MINIA UNIVERSITY
FACULTY OF AGRICULTURE
FOOD SCIENCE DEPARTMENT

CHEMICAL AND TECHNOLOGICAL STUDIES ON SOME VEGETABLE OILS

BY

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THESIS

Submitted in partial fulfillment of the requirements for the degree of

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A thesis submitted for the Master Science Degree

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FOOD SCIENCE

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DEDICATION

THIS THESIS IS DEDICATED TO:-

The soul of my father…

My lovely mother……

My brother's; Ahmed, Mohamed, Mosbah, Youssef, my sister and their families……

My small family; my wife,

My son Mostafa and my daughter lamia

My friends

All who taught me a letter from first day of school till now.

Abul-Hamd .E. Mehanni

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ABBREVIATIONS

Abbreviate	**Definition**
AOAC	Association of Official Analytical Chemists
AOCS	American Oil Chemists Society
AOM	Active oxygen method
AV	Acid Value
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
cm	Centimeters
Ctrl.	Control
E.O.S	Egyptian Organization for Standardization
EG	Eggplant
FA	Fatty acid(s)
FAO	Food and Agriculture Organization
FDA	Food and Drug Administration
FFA	Free fatty acid(s)
g	Gram
GLC	Gas liquid chromatography
INFORM	International News on Fats, Oils and Related Materials
IV	Iodine value
Kg	Kilogram
LEAR	Low erucic acid
mg	Milligram
mPa.Sec	Milli-Pascal Second
MPOPC	Malaysian Palm Oil Promotion Council
MUFA	Mono unsaturated fatty acids

^{o}C	Degree of Celsius
PG	Propyl gallate
PO	Potatoes
PUFA	Poly unsaturated fatty acids
PV	Peroxide value
RBD	Refined bleached deodorized
RBW	Refined bleached winterized
RI	Refractive index
S/U	Saturated / Unsaturated ratio
SFA	Saturated fatty acids
Sp. Gr.	Specific gravity
SQ	Squash
SV	Saponification value
TAG	Triacylglcrol
TBA	Thiobarbituric acid
TBHQ	Tertiary butylhydroquinone
TS	Total saturated
TSFA	Total saturated fatty acids
TUFA	Total unsaturated fatty acid

INTRODUCTION

1 – INTRODUCTION

The functions of oils and fats fall into two distinct parts, technically and nutritional. Technologically, oils and fats play various roles in foods. They are usually used in frying, cooking, salad oils and mayonnaise. Besides, large amount of edible oils used in so-called convenience foods such as potato chips, roasted nuts, popcorn and many others which is expected to increase this category further **(Swern, 1979).** From the nutritional point of view, oils and fats are a structural component of the membranes, which enclose living cells. Oils and fats constitute one of the three major classes of food constitutes besides proteins and carbohydrates **(Lawson, 1995).** Both plants and animals utilize fats as a major source of energy, and for this purpose oils and fats form depots or reserve store in the tissues. As fuel, fats are more than twice as efficient as carbohydrates and proteins. In addition, certain components of fats have essential metabolic functions, being transformed into prostaglandins and hormones. While animals can synthesis some fats, others have to be supplied in the food particular the essential fatty acids and as a carrier for the fats–soluble vitamins **(Khalaf, 1993** and **Berger, 1996).** Furthermore, several studies showed the role of fats and oils in many diseases e.g. cardiovascular diseases, cancer, hypertension and obesity **(McDonald, 1995; and El-Sharnouby, 1999a).**

World consumption of the major oils and fats with their projection to 2020 is given in Table (1) **(Chow, 1998).** World demand for 11 vegetable oils increased from 37.73 million tonnes in 1980 to 59.58 million tonnes 1990, a growth rate at of about 2.2 million tonnes per year. Since 1990-demand increase at an average rate of 2.5 million tonnes per year to 74.37 million tonnes 1996. Demand is expected to increase at higher rate in the near future. The total vegetable oil demand is estimated

Table (1): World Consumption of Major Oils and Fats (Million tonnes)*

Year	Palm	Palm kernel	Soya	Sunflower	Cotton	Peanut	Rapeseed	Olive	Coconut	Corn	Sesame	Total 11 vegetable oils	Lord	Tallow	Butter	Fish	Total animal	Total 15 oils & fats
1980	4.57	0.61	12.71	4.98	3.02	2.69	3.94	1.71	2.58	0.86	0.51	**37.73**	4.96	6.31	5.78	1.16	18.21	**55.94**
1990	11.08	1.37	16.13	7.89	3.80	3.99	8.20	1.85	3.21	1.45	0.61	**59.58**	5.48	6.87	6.43	1.54	20.32	**79.90**
1995	14.68	1.49	19.48	8.6	3.89	4.20	10.54	1.94	3.26	1.76	0.74	**71.03**	5.81	7.41	5.84	1.41	20.47	**91.50**
1996	15.78	2.07	20.15	9.27	4.08	4.17	11.43	1.85	3.00	1.83	0.74	**74.37**	6.05	7.59	5.74	1.32	20.70	**95.07**
1997	16.38	2.29	20.21	9.20	4.14	4.57	12.18	2.04	3.17	1.95	0.72	**76.35**	5.98	7.59	6.12	1.31	21.00	**97.85**
2000	19.26	2.79	21.85	9.96	4.32	5.00	14.24	2.10	3.23	2.22	0.77	**85.54**	6.22	7.87	6.07	1.26	21.42	**107.16**
2005	24.60	3.77	24.6	11.25	4.63	5.81	18.12	2.21	3.31	2.74	0.85	**101.95**	6.62	8.37	5.10	1.13	22.03	**123.98**
2010	30.85	4.92	27.56	12.58	4.96	6.75	22.57	2.33	3.37	3.32	0.94	**119.90**	7.04	8.88	5.66	0.94	22.52	**142.42**
2015	37.16	6.31	30.57	13.96	5.30	7.83	27.62	2.44	3.41	3.98	1.04	**139.62**	7.47	9.41	5.31	0.70	22.89	**162.51**
2020	44.26	7.08	33.71	15.41	5.65	9.05	33.30	2.57	3.42	4.72	1.15	**161.12**	7.92	9.97	4.85	0.39	23.13	**184.52**

*** Source: Chow, (1998)**

to reach 85 million tonnes in 2000, over 100 million tonnes by 2005 and about 120 million tonnes by 2010. The total demand will probably be over 160 million tonnes by 2020, more than double the current demand.

The per capita consumption for the major vegetable oils was 5.52 kg/year. in 1960. It doubled to 11.50 kg/year in 1990 and increased to 13.21 kg/year in 1996 (Table 2). The per capita consumption for developed countries (Europe and US) is as high as 45.00 kg/year **(Chow, 1998).** In Egypt, the total per capita consumption of edible fats and oils in 1994 was 21.35kg/year (15.45 kg. vegetable origin and 5.90 kg. animal origin) **(FAO, 1994).** On the other hand, Table (4) shows the production and imports of vegetable oils and fats in Egypt till 2003.

