of control (C), oleoresin rosemary at 0.2% (R2) and 0.5% (R5), and tertiary butylhydroquinone (Q) on conjugated diene values of canola (A) and corn (B) oils extracted from the first replication of potato chips after 2,4,6,8, and 10 weeks of storage*.

*All values represent the average of two storage temperatures (23.9°C and 32.2°C).

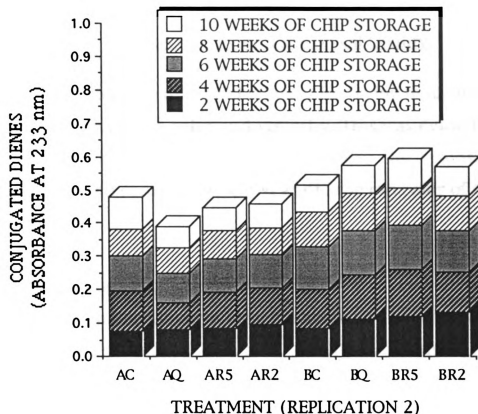


Figure 5. Effects of control (C), oleoresin rosemary at 0.2% (R2) and 0.5% (R5), and tertiary butylhydroquinone (Q) on conjugated diene values of canola (A) and corn (B) oils extracted from the second replication of potato chips after 2,4,6,8, and 10 weeks of storage*.

*All values represent the average of two storage temperatures (23.9°C and 32.2°C).

rosemary appeared to have a slightly higher conjugated diene content than the others.

FRYING STUDY

Effect of Frying Time on Oil Quality

Over time the quality of oil used for frying tends to decrease as shown by change in color and viscosity. This was evident in a study conducted by Huang et al. (1981) where the viscosity of both sunflower and corn oils increased as did the red color of the oils over frying time.

Effect of Color

The Hunter "L" value measure lightness (100) and darkness (0). In the present study, the corn oil which was continually heated for six hours with chips being fried every three hours caused the Hunter "L" values to increase. This indicates that the oil was getting lighter in color (Figure 6). This is not the expected outcome and is in contrast to the results of Prior et al. (1991), Marquez (1986), Robertson et al. (1978) and Tangel et al. (1977). The differences between this study and others may be due to different time spans. For the frying study, six hours of frying was chosen because in preliminary tests, the color and viscosity of the oils were similar under the following conditions: a) heating oil for two hours daily for seven days with potato chips fried for one hour; b) heating the oil for six continuous hours for one

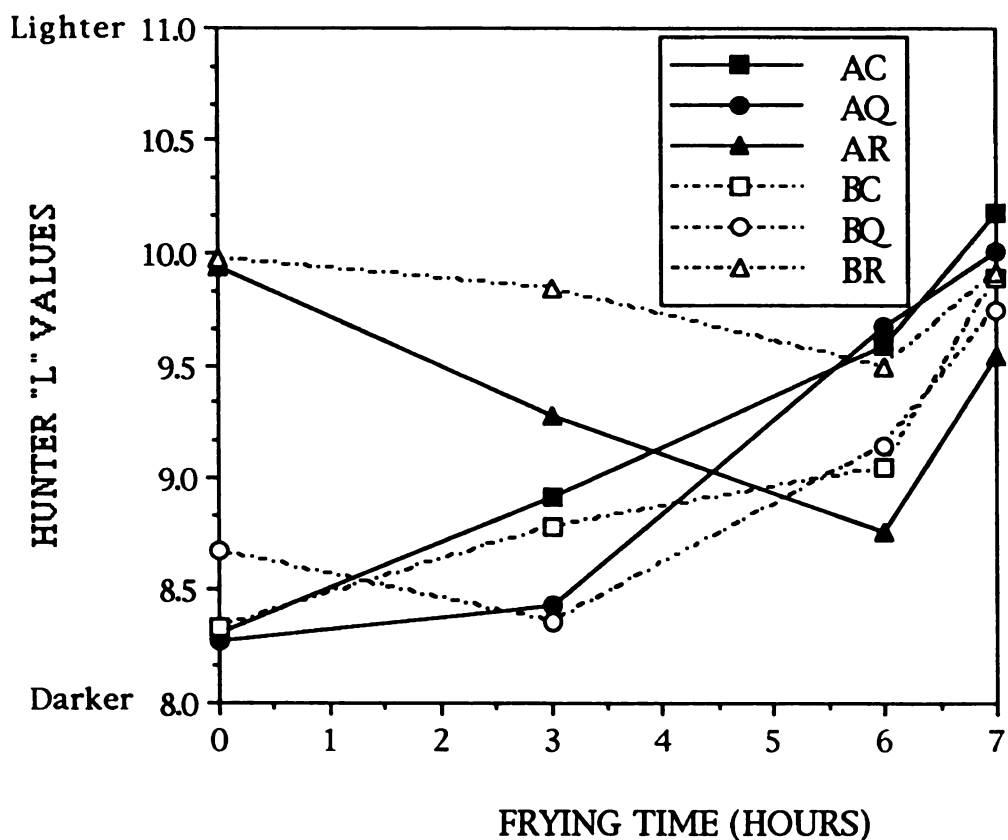


Figure 6. Effects of oleoresin rosemary (R) at 0.5%, TBHQ (Q) at 0.02%, and control (C) on the Hunter "L" values of the canola (A) and corn (B) oils continually heated for six hours^{1,2,3}.

¹All values represent the average of two replicated experiments with the average of the treatments.

²L=0 (Black); L=100 (White)

³Highly significant statistical differences ($P < 0.01$) were found among frying time and antioxidants.

day, frying chips every three hours. A study done by Prior et al. (1991) extended the time to a 14 day time period. Robertson et al. (1978) conducted a study over multiple weeks of oil storage and reported chips fried in palm, sunflower, and cottonseed oils to lighten over the first few weeks of storage and then darken upon storage. Tangel et al. (1977) also showed butteroil to pale over the first three days before darkening progressively over 8 days of frying. Additionally, when methylsiloxane was incorporated into the butteroil, the butteroil remained lighter than the control over time. Corn oil was lighter than canola only when rosemary was added to the oil. Rosemary caused both oils to be lighter than the control or the TBHQ oils (Figure 6).

As an oil carbonizes or "cokes" a red pigment is produced, causing the oil to increase in redness as it degrades (Blumenthal, 1991). In the Hunter CDM system, red and green appear on the same axis but at opposite ends of the measurement scale for "a" value. In this study, the change in "a" value indicates a decrease in the greenness of the oil over time (Figure 7). From this information a conclusion may be drawn that there may have not been enough time for the red pigment to develop. But it is apparent that corn oil is highly significantly ($P < 0.01$) less green than canola oil and when the rosemary was incorporated into the canola oil, it was more green than the corn oil. This may be due to a higher chlorophyll level in the canola oil.

The corn oil, in this study, was significantly ($P < 0.05$) more yellow than the canola oil (Figure 8); the rosemary oils were highly significantly ($P < 0.001$) more yellow than both the control and the