In Egypt, cottonseed oil is the most familiar edible oil. Now after the population arrived to over 70 millions, the production of oil is not enough to consumption. There is a great shortage in the edible oils and large amounts are annually imported to cover the shortage in local consumption market. Many investigators studied the physical and chemical properties of traditional and untraditional oil in their attempts to face the high consumption of oil all over the world including Egypt. Cultivating of new short season oil crop such as canola seed in the new Egyptian reclaimed soils seems to be one of the most promising solutions in Egypt. Plant breeders are being worked for producing low erucic acid and low level glucosinolates rapeseed to cover this shortage **(Eskander, *et al.* 1984; Rady, *et al.* 1990 and El-Sharnouby, 1999a).** As a result of increased utilization of rapeseed oil for cooking and for manufacture of margarine, shortening and salad oil, rapeseed (canola) is now ranked third among all vegetable oil seeds, after soybean and palm oils, in total world tonnage. The rapeseed cultivars now grown in Canada, known as "canola" ***(Brassica napus),*** have been genetically improved to contain low level erucic acid (< 1%) in the oil and glucosinolates (> 30 μM/gm)

Table (2): Per Capita Consumption of Major Oils and Fats (Kg/year)*

Year	Palm	Palm kernel	Soya	Sunflower	Cotton	Peanut	Rapeseed	Olive	Coconut	Corn	Sesame	Total 11 vegetable oils	Lord	Tallow	Butter	Fish	Total animal	Total 15 oils & fats
1960	0.43	0.14	1.10	0.62	0.78	0.76	0.39	0.43	0.26	0.14	0.11	**5.52**	1.04	1.14	1.37	0.16	3.71	**9.23**
1970	0.47	0.11	1.66	0.97	0.71	0.73	0.47	0.42	0.55	0.13	0.14	**6.36**	1.04	1.31	1.38	0.27	4.00	**10.38**
1980	1.04	0.14	2.90	1.14	0.69	0.61	0.80	0.39	0.59	0.12	0.20	**8.62**	1.03	1.44	1.32	0.26	4.15	**12.79**
1990	2.14	0.26	3.12	1.52	0.73	0.77	1.58	0.36	0.62	0.12	0.28	**11.50**	1.06	1.33	1.24	0.30	3.93	**15.44**
1995	2.62	0.34	3.49	1.54	0.69	0.76	1.91	0.35	0.60	0.13	0.32	**12.75**	1.04	1.32	1.04	0.25	3.65	**16.42**
1996	2.83	0.37	3.57	1.62	0.72	0.75	2.03	0.33	0.54	0.13	0.32	**13.21**	1.07	1.34	1.01	0.23	3.65	**16.85**
1997	2.86	0.40	3.53	1.61	0.72	0.80	2.13	0.36	0.55	0.13	0.34	**13.43**	1.05	1.33	1.07	0.23	3.68	**17.11**
2000	3.23	0.47	3.67	1.67	0.72	0.84	2.39	0.35	0.54	0.13	0.37	**14.38**	1.04	1.32	1.02	0.21	3.59	**17.98**
2005	3.86	0.59	3.87	1.76	0.73	0.91	2.84	0.35	0.52	0.13	0.43	**15.99**	1.04	1.31	0.93	0.18	3.46	**19.45**
2010	4.49	0.73	4.05	1.85	0.73	0.99	3.32	0.34	0.49	0.14	0.49	**17.62**	1.03	1.30	0.83	0.14	3.30	**20.93**
2015	5.13	0.87	4.22	1.93	0.73	1.08	3.81	0.34	0.47	0.14	0.55	**19.27**	1.03	1.30	0.73	0.10	3.16	**22.42**
2020	5.74	1.02	4.37	2.00	0.73	1.17	4.32	0.33	0.44	0.15	0.61	**20.88**	1.03	1.29	0.63	0.05	3.00	**23.89**

*** Source: Chow, (1998)**

in the meal. Canola plants characterized by a high seed yield, about 900 – 1000kg/fed. The seeds contain about 40-45 % oil, 20-25 % protein and 30-40 % carbohydrates, yielding meal containing up to 50 % protein after oil extraction. **(Daun, *et al.* 1986, Prior, *et al.*1991 and El-Sharnouby, 1998).** Tables (3) and (4) illustrate the world production of some vegetable oils in the world and Egypt **(FAO, 2004a, b).**

Table (3) World production of some vegetable oils (Metric ton)*

Source / Year	Soybean oil	Palm oil	Canola oil	Cottonseed oil
1990	15 655 903	11 445 581	8 172 922	3 828 649
1995	19 751 188	15 923 981	10 667 849	3 850 001
2000	25 081 002	22 443 006	13 450 449	3 801 436
2001	27 419 641	24 312 519	12 512 846	3 917 294
2002	30 102 345	25 721 405	12 386 307	3 786 754
2003	31 063 276	28 077 905	11 903 321	3 812 932
2004	31 123 765	30 103 549	12 602 109	3 120 186

***(FAO, 2004a).**

Table (4) Production and imports of vegeTable oils and fats (Metric ton)* in Egypt.

Year	*Production*	*imports*	year	*Production*	*Imports*
1961	136 804	17 708	**1990**	181 748	748 187
1965	212 989	32 890	**1995**	189 626	727 187
1970	300 182	112 583	**2000**	223 128	631 711
1975	375 714	263 629	**2001**	284 011	679 023
1980	237 889	275 403	**2002**	298 133	665 088
1985	184 170	534 108	**2003**	247 221	689 223

***(FAO, 2004b).**

Canola seed differs from soybean or cottonseed in many particulars such as size, colour, fatty acid composition, oil content, presence of glucosinolates and absence of trypsin inhibition. Thus, methods appropriate to soy or even flax do not necessarily apply **(Blake, and Marianchuk, 1984).** However, the Food and Drug Administration **(FDA, 1982)** reported that the Research Branch of Agriculture Canada had petitioned for generally recognized as safe list (GRES) status for low erucic acid (< 2%) rapeseed oil as a food ingredient. The petition proposes that low erucic acid rapeseed oil and hydrogenated low erucic acid rapeseed oil be used as food ingredients similarly to other edible fats and oils. Plant breeders have been succeeded in developing low erucic acid cultivars which are more acceptable for edible oil market **(Downey and Klassen, 1977**). Low erucic acid rapeseed (LEAR) oil is being used for cooking and other edible uses **(Riiner and Ohlson, 1971; Bernard 1971 and Craig, 1977)**, while the traditional high erucic acid rapeseed (HEAR) one is still marketable for industrial purposes **(Ohlson, 1983 and Daun, *et al.* 1986).** The Canadian plant breeders are being worked to produce new rapeseed cultivars free or contain very low level of glucosinolaes and also zero erucic acid, double zero rapeseed, this, type of rapeseed will completely replace soybean meal in feed formulation **(Clandinin, 1981).**