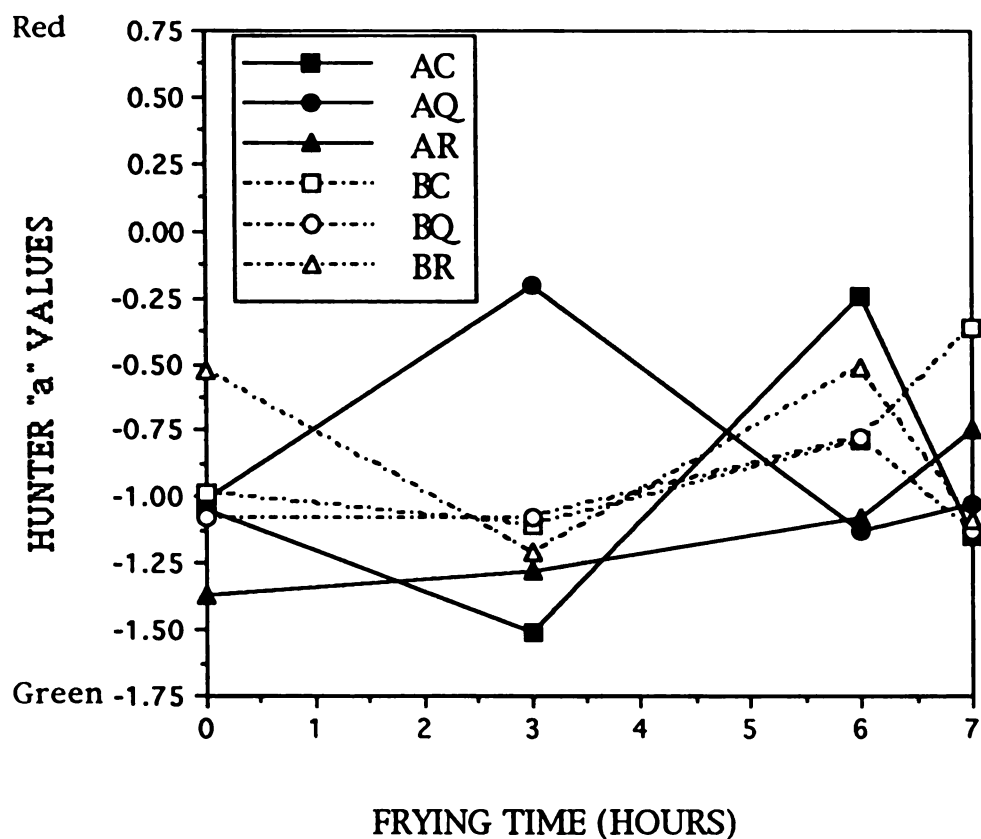


Figure 7. Effects of oleoresin rosemary (R) at 0.5%, TBHQ (Q) at 0.02%, and control (C) on the Hunter "a" values of the canola (A) and corn (B) oils continually heated for six hours^{1,2,3}.

¹All values represent the average of two replicated experiments with the average of the treatments.

²+a=red; -a=green

³Highly significant differences ($P < 0.01$) were found among the oil type and significant differences ($P < 0.05$) between the frying times.

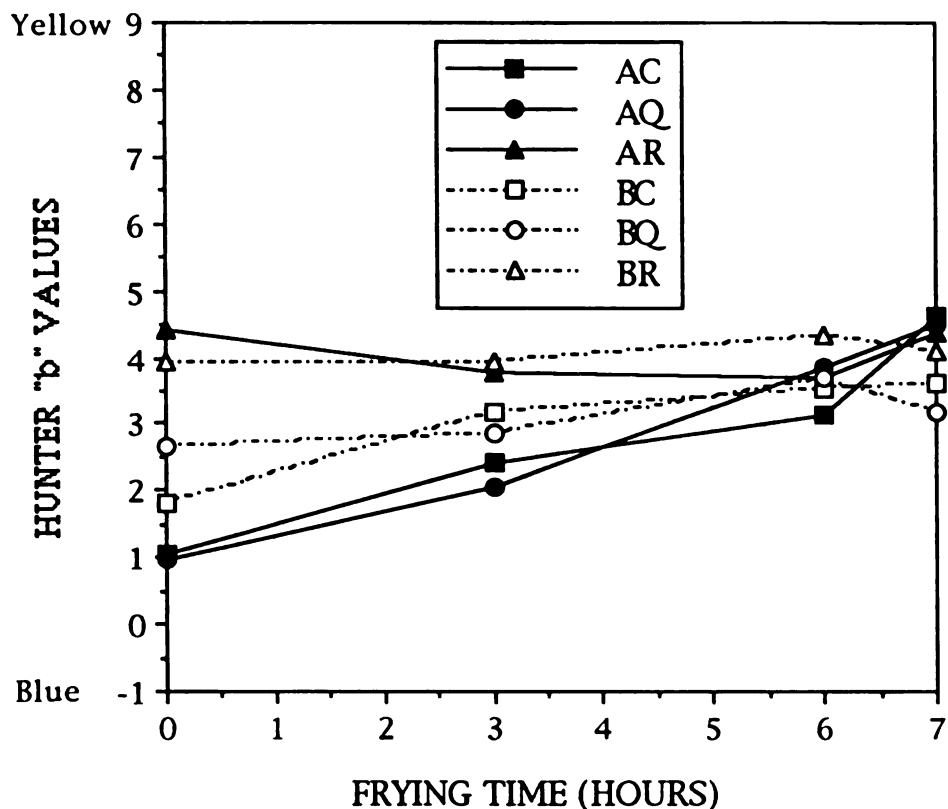


Figure 8. Effects of oleoresin rosemary (R) at 0.5%, TBHQ (Q) at 0.02%, and control (C) on the Hunter "b" values of the canola (A) and corn (B) oils continually heated for six hours^{1,2,3}.