Frying is a mainstay of any successful fast –food operation and is one of the most commonly used procedures for the preparation and production of food in the world. Potato chips, corn chips and similar products after fried and packaged to be consumed within a few days after preparation **(Weiss, 1970 and Vincent, 1979).** During frying, the fat or oil is kept hot (about 180 ^{o}C) for long periods of time and is exposed to both moisture and oxygen. Complex chemical and physical changes occur under these conditions, causing fat deterioration which may reach a point

where the flavour, odor, colour, nutritional value and safety of the food may be affected **(Edward, 1967; Smith, *et al.* 1986; Iskandar, 1991 and 1992).** It should be noted that some food processes maintain their frying oil in good quality while others abuse and seriously damage them. Such deteriorated oils not only may have an adverse effect upon human nutrition, but also cause poor texture, flavour and flavour stability of the fried foods **(Stephen, 1967).** There are many evidences indicating the formation of harmful substances such as malonaldehyde which is reported to be carcinogenic **(Shamberger, *et al.* 1974; Vincent, 1979; Carroll, 1981 and Brown, 1983).** The deterioration of oil during frying has been evaluated by conventional methods such as free fatty acid content, colour, peroxide value and flavour values which are standard in the fat and oil industry. Thiobarbituric acid test can be quite useful in supplementing the flavour evaluation incoming frying oils. Furthermore, the change in iodine value was used as a simple and highly precise tool for determining the formation of polymeric materials in the heated oils **(Jacobson, 1967; Vincent, 1979 and Iskandar, 1991).**

AIM OF INVESTIGATION

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The objectives of the present study were:

- **To** determine some physical and chemical properties, fatty acids composition, stability and unsaponifiable matters of canola oil extracted from varieties which planted under Egyptian environmental conditions and compare this oil with cottonseed oil which represents the main Egyptian edible oil.

- **To** study the effect of storage conditions on the physical and chemical properties of the cottonseed oil and canola oils during storage.

- **To** evaluate the keeping quality and stability of the studied oils by addition of some commercially available antioxidants.

- **To** evaluate and determine the changes that take place in cottonseed and canola oils when used to fry Eggplant, Squash and Potato.

- **To** evaluate the alteration level in heated cottonseed and canola oils, differentiating the three important classes of degradation implicated in the total alteration: hydrolytic, thermal and oxidative.

REVIEW OF LITERATURE

2 – REVIEW OF LITERATURE

2.1 – Physical and chemical characteristics of some vegetable oils:

Physical properties nearly help to identify and to recognize of vegetable oils, which also have economical and industrial benefits. In addition, chemical characteristics are a measure of several specific chemical properties of vegetable oils. Characteristics are widely used in fat and oil industry because they are useful for describing the characteristics of lipid mixtures used in food manufacturing and processing. The composition of oils and fats is affected by cultivar and growing conditions, as well as handling and processing. Chemical characteristics are a practical way of describing and quantifying this diversity. They are, however, seldom used for the characterization of individual vegetable oils because, in isolation, they do not provide proof of the identity or purity of an individual compound **(Nichols and Sanderson, 2003).**

2.1.1 – Cottonseed oil:-

Van Oss (1975) reported that the refractive index of cottonseed oil was 1.468 – 1.472 at 25 ^{o}C. **Swern (1979)** showed the following characteristics for cottonseed oil: Sp. Gr. (at 25 ^{o}C) 0.916 – 0.918 and RI (at 25 ^{o}C) 1.468 – 1.472.

Du Plessis, *et al* (1981) found that the peroxide and free fatty acid values of cottonseed oil were 0.7 and 0.2, respectively.

Krishnamurthy (1982) showed the following characteristics for cottonseed oil: of R.I. at 60 ^{o}C 1.4572, smoke point ^{o}C (^{o}F) 226.6 (440) and lovibond colour (Y/R) 20/2.5, iodine value 108 and free fatty acids (as % oleic acid) 0.03.

Moharram and Moustafa (1982) reported the following properties for cottonseed oil: specific gravity at 20^{o}C 0.925, melting point 194,

refractive index at 20 °C 1.4717, iodine value 104.5, saponification value 196 and acid value 0.7, respectively.

Badawy (1986) showed that the refractive index at (25°C), viscosity (poises) and specific gravity at (25°C) were 1.4691, 41.03 and 0.9154, respectively.

Rady, *et al.* (1990) evaluated the physical properties of cottonseed oil. They found that the specific gravity (25°C), refractive index RI (20 °C), colour yellow, and colour red were 0.9163, 1.48682, 35 and 6.5, respectively.

The Egyptian Organization for Standardization (**E.O.S., 1993**) reported the following values for cottonseed oil: specific gravity at 20/20 0.9159 – 0.9300, colour (lovibond Y/R 5.25 in. cell) 35/7, and refractive index at 20°C 1.4717 – 1.4727; iodine value 101 – 115, saponification value 190 – 199 and free fatty acids as % oleic acid 0.2, respectively.

Hui (1996) showed the following characteristics for cottonseed oil: smoke point 232 °C (450 °F), specific gravity (25°C) 0.914 – 0.917, viscosity (at 37 °C) 35.88, colour (red) 2.0 – 2.5, refractive index RI (40 °C) 1.4648, iodine value 103 – 112, free fatty acids (%) 0.05% and unsaponifiables and 0.5 – 0.7%.

El-Sharnouby (1999a) reported the following properties for cottonseed oil: specific gravity at 25°C 0.9210, refractive index at 25°C 1.4720; colour (Y/R) 35/5; acid value (as % oleic acid) 0.13, saponification value 189, iodine value 108, peroxide value (meq/kg oil) 0.9 and unsaponifiable matter (U.S %) 0.6.

Francis (2000) reported the values of refractive index, specific gravity, iodine number and saponification number for cottonseed oil as follow: 1.468 – 1.472, 0.916 – 0.918, 99 – 115 and 189 – 198, respectively. On the other hand, **Yaghmur, *et al.* (2001)** showed the following

characteristics for cottonseed oil: peroxide value (meq. /kg oil) 1.2 and acid value (mg KOH/g oil) 0.3.

Noor Azian, *et al.* (2001) reported that the viscosity is an important a phenomenon of fluids. It affects strongly by the change of temperatures. Vegetable oils have high viscosities according to the intermolecular attractions of the long chains of glyceride molecules. However, the viscosity increases with molecular weight but decreases with increases in unsaturation and temperature.

The following values were found for cottonseed oil: specific gravity (25/25°C) 0.916 to 0.918, refractive index (25°C) 1.468 to 1.472, melting point (°C) 10 to 16; iodine value 98.0 to 118.0, saponification number 189 to 198 and unsaponifiable number <1.5 (**Bennion and Schedule, 2004)**.

Thomas (2005) reported that cottonseed oil had the following characteristics: density (**g/cm^3)** 0.917 – 0.931; refractive index (40 ^{o}C) 1.472 – 1.477, viscosity (mPa · s) 80 (at 20 ^{o}C), saponification value 190 – 198, iodine value 100 – 117 and nonsaponifiable matter 0.5 – 1.5 %.

2.1.2 – Canola oil:-

Moharram, *et al.* (1982) reported the following properties for rapeseed oil: specific gravity at 25 ^{o}C 0.9120, refractive index at 25 ^{o}C 1.4693, saponification number 168 and unsaponifiable matter 1.43 %.

Vaisey-Genser and Eskin (1982) studied the iodine value (IV) and saponification value (SV) of low erucic acid rapeseed and high erucic acid rapeseed oils. They found the low erucic acid rapeseed oil had higher SP (188 – 192) and IV (112) than that of high erucic acid SP (168 – 181) and IV (81.4).

Ackman (1983) cited that the chemical characteristics of the edible low erucic acid rapeseed oil were: saponification value (mg KOH/g oil)

188 – 193; iodine value 110 – 126; unsaponifiable matter not more than 20 g/kg, acid value not more than 0.6 mg KOH/g oil; peroxide value not more than 10 meq /kg oil and erucic acid not more than 5 % of the total fatty acid composition.

Ohlson (1983) reported the following characteristics for high erucic acid rapeseed oil: relative density (20 ^{o}C/water at 20 ^{o}C) 0.910 – 0.920; refractive index (nD 40 ^{o}C) 1.465 – 1.469; saponification value (mg KOH/g oil) 168 – 187; iodine value (Wijs) 94 – 120; unsaponifiable matter not more than 20 g/kg; erucic acid more than 5 % (m/m) of the component fatty acid composition. In addition, **Mag (1983)** mentioned that the free fatty acids content and unsaponifiables of crude canola oil were 0.4 – 1 % and 0.5 – 1.2 %, respectively.

Campbell (1984) reported that the free fatty acid (as % oleic acid) content of crude canola oil should be not more than 1.0 according to the specifications of the national standards of canola. On the other hand, **Diosady *et al.* (1984)** reported the free fatty acids FFA as % oleic acid, peroxide value PV and iodine value IV of crude canola oil, were 0.7, 4.62 and 120.8, respectively.

Daun *et al.* (1985) found the free fatty acids FFA as % oleic acid and iodine value IV of canola oil, were 1.26 and 112, respectively. Also, **Abraham and DeMan (1987)** reported that the iodine value of the crude canola oil was 125.

Köseoglu and Lusas (1990) reported that the free fatty acids FFA as % oleic acid and iodine value IV of canola oil were 0.4 – 1.00 and 112 – 131, respectively.

Rady, *et al.* (1990) stated the physical and chemical properties of some varieties of crude rapeseed oil as mentioned in the following:-

Characteristics	Rapeseed varieties			
	Cresor	Brutor	A.D-201GI	Iraq
Specific gravity at 25°C.	0.9204	0.9196	0.9209	0.9141
Refractive index at 25°C.	1.4720	1.4712	1.4721	1.4718
Colour yellow	35	35	35	35
red	4.9	4.4	5.9	4.4
Iodine value (Hanus)	111	104	112	101
Saponification value	190	191	192	175
Acid value (% oleic acid)	0.30	0.36	0.21	4.09
Peroxide value (meq/kg.)	0.66	0.50	0.48	0.47
Unsaponifiable matter %	1.0	1.1	1.1	1.1
Induction period (11.3 in hrs. at 100 °C).	11.3	16.5	15.8	15
Oil %	47.08	44.5	42.0	37.4

Lang, *et al.* (1992) studied that the viscosity of refined, bleached, deodorized (RBD) and refined, bleached, winterized (RBW) canola oils at range of temperatures from 4 to 100 °C. The viscosity was exponentially related to the oil temperature and the viscosity of RBW oil was slightly greater than of the RBD oil when the temperature < 15 °C.

Przybyski (1994) reported the following values for the canola: relative density (g/cm^3; 20 °C/water at 20 °C) 0.914 – 0.917; refractive index (nD40 °C) 1.465 – 1.467; viscosity (kinematic at 20 °C, mm^2/sec) 78.2; free fatty acids (%) 0.4 – 1.2; iodine value 110 – 126; saponification value 188 – 192 and unsaponifiables 0.5 – 1.2 %.

Wanasundara and Shahidi (1994) stated the iodine value and peroxide value of refined-bleached (RB) canola oil were 112 and 0.2,

respectively. In addition, **Hawrysh, *et al.* (1995)** reported that the peroxide value, iodine value and free fatty acids as % oleic acid of fresh canola oil were 0.2, 125.96 and 0.0, respectively. On the other hand, the following properties were found for canola oil **(Hui, 1996)**: relative density (g/cm^3; 20 ^oC/water at 20 ^oC) 0.914 – 0.917; refractive index (nD 40 ^oC) 1.465 – 1.467; viscosity (kinematic at 20 ^oC, mm^2/sec) 78.2; smoke point (^oC) 220 – 230; free fatty acids (%)0.4 – 1.2; triglycerides (%)94.4 – 99.1; crismer value 67 – 70 and unsaponifiables 0.5 – 1.2%.

E.O.S (1997) reported the following characteristics for rapeseed oil: colour (Y/R in 5.25 inch cell) 35/3; specific gravity (20/20 ^oC) 0.914 – 0.917; RI (40 ^oC) 1.465 – 1.467; saponification value (mg KOH/g oil) 188 – 193; Iodine value 110 – 126; crismer value 67 – 70; unsaponifiable matter not more than 20 g/kg ; acid value not more than 0.6 mg KOH/g oil; peroxide value not more than 10 meq /kg oil; brassicasterols not more than 5 % of the total sterols and erucic acid not more than 2 % of the total fatty acid composition.

Hawrysh (1998) found that the iodine value, peroxide value, and free fatty acids as % oleic acid of commercial canola oil were 119.92, 0.63 and 0.0, respectively. In addition, **Vaisey-Genser, *et* al. (1998)** determined the iodine value of the regular and low erucic linolenic acid canola oil. The results showed that the iodine values were 122 and 110 for regular and low erucic linolenic acid canola oil, respectively.

El-Sharnouby (1999b) showed the following characteristics for canola oil: specific gravity at 25^oC 0.9201; refractive index at 25^oC 1.4700; colour (Y/R) 35/0.5; acid value (as % oleic acid) 0.16; saponification value 188; peroxide value 0.5; iodine value 112 and unsaponifiable matter (%) 0.9.

Ibrahim (2000) studied that the physical and chemical characteristics of some varieties of canola oil grown under Egyptian

environmental. He reported the following values: specific gravity (at 25/25°C) 0.914 – 0.915; refractive index (nD 40 °C) 1.465 – 1.467; acid value (mg KOH/g oil) 0.58 – 1.23; saponification value 191.6 – 193.4; peroxide value 1.23 – 2.03; iodine value 117.7 – 125.1 and unsaponifiable matter (%) 1.26 – 1.54. On the other hand, **Francis (2000)** showed that the refractive index and specific gravity values of rapeseed oil ranged from 1.470 – 1.474 and 0.906 – 0.914, respectively. In addition, he found that the specific gravity of low-erucic acid rapeseed was 0.916 – 0.9176.