¹All values represent the average of two replicated experiments with the average of the treatments.

²+b=yellow; -b=blue

³Highly significant statistical difference ($P < 0.001$) were found among the frying time and antioxidants and significant differences ($P < 0.05$) were found among the oil types.

TBHQ oils (Figure 8). The oils also show a significant ($P < 0.01$) increase in yellowness with increased frying times except for the rosemary which stayed close to the same over time (Figure 8).

Effect on Viscosity

As an oil degrades, polymers are formed along with flammable ketones and ethers. This causes an increase in the rate of oxygenation and an increase in the stability of steam domes and foaming. Fats form carbon-carbon linkages in the absence of oxygen, resulting in polymers with a high molecular weight. As the amount of polymers increase, the viscosity of the oil increases. In this study, there were highly significant ($P < 0.001$) differences among the viscosity readings over time (Figure 7). Viscosity measured at 30°C increased with time and these results are similar to those obtained by Morrison et al. (1973) with sunflower oils from different growing regions. The present study also resulted in a highly significant difference ($P < 0.01$) between viscosity of the canola (155.1 cps) and corn (138.7 cps) oils. Eskin (1986) reports similar results with corn oil (73.6 cps) having a lower viscosity than canola oil (77.3 cps) when was measured at 21°C. These data are logical in light of the fact that corn oil contains more polyunsaturated fatty acids than canola oil, which is likely to make it more viscous at room temperature.

Sensory Evaluation of Potato Chips

One of the objectives of this study was to determine if there was a perceivable difference in canola oil flavor in potato chips fried

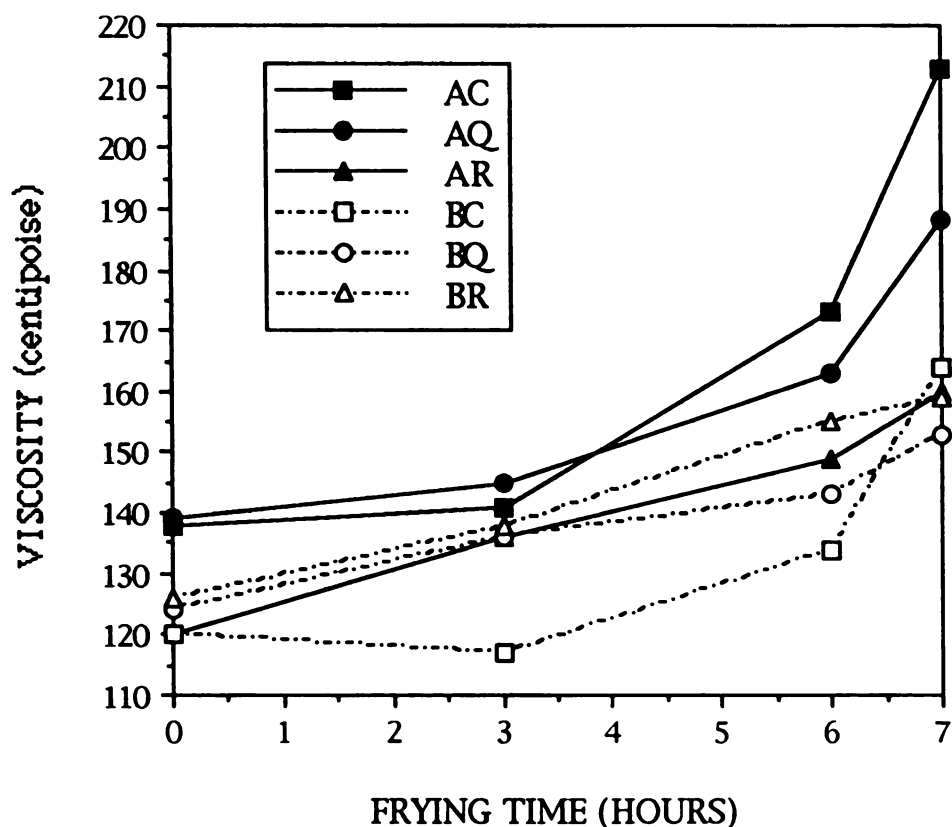


Figure 9. Effects of oleoresin rosemary (R) at 0.5%, TBHQ (Q) at 0.02%, and control (C) on the viscosity of the canola (A) and corn (B) oils continually heated for six hours^{1,2}.

¹All values represent the average of two replicated experiments with the average of the treatments.

²Highly significant difference ($P < 0.001$) were found between the viscosity readings over time and also between the oil types.

at three hour intervals in oils which were continuously heated for six hours. Sensory panelists did perceive some flavor differences (Figure 10) and a preference between chip treatments was detected (Figure 11). The potato chips that panelists sampled were those subjected to two frying conditions: a) chips were fried in one hour old oil (termed one hour chips) and b) chips were fried after six hours of heating the oil (termed six hour chips).

Panelists Perception of Rancidity

Panelists used their own perception of rancidity on which to base this evaluation. Therefore, variations in the term rancidity may be greater than if a trained sensory panel were used. The panelists perceived highly significant differences ($P < 0.001$) in rancidity between the chips treated with the various antioxidants. A rating of 5 indicates the panelists perceived the sample to be equal to the reference sample, 1 indicates the sample is perceived as more rancid than the reference, and 9 indicates the sample is perceived as less rancid than the reference. In Figure 10, the panelists rated one hour chips from canola oil with TBHQ (AQS) and one hour chips from corn oil with TBHQ (BQS) as the least rancid treatments. One hour chips from canola oil with rosemary (ARS) were highly significantly more rancid than the other treatments (Figure 10). When looking at the general category of antioxidants, significant differences were observed with TBHQ samples rated as the least rancid of the treatments (Table 8). Table 8 shows the panelists also detected the one hour chips to be rated as less rancid than the six hour chips. The

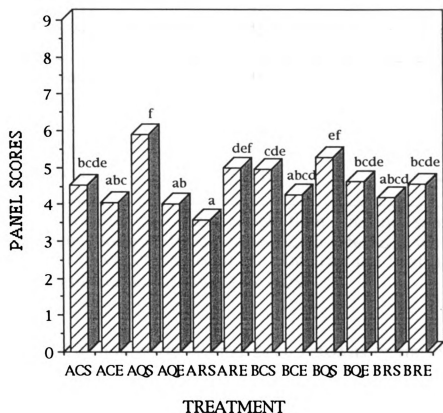


Figure 10. Sensory scores of panelists perceived rancidity in one hour chips (S) and six hour chips (E)^{1,2,3,4}.

¹All values represent the average of two replicated experiments with the average of the treatments.

²Panel Scores: 1=More rancid than the reference; 5=Equal to the reference; 9=Less rancid than the reference.

³All numbers bearing the same letter do not differ significantly at $P < 0.001$.

⁴Treatments: A=Canola oil; B=Corn oil; C=Control; Q=TBHQ; R=Oleoresin rosemary.

Table 8. Effect of antioxidant, oil age, and oil type on potato chip rancidity as detected by the sensory panelists.

Treatment	Panelists Rating of Rancidity ¹	Effect ²
Control	4.45	a
TBHQ	4.95	b
Rosemary	4.33	a
One hour chips	4.73	b
Six hour chips	4.42	a
Canola Oil	4.51	a
Corn Oil	4.65	a

¹Panelist rating of 1=More rancid than reference sample; 5=Equal to reference sample; 9=Less rancid than reference sample.

²Within an effect, values in the same row not bearing the same letter are significantly different ($P < 0.05$).

corn oil also appears to have been rated as being slightly less rancid than the canola oil samples (Table 8).