Nichols and Sanderson (2003) found that the following properties of canola oil: specific gravity (20/20°C) 0.914 – 0.920 and refractive index **(**40°C) 1.465 – 1.467, iodine value 110 – 126 and saponification value 182 – 193. On the other hand, the following properties found for canola oil: iodine value 110.0 to 126.0; saponification number 182 to 193; unsaponifiable number 0.5 to 1.2 and AOM stability (hours) 12 to 20 **(O'Brien (2004)**.

Thomas (2005) reported the following values for rapeseed oil: smoke point 200.08 °C, flash point 218 °C, and fire point 317 °C; density **(g/cm^3)** 0.910 – 0.917, refractive index (40 °C) 1.472 – 1.476, and viscosity (mPa · s) 85 (at 20 °C). The same author **(2005)** mention that the smoke, flash and fire points of oils and fats are effects measures of their thermal stability when heated in air.

2.2 – Fatty acids composition of some vegetable oils:-

2.2.1 – Cottonseed oil:

Lawhon, *et al.* (1977) mentioned the composition of fatty acids in cottonseed oil varieties as follow: 0.7 – 0.9 % myristic, 22.6 – 23.0 % palmitic, 2.1 – 2.2 % stearic, 17.6 – 17.7 % oleic, 55.8 – 56.6 % linolenic, and 0.3 – 0.4 % unknown fatty acids. On the other hand, **Padley, *et al.***

(1986) reported the following fatty acid composition of cottonseed oil: C14:0 (0.8 %), C16:0 (27.3 %), C18:0 (2.0 %), C20:0 (0.3 %), C16:1(0.8 %), C18:1 (18.3 %), C18:2 (50.2 %) and C18:3 (tr.).

Habib (1986) reported the principal fatty acid composition of cottonseed oil: as follows: C8:0 (1.24 %), C10:0 (1.10 %) C12:0 (0.73 %), C13:0 (0.93 %), C14:0 (1.33 %), C15:1 (0.53 %), C16:0(19.0 %), C16:1(0.88 %), C18:0 (7.1 %), C18:1 (26.0 %), C18:2 (41.2 %).

King and Camire (1989) reported that fatty acid profile of cottonseed oil generally consists of 22 % saturated fatty acids, primarily palmitic; 18 % oleic, a monounsaturated fatty acid; and approximately 54 % linoleic acid, which is an essential fatty acid. In addition, **Rady, *et al.* (1990)** mentioned that the major fatty acid contents of cottonseed oil were: C14:0 (1.97 %), C16:0 (26.72 %), C18:0 (3.52 %), C18:1 (16.87 %), C18:2 (51.0 %), total saturated (32.21%) and total unsaturated (67.87%).

Abidi and Warner (1996) reported the main fatty acids (%) 16:0, 18:0, 18:1, 18:2, and 18:3 of cottonseed oil were 24.3, 2.20, 16.5, 54.9, and 0.10, respectively. Also, **Hui (1996)** mentioned that the fatty acid composition of cottonseed oil: C14:0 (0.8 %) of the total fatty acids, C16:0 (27.0 %); C18:0 (2.0 %); C20:0 (0.3 %); C16:1 (0.8%); C18:1 (18.3 %); C18:2 (50.5 %) and C18:3 (trace).

Takeoka, *et al.* (1997) reported the following fatty acids for cottonseed oil: C8:0 (0.01 %), C12:0 (0.02 %), C14:0 (0.94%), C16:0 (26.96 %), C18:0 (2.47 %); C20:0 (0.30 %); C22:0 (0.18 %); C24:0 (0.19 %); C16:1 (0.63 %), C18:1 (26.0 %), C18:2 (54.19 %); and C18:3 (0.54 %).

El-Sharnouby (1998; 1999a) investigated the fatty acid content of cottonseed oil. The results were as follow: capric (0.13%); lauric (0.70 %); myristic (0.50 %); palmitic (23.20 %) ; palmitoleic (1.60 %); stearic (21.53 %); oleic (52.06 %); linolenic (0.05 %); total saturated fatty acids (26.36

%); total unsaturated (73.64 %); total monounsaturated (21.58 %) and total diounsaturated (52.06 %).

Lolos, *et al.* (1999) mentioned that the fatty acids composition of cottonseed oil as frying oil were 0.7 % myristic, 22.9 % palmitic, 1.9 % stearic, 15.4 % oleic, 58.1 % linoleic, and 0.1 % linolenic of total fatty acids, respectively.

Francis (2000) reported the fatty acid content of cottonseed oil in weight percent as follow: capric C10:0 (0.5 %); lauric C12:0 (0.4 %); myristic C14:0 (0.8 %); palmitic C16:0 (19.9 %); stearic C18:0 (3.1 %); oleic C18:1 (25.1 %); linolenic C18:2 (48.5 %); linolenic C18:3 (0.1 %); total saturated fatty acids (24.7 %); total unsaturated (74.3 %).

Jahaniaval, *et al.* (2000) reported that the fatty acids of cottonseed oil were as follows: C14:0 (1.00 %); C16:0 (25.7 %); (0.53 %); C18:0 (2.45 %); C18:1 (17.7 %); C18:2 (52.1 %); C18:3 (0.22 %); C20:0 (0.25 %); C20:1 (0.05 %); C22:0 (0.05 %); C22:1 (0.05 %) and saturated/ unsaturated ratio 0.41.

Yaghmur, *et al.* (2001) reported the following composition of fatty acids for cottonseed oil: myristic C14:0 (0.7 %); palmitic C16:0 (22.8 %); palmitoleic C16:1 (0.8 %); stearic C18:0 (2.4%); oleic C18:1 (19.8%); linoleic C18:2 (52.0%); ∞-linolenic C18:3 (0.6%); arachidic C20:0 (0.4%); gondoic C20:1 (0.5%); saturated fatty acids (SFA) (26.3%); monounsaturated acids (MUFA) (21.3%) and polyunsaturated fatty acids (PUFA) (52.6 %).

O'Brien (2004) reported the fatty acid composition of cottonseed oil were as follow: myristic C14:0 (0.6 to 1.0 %); palmitic C16:0 (21.4 to 26.4 %); palmitoleic C16:1 (0 to 1.2 %); stearic C18:0 (2.1 to 3.3 %); oleic C18:1 (14.7 to 21.7 %); linoleic C18:2 (46.7 to 58.2 %); linolenic C18:3 (0 to 1.0 %); arachidic C20:0 (0.2 to 0.5 %); gadoleic C20:1 (0 to 0.1 %); behenic C22:0 (0 to 0.6 %); erucic C22:1 (0 to 0.3 %); lignoceric

C24:0 (0 to 0.1 %); trisaturated (0 to 0.1 %); disaturated (14.0 %); monosaturated (50.0 to 58.0 %) and triunsaturated (28.0 to 36.0 %).

2.2.2 – Canola seed oil:

Thomas (1982) found that the fatty acid composition of low erucic acid rapeseed oil as follows: palmitic (3 – 4 %); stearic (1 – 2 %); oleic acid (60 %); linoleic (20 %); linolenic acid (9 – 13 %); gladoleic (2 – 3 %) and erucic acid (< 5 %).