Panelists Preference

Panelists rated the potato chips as anywhere from extremely disliked (1), neither liked nor disliked (5), or extremely liked (9). The panelists preferred the six hour chips from corn oil with rosemary (BRE) and six hour chips from corn oil with TBHQ (BQE) (Figure 11). They disliked, to some extent, the one and six hour chips from corn oil without any antioxidant (BCS) (BCE), one hour chips from corn oil

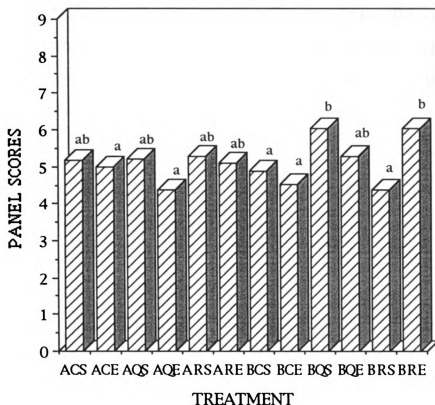


Figure 11. Sensory scores of panelists' preference of one hour chips (S) and six hour chips (E)^{1,2,3,4}.

¹All values represent the average of two replicated experiments with the average of the treatments.

²Panel scores: 1=Extremely disliked, 5=Neither liked nor disliked, and 9=Extremely liked.

³All numbers bearing the same letter do not differ significantly at $P < 0.001$.

⁴Treatments: A=Canola oil; B=Corn oil; C=Control; Q=TBHQ; R=Oleoresin rosemary.

with rosemary (BRS), six hour chips from canola oil without any antioxidant (ACE), and six hour chips from canola oil with TBHQ (AQE) samples (Figure 11). Two panelists noted a rosemary flavor in the potato chips. Also, the preference of the chips is based on what the panelists previous experiences were with potato chips and lipid oxidation. Therefore, the reason for like or dislike may not be due to an increase in oil rancidity or the rosemary flavoring, but due to panelists experiences. For future research, this experimental error due to panelists can be compensated for by increasing the number of panelists.

CONCLUSIONS

There were three objectives in this investigation. The first was to assess the suitability of canola oil as a frying medium for potato chips. The second was to determine the effectiveness of oleoresin rosemary (OR) and TBHQ in retarding oxidative rancidity in potato chips when added directly to the frying oil. The final was to determine if there was a perceivable difference in canola oil flavor over a continual oil heating period.

The results of this study show that the canola oil had consistently lower peroxide values, significantly lower conjugated diene values, lower percent oil absorbed, and significantly lighter chips than corn oil. Unfortunately, the canola oil showed a greater increase in viscosity with continual heating which indicates more breaking down of the oil over time. The color of the oils varied with the heating. Overall the canola appears to be a better oil than corn as a frying medium.

As for the antioxidants, 0.5% OR in corn oil (BR5) gave the lowest peroxide values but the TBHQ in canola oil (AQ) was only slightly higher. Comparing these treatments to 0.5% OR in canola oil (AR5) and TBHQ in corn oil (BQ), where higher peroxide values were observed, there is a difference due to oil type and treatment. The lowest conjugated diene value was found in the TBHQ incorporated into canola (AQ) while the 0.5% OR in corn (BR5) was the highest.

This shows a conflict between the 0.5% OR's conjugated diene values and the peroxide values giving mixed results. The Agtron values for potato chips show that in every instance, the antioxidants gave lighter colored chips with canola oil except the controls where corn oil produced lighter chips. These values were very similar, most likely not indicating any detectable visual differences. TBHQ chips were the lightest of all the antioxidants used in the chips. Combining all of the data, it can be concluded that the TBHQ produced the best potato chips. OR proved to be better than the control in some cases and less effective than the TBHQ in most cases. OR appears to not be suited for use in canola oil or corn oil for potato chips. A level greater than 0.5% OR has not been tested for toxicity and in addition may cause a notable rosemary flavor, so it is probably not suitable for use in potato chips. For less bland snack foods, the rosemary flavor may not show through.

Taste panelists rated one hour chips from canola oil with TBHQ (AQS) and one hour chips from corn oil with TBHQ (BQS) to be significantly less rancid than the other treatments (Figure 10). The one hour chips from canola oil with rosemary (ARS) were significantly more rancid than the other treatments (Figure 10). The panelists preferred the six hour chips from corn oil with rosemary (BRE) and six hour chips from corn oil with TBHQ (BQE). They disliked, to some extent, the one and six hour chips from corn oil without any antioxidant (BCS)(BCE), one hour chips from corn oil with rosemary (BRS), six hour chips from canola oil without any antioxidant (ACE), and six hour chips from canola oil with TBHQ (AQE)

samples (Figure 11). It appears the panelists have different preferences for the oils, as well as the antioxidant treatments.

APPENDIX A

Sensory Evaluation of Potato Chips

NAME _____ DATE _____

You are receiving samples of potato chips to compare for the degree of product freshness. You have been given a reference sample, marked R, with which you are to compare each sample. Taste each sample; determine whether it is fresher than, comparable to, or more rancid than the reference. Then mark the amount of difference that exists.

Sample number _____

Fresher than R _____

Equal to R _____

More Rancid than R _____

Amount of difference:

None _____

Slight _____

Moderate _____

Much _____

Extreme _____

Comments:

Sensory Evaluation of Potato Chips

NAME _____ DATE _____

Using the same samples, taste the samples and check how much you like or dislike each one.

<u>Sample number</u>	_____	_____	_____	_____	_____	_____
like extremely	_____	_____	_____	_____	_____	_____
like very much	_____	_____	_____	_____	_____	_____
like moderately	_____	_____	_____	_____	_____	_____
like slightly	_____	_____	_____	_____	_____	_____
neither like nor dislike	_____	_____	_____	_____	_____	_____
dislike slightly	_____	_____	_____	_____	_____	_____
dislike moderately	_____	_____	_____	_____	_____	_____
dislike very much	_____	_____	_____	_____	_____	_____
dislike extremely	_____	_____	_____	_____	_____	_____

Comments:

APPENDIX B

Table 1B. Analysis of variance for peroxide values of potato chips during storage study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication(R)	1	2.083	2.083	0.725	ns
Oil Type(A)	1	12.233	12.233	3.621	ns
Antioxidant(B)	3	42.118	14.039	4.156	ns
AB	3	16.447	5.482	1.623	ns
RAB	7	23.649	3.378		
Temperature(C)	1	3.987	3.987	0.079	ns
Time(D)	3	153.991	51.330	1.019	ns
CD	3	3.121	1.040	0.021	ns
RCD	7	352.556	50.365		
AC	1	0.00004	0.00004	0.00001	ns
AD	3	37.888	12.629	4.394	<0.01
BC	3	9.576	3.192	1.111	ns
BD	9	20.514	2.279	0.793	ns
Residual	79	227.008	2.874		
Total	127	905.171			

Table 2B. Analysis of variance for conjugated diene values of potato chips during storage study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication(R)	1	0.010	0.010	55.556	<0.001
Oil Type(A)	1	0.018	0.018	18.000	<0.01
Antioxidant(B)	3	0.007	0.002	2.000	ns
AB	3	0.002	0.001	1.000	ns
RAB	7	0.004	0.001		
Temperature(C)	1	0.00003	0.00003	0.030	ns
Time(D)	4	0.012	0.003	3.000	ns
CD	4	0.002	0.0004	0.400	ns
RCD	9	0.009	0.001		
AC	1	0.00006	0.00006	0.333	ns
AD	4	0.0003	0.00006	0.333	ns
BC	3	0.0000	0.00002	0.111	ns
BD	12	0.006	0.0005	2.778	<0.01
Residual	106	0.019	0.00018		
Total	159	0.089			

Table 3B. Analysis of variance for Agtron values of potato chips during storage study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication(R)	1	2.220	2.220	6.727	<0.01
Oil Type(A)	1	18.550	18.550	7.599	<0.05
Antioxidant(B)	3	278.484	92.828	38.029	<0.001
AB	3	58.004	19.335	7.921	<0.05
RAB	7	17.088	2.441		
Temperature(C)	1	1.402	1.402	5.434	ns
Time(D)	2	0.252	0.126	0.488	ns
CD	2	0.808	0.404	1.566	ns
RCD	5	1.288	0.258		
AC	1	0.844	0.844	2.558	ns
AD	2	0.004	0.002	0.006	ns
BC	3	1.789	0.596	1.806	ns
BD	6	1.838	0.306	0.927	ns
Residual	58	19.114	0.330		
Total	95	401.685			