Mag (1983) reported that the fatty acid composition of canola oil (wt/wt %) was palmitic 4 %, stearic 2 %, oleic 60 %, linoleic 20 %, linolenic 10 %, eicosenoic 2 %, and erucic acid 2 %. In addition, **Daun, *et al.* (1985)** stated that the main fatty acids in canola oil were palmitic acid (4.1 – 4.5 %) and stearic acid (9.9 – 10.5 %) of total fatty acids. On the other hand, **Gunstone, *et al.* (1986)** summarized the fatty acid composition of two examples of rapeseed oil as cited in the following:-

Canola oil	**Fatty acid (wt. %)**								
model	16:0	18:0	20:0	22:0	18:1	18:2	18:3	20:1	22:1
High erucic acid	3	1	1	tr.	16	14	10	6	49
Low erucic acid	4	2	tr.	tr.	56	26	10	2	tr.

Abraham and DeMan (1987) mentioned that the fatty acid composition of crude canola oil were palmitic, stearic, oleic, linoleic, and linolenic acids: 3 – 9 %, 1.8 %, 60.3 %, 23 % and 9.6 % of total fatty acids, respectively. **Yoshida and Alexander (1989)** studied the fatty acid content of canola oil. The results indicated that the fatty acids were myristic 0.5%, palmitic 4%, palmitoleic 0.4% stearic 1.7%, oleic 57.2%, linoleic 23.6%, gadoleic 1.8%, linolenic 9.7%, erucic 1.0% and ligboceric acid 0.1%.

Eskin, *et al.* (1989) reported that the fatty acid composition of high linolenic acid laboratory refined canola oil were 4.5 % palmitic, 1.9 % stearic, 62.7 % oleic, 17.5 % linoleic, 9% linolenic, 0.6% arachidic, 1% gadoleic, 0.3 % behenic and 0.1 % erucic. In addition, **Köseoglu and Lusas (1990)** studied the fatty acid composition of canola oil. They found that the main fatty acids stearic, oleic, linoleic and linolenic were 1.7%, 60.1 %, 22.7% and 10.5% of total fatty acids, respectively.

Hyvonen, *et al.* (1993) reported that the fatty acid composition of rapeseed oil was as follow: C14:0 (0.07 %), C16:0 (3.73 %), C18:0(1.37 %), C20:0 (0.38 %), C22:0 (0.18 %); C16:n9 (0.04 %), C17:1 (0.18 %), C18:1n-9 (53.38 %), C18:1n-7 (2.39 %), C18:2n-6 (22.1 %), C18:3n-3 (10.9 %), C20:1n-9 (1.25 %) and C22:1n-9 (0.70 %).

Gustafsson, *et al.* (1993) mentioned that the fatty acid in rapeseed oil were myristic 0.8%, palmitic 4.59%, palmitoleic 0.29 %, stearic 1.7%, oleic 60.08%, linoleic 21.42% and linolenic 11.37.

Warner and Mounts (1993) found that the fatty acid composition of canola oils (low-erucic acid) as listed in the following:-

Fatty acid composition of canola oils:

Fatty acid	% of total fatty acid	
	Standard canola oil	**Low-erucic acid canola oil**
C16:0	4.3	5.1
C18:0	1.7	1.9
C18:1-cis	60.5	65.6
C18:1-trans	-	-
C18:2-cis	20.8	24
C18:2-trans	10.1	1.7
C20:1	1.3	0.8
C22:1	0.5	0.0

Wanasundara and Shahidi (1994) investigated that the fatty acid composition of refined-bleached canola oil. The results were 4.2%

palmitic, 0.2% palmitoleic, 1.9% stearic, 57.7%oleic, 23.5% linoleic, 9.4% linolenic, 0.6% arachidic, 1.8% gadoleic, 0.3 % behenic, and 0.3% erucic acid of total fatty acids. **Neff, *et al.* (1994b)** reported that the principal fatty acid content of canola oil were 0.0 – 0.2 % myristic, 2.7 – 3.9 % palmitic, 0.0 – 0.2% palmitoleic, 1.8 – 2.5 % stearic, 60.0 – 81.3 % oleic, 6.5 – 23.1 % linoleic, 2.1 – 8.8 % linolenic, 0.6 – 1% arachidic, 1.1 – 1.9% gadoleic, 0.2 – 0.8 % behenic, 0.0 – 0.2 % erucic and 0.0 – 0.5 % lignoceric acid of total fatty acids.

Daun, *et al.* (1994) studied the fatty acid composition of canola oil were Palmitic 0.3%, stearic 0.2%, oleic 61.4%, linoleic 19.5%, linolenic 9.4%, erucic 0.6% and saturated acids 5.6%. **Fillières, *et al.* (1995)** investigated the fatty acid composition of edible rapeseed oil. The results showed that palmitic 5.56%, palmitoleic 0.12%, stearic 1.38%, oleic 58.25%, linoleic 22.17%, linolenic 8.9%, arachidic 0.22%, gadoleic 1.88%, behenic 0.16% and erucic acid 1.2 % of total fatty acids. **Hawrysh, *et al.* (1995)** showed that the fatty acid composition of canola oil were (% of total fatty acids) 4.0% palmitic, 0.2% palmitoleic, 1.9% stearic acid, 58.5% oleic, 21.3% linoleic, 9.9 % linolenic, 0.6% arachidic, 1.6 % gadoleic, behenic, 0.6% erucic acid and 0.2 % lignoceric of total fatty acids. **Ackman (1983, 1990) and Hui (1996)** reported that the major fatty acids in canola oil as a follow: C14:0 (0.1 %), C16:0 (3.5 %), C18:0 (1.5 %), C20:0 (0.6 %), C22:0 (0.3 %), C16:1 (0.2 %), C18:1 (60.1 %), C20:1(1.4 %), C22:1(0.2 %), C18:2n-6 (20.1 %) and C18:3n-3 (9.6 %).

Shen, *et al.* (1997) found the polyunsaturated fatty acids, monounsaturated fatty acids; saturated fatty acids and transisomers of linoleic acid and ∞-linolenic acid were 29.9± 0.1 %, 58.4 ± 0.1%, 6.9 ± 0.1 %, and 4.7 %, of total fatty acids of canola oil, respectively. On the other hand, **Takeoka, *et al.* (1997)** reported that the main fatty acids of canola salad oil and canola liquid frying shortening oil as follow:

Fatty acid of canola salad oil and canola liquid frying shortening oil:-

Fatty acid type	Canola salad oil (%)	Canola liquid frying shortening oil (%)
12:0	0.02	0.12
14:0	0.06	0.12
16:0	4.20	5.99
16:1	0.23	0.22
18:0	1.70	5.21
18:1	58.51	60.82
18:2	21.19	18.34
18:3	10.12	4.96
20:0	0.59	0.55
20:1	1.40	1.14
22:0	0.32	0.29
22:1	0.50	0.33

Deng and Scarth (1998) reported that the content of fatty acids of canola oil were 0.0 – 0.1 % myristic, 4.5 – 5.0 % palmitic, 0.1 – 1.8 % stearic, 54.3 – 59.7 % oleic, 18.6 – 21.0 % linoleic, 7.3 – 9.2 % linolenic, 0.6 % arachidic, 1.3 – 1.5 % gadoleic, 0.3 – 0.4 % behenic, 0.1 – 0.4 % erucic and 0.1 % lignoceric of total fatty acids.

Woodbury, *et al.* (1998) reported that the fatty acid composition of rapeseed oil were 0.0 – 0.1 % myristic, 4.5 – 5% palmitic, 0.1 – 1.8 % stearic acid, 54.3 – 59.7 % oleic, 18.6 – 21 % linoleic, 7.3 – 9.2 % linolenic, 0.6 % arachidic, 1.3 – 1.5 % gadoleic, 0.3 – 0.4 % behenic, 0.1 – 0.4 % erucic and 0.1 % lignoceric of total fatty acids.

Xu, *et al.* (1999) investigated the fatty acid composition of four types of canola oils before deep frying. They found the fatty acid as follow:-

Fatty acid	Low-linolenic canola oil	Medium-linolenic canola oil	High-linolenic canola oil	Partially hydrogenated canola oil
C16:0	4.1	3.9	4.1	5.1
C18:0	1.9	1.6	2.2	10.0
18:1trans	0.0	0.0	0.0	26.7
18:1n-9	65.4	67.6	66.5	41.2
18:1n-7	3.3	3.3	2.8	3.2
18:2n-6	20.1	16.5	13.8	2.8
18:3n-6	0.3	0.4	1.1	0.0
18:3n-3	2.2	4.0	5.7	0.5
20:1n-9	1.1	1.1	1.2	0.2
SFA	6.6	6.0	6.9	17.2
MUFA	70.0	72.1	70.8	74.9
PUFA	22.9	21.1	21.2	4.1
n-3PUFA	2.4	4.2	6.0	0.8

Where: SFA, total saturated fatty acids; MUFA, total mono unsaturated fatty acids, and PUFA, total polyunsaturated fatty acids.

Ibrahim, (2000) investigated the fatty acid composition of three varieties of canola oil; the results were as listed in the following:-

Fatty acid	Carbon chain	% of total fatty acids
Myristic	14:0	0.085 – 1.004
Palmitic	16:0	0.839 – 6.244
Palmitoleic	16:1	0.093 – 1.201
Stearic	18:0	1.546 – 2.674
Oleic	18:1	53.141 – 60.398
Linoleic	18:2	18.582 – 25.837
Linolenic	18:3	6.420 – 11.867
Arachidic	20:0	0.176 – 3.151
Gadoleic	20:1	0.686 – 1.636
Behenic	22:0	0.033 – 3.210
Erucic	22:1	0.254 – 0.785

Francis (2000) reported the main fatty acid composition of canola and rapeseed oils as follow:-

Fatty acid type	Canola	Rape
Myristic C14:0	0.1	0.1
Palmitic C16:0	5.7	2.9
Stearic C18:0	2.1	1.4
Arachidic C20:0	0.2	
Behenic C22:0	0.2	0.5
Total saturates	***8.3***	***4.9***
Oleic C18-.1	57.7	33.0
Linoleic C18:2	24.6	15.4
Linolenic C18:3	7.9	6.2
Gadoleic C20:l	1.0	12.2
Erucic C22:l	0.2	25.5
Total unsaturates	***91.4***	***92.3***

Kochhar (2001) summarized the fatty acid composition of refined and deodorized rapeseed oil which used as frying oil as follow: C16:0 (4.5 %), C18:0 (1.5 %), C18:1 (59.0 %), C18:2 (21.01 %), C18:3 (11.0 %) and others acids (3.0 %). In addition, **Knothe (2002)** investigated the fatty acids compositions of low erucic acid (LEAR) canola oil and rapeseed oil as follow:-

Vegetable oil	Fatty acid (wt. %)						
	14:0	16:0	18:0	18:1	18:2	18:3	22:1
Canola LEAR	<0.2	3.3-6.0	1.1-2.5	52-66.9	16.1-24.8	6.4-14.1	0-2
Rapeseed	<0.2	1.5-6.0	0.5-3.1	8-60	11-23	5-13	5-60

Önal and Ergin (2002) mentioned the main fatty acid of fresh RBD canola oil used in frying as a follows: C16:0 (4.9±0.00 %), C18:0 (2.0± 0.07 %), C18:1 (62.5± 0.07 %), C18:2 (19.9 ± 0.00 %), C18:3 (7.5 ± 0.07 %), others (arachidic acid + behenic acid + erucic acid) (3.2 ± 0.00 %), total saturated, fatty acids (7.5 ± 0.07 %), total unsaturated fatty acids (92.6 ± 0.07 %) and C18: 2/16: 0 ratio (4.04 ± 0.00 %).

Knauf and Del Vecchio (2002) reported the fatty acid composition of canola oil and laurate canola oil as follow:

Fatty acids	Laurate canola	Canola
Lauric	38.0	0.0
Myristic	4.0	0.1
Oleic	31.0	61.5
Linoleic	11.0	20.0
Other	16.0	18.4
Total	100.0	100.0

Fullana, *et al.* (2004) reported the following values of typical fatty acid composition of canola; palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2), linolenic (18:3) and eicosenoic (20:1) were canola 4.1 % , 1.8%, 63.0%,20.0%,8.6%,and1.9%.

O'Brien (2004) illustrated the fatty acid composition of some genetically varieties of canola oils:-

Fatty Acid (%)	Canola	Low-Linolenic Canola	High Oleic Canola	Lauric Canola
Lauric (C-12:0)	0.0	0.0	0.0	37.0
Myristic (C-14:0)	0.1	0.1	0.1	4.4
Palmitic (C-16:0)	4.2	3.8	3.0	3.2
Palmitoleic (C-16:1)	0.3	0.3	0.3	0.3
Stearic (C-18:0)	2.3	2.4	2.0	1.3
Oleic (C-18:1)	62.5	64.1	73.7	31.5
Linoleic (C-18:2)	19.2	23.8	14.4	13.1
Linolenic (C-18:3)	7.9	2.1	2.9	6.7
Arachidic (C-20:0)	0.7	0.7	0.7	0.5
Gadoleic (C-20:1)	1.3	1.2	1.4	1.0
Eicosadienoic (C-20:2)	0.1	0.1	0.1	0.1
Behenic (C-22:0)	0.3	0.3	0.3	0.3
Erucic (C-22:1)	0.3	0.3	0.1	0.2
Lignoceric (C-24:0)	0.0	0.0	0.2	0.0
Nervonic (C-24:1)	0.2	0.2	0.2	0.1

2.3 – Effect of frying process on the keeping quality of some vegetable oils:

Frying is one of the fastest, oldest and simplest methods of food cooking, since it involves heating an edible oil or fat and simply using the hot oil to cook the food. It was probably invented by the ancient Chinese

but became so popular that it is now used throughout the world in domestic, restaurant and industrial establishments. Frying is useful in cooking all types of food, viz. meat, fish and vegetables **(Smith, *et al.* 1986; Iskander, 1991 and 1992).** In fact, a single vegetable, the potato, is probably the food most closely associated with frying, since potatoes are used to generate both French fries and crisps **(Rossell, 2001)**. Cottonseed oil has been popular oil for frying. Its main problem is that it has a moderately high amount of saturated fatty acid, namely 21–26% palmitic together with up to 4% of longer chain length saturated acids. This leads to the oil developing an unsightly deposit of solid fat when stored at refrigerator temperatures – an aspect criticized by consumers. It was discovered that cottonseed oil that had been allowed to stand out of doors during the winter in unlagged tanks did not suffer this problem, and 'winterized' cottonseed oil became preferred. Nowadays, oils that have been industrially processed to remove high-melting triglycerides are still called 'winterized'.

Rapeseed oil has high iodine value and low level of saturated fatty acids, and is fully fluid even at low ambient temperatures. The main difficulty rapeseed oil is the 5–14 % or so of linolenic (C18:3) acid present, as this makes factors affecting the quality of frying oils and fats. Then this oil will be prone to oxidation and off-flavour development. In this respect, it must be remembered that, with industrial frying, it is not only oxidation during the frying process that must be considered but in many cases also oxidation of the oil during subsequent storage of the fried food. Crisps (chips in USA parlance) are a particular problem in this respect as it contains a high level of absorbed oil, are often stored in transparent bags and expose the oil on a large surface area to the surrounding atmosphere. However, rapeseed oil and is cheap and are widely used in many frying operations, especially in the fast-food area,

where storage of the fried product is not necessary **(Rossell, 2001)**. Frying is the process of cooking foods using oil as the heating medium and can be classified as pan-frying and deep-fat frying. In pan-frying, the food is moistened with fat, but not soaked. A little amount of oil is used in pan-frying so that the food is cooked until golden brown and crisp. In deep-fat frying, the food is immersed in the oil, which should be enough to cover the food by at least 2 cm. Deep-fat frying is a common method of food preparation that imparts desired sensory characteristics of fried food flavour, golden brown colour, and crisp texture. During frying, at approximately 190 ^{o}C, as oils thermally and oxidatively decompose, volatile and nonvolatile products are formed that alter functional, sensory, and nutritional qualities of oils (**Warner, 2002)**.

The objective of deep-fat frying is to seal the food by immersing it in hot oil so that all the flavours and juices are retained in a crisp crust. The frying technology is important to many sectors of the food industry, including suppliers of oils and ingredients, food service operators, and manufacturers of frying equipment. The United States produce more than 2.5 million tons of snack food per year, the majority of which are fried. Commonly fried products in the United States include: potato chips, French fries, doughnuts, extruded snacks, fish sticks, and the traditional fried chicken products. The term frying is interpreted broadly in this article and includes only the process of deep-fat frying **(Moreira 2003).**

2.3.1 – Oxidative stability:-

During frying, the fat or oil is kept hot (about 180 ^{o}C) for long periods of time and is exposed to both moisture and oxygen. Complex chemical and physical changes occur under these conditions, causing fat deterioration which may reach a point where the flavour, odour, colour, nutritional value and safety of the food may be affected **(Edward, 1967).**

Stephan, (1967) noted that some food processors maintain their frying oils in good quality while others abuse and seriously damage theirs. Such deteriorated oils not only may have an adverse effect upon human nutrition, but also may cause poor texture, flavour and flavour stability of the fried foods. The deterioration of oil during frying has been evaluated by conventional methods such as free fatty acid content, colour, peroxide value and flavour. Thiobarbituric acid test can be quite useful in supplementing the flavour evaluation of incoming frying oils **(Jacobson, 1967 and Vincent, 1979).** There are many evidences indicating the formation of harmful substances such as malonaldehyde which is reported to be carcinogenic **(Vincent, 1979 and Carroll, 1981).**

Vegetable oil shelf life is the period of time before deterioration changes. The oxidative tests include thermal analysis and a variety of accelerating ageing techniques **(Jackson, 1981).** However, the oxidation degree of vegetable oil examines the shelf life of oil. It also, the tolerance of consumers to degrees of oxidation of vegetable oils is useful for the definition of the sensory limits of shelf life and may prove instructive for food safety **(Vaisey-Genser *et al.* 1994)**. They also suggested that the sensory induction period of 2 – 4 days at 60 – 65 ^{o}C of canola oil may be expected to remain perceptible unchanged in flavour quality for at least 16 weeks if held in light-proof containers at room temperature. **Hawrysh *et al.* (1989)** studied the sensory induction period for 2-4 days at 60 – 65 ^{o} C of canola oil. They found unchanged in flavour quality for at least 16 weeks if held in light proof containers at ambient temperature.

Sosulski and Sosulski (1993) studied the degree of rancidity by determine the peroxide value of canola and rapeseed enzyme-treated oils at 60 ^{o}C for up to 15 days. The results showed the development of rancidity at the same degree of both control and treated oils. On the other hand, **Przybylski *et al.* (1993)** studied the stability of rapeseed oil with reduced

linolenic acid content (3.1% C18:3 of the total fatty acids) to that of commercial rapeseed oil (11.5% C18:3 of the total fatty acids) after accelerated dark storage at 60 ^{o}C. The results indicated that low linolenic rapeseed oil exhibited improvement in stability during accelerated at 60 ^{o}C. **Neff *et al.* (1994a, b)** found that the rate of peroxide formation increased with an increase in the number of double bonds on fatty acid compositions in soybean and canola oils. In addition, **Malcolmson *et al.* (1996)** investigated the consumer acceptability of rapeseed oil; however it decreases with increasing of painty odour, peroxide value, total volatile compounds, total carbonyl compounds, unsaturated carbonyl compounds and dienals in rapeseed oil.

Hawrysh (1998) determined the changes in peroxide values of commercial canola oil during storage at 65 ^{o}C for 15 days and found that the peroxide value increased from 1.46 at zero time to 39.41 at the end of storage. It also, the conjugated diene and conjugated triene values increased from 5.16 to 7.21 and 0.74 to 0.97, respectively. **Lampi and Piironen (1999)** studied the oxidation at 40 ^{o}C of rapeseed oil and butter oil. The results shown that the rapeseed oil triacylglycerols hydroperoxidases and p-ansidine reactive compounds were formed than in the butter oil because the difference of the double bond content in fatty acid compositions.

Xu *et al.* (1999) monitored that the fatty acid composition of oil has marked effects on its frying performance as well as on its physical and chemical behavior. During deep frying, fatty acids of frying oils change to cyclization, polymerization and pyrolytic, hydrolytic, oxidative and other chemical reactions promoted by frying conditions. It also the reducing of linolenic acid increased the oxidative stability of the oils. However, the 18:3n-3 is critical phenomenon in frying performance and stability of canola oils and the flavour and overall quality of fried food. On the other hand, linoleic acid 18:2n-6 is the major of poly unsaturated fatty acid

(PUFA) in frying oils and it is not negative in oil stability and sensory ranking of the fried food.

Tian and Dasgupta (1999) reported that evaluation of the oxidative stability