Table 4B. Analysis of variance for percent oil values of potato chips during storage study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication(R)	1	83.191	83.191	46.192	<0.001
Oil Type(A)	1	11.019	11.019	0.584	ns
Antioxidant(B)	3	36.341	12.114	0.643	ns
AB	3	71.455	23.818	1.263	ns
RAB	7	131.979	18.854		
Temperature(C)	1	20.050	20.050	22.452	<0.01
Time(D)	9	13.219	1.469	1.645	ns
CD	9	5.444	0.605	0.678	ns
RCD	19	16.970	0.893		
AC	1	0.203	0.203	0.113	ns
AD	9	16.061	1.785	0.991	ns
BC	3	41.486	13.829	7.679	ns
BD	27	30.828	1.142	0.634	ns
Residual	226	406.980	1.801		
Total	319	885.226			

Table 5B. Analysis of variance for Hunter "L" values of frying oil during frying study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication(R)	1	0.010	0.010	0.0004	ns
Oil Type(A)	1	0.007	0.007	0.241	ns
Antioxidant(B)	2	2.840	1.420	48.966	<0.001
AB	2	1.005	0.503	17.345	<0.01
RAB	5	0.143	0.029		
Time(C)	3	7.273	2.424	42.526	<0.01
RC	3	0.172	0.057		
AC	3	0.160	0.053	0.002	ns
BC	6	6.801	1.133	0.00004	ns
Residual	37	1028.519	27.798		
Total	63	1046.930			

Table 6B. Analysis of variance for Hunter "a" values of frying oil during frying study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication(R)	1	0.144	0.144	0.050	ns
Oil Type(A)	1	0.111	0.111	15.857	<0.01
Antioxidant(B)	2	0.051	0.026	3.714	ns
AB	2	0.457	0.229	31.806	<0.001
RAB	5	0.036	0.007		
Time(C)	3	0.654	0.218	12.111	<0.05
RC	3	0.055	0.018		
AC	3	0.265	0.088	0.031	ns
BC	6	1.692	0.282	0.098	ns
Residual	37	12.903	2.868		
Total	63	16.368			

Table 7B. Analysis of variance for Hunter "b" values of frying oil during frying study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication(R)	1	0.0002	0.0002	0.00005	ns
Oil Type(A)	1	0.319	0.319	8.622	<0.05
Antioxidant(B)	2	13.625	6.813	184.135	<0.001
AB	2	0.149	0.074	2.000	ns
RAB	5	0.187	0.037		
Time(C)	3	18.033	6.011	82.342	<0.01
RC	3	0.218	0.073		
AC	3	4.538	1.513	0.409	ns
BC	6	9.763	1.627	0.440	ns
Residual	37	136.176	3.696		
Total	63	183.008			

Table 8B. Analysis of variance for the viscosity of frying oil during frying study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication(R)	1	21.333	21.333	0.003	ns
Oil Type(A)	1	3234.083	3234.083	42.479	<0.01
Antioxidant(B)	2	466.292	233.146	3.062	ns
AB	2	2622.792	1311.396	17.225	<0.01
RAB	5	380.667	76.133		
Time(C)	3	14399.500	4799.833	152.914	<0.001
RC	3	94.167	31.389		
AC	3	711.417	237.139	0.034	ns
BC	6	1664.375	277.396	0.040	ns
Residual	37	259635.120	7017.166		
Total	63	283229.750			

Table 9B. Analysis of variance for the multiple comparison of the degree of rancidity perceived in the treatments during frying study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication	1	0.587	0.587	0.203	ns
Treatments	11	201.935	18.358	6.359	<0.001
Judges	22	73.721	3.351	1.161	ns
Residual	517	1492.562	2.887		
Total	551	1768.804			

Table 10B. Analysis of variance for the preference of the treatments during frying study.

Source of Variation	Degree of Freedom	Sum of Square	Mean Square	F Value	Probability
Replication	1	2.219	2.219	0.596	ns
Treatments	11	150.759	13.705	3.682	<0.001
Judges	22	188.286	8.558	2.299	<0.001
Residual	517	1924.647	3.723		
Total	551	2265.911			

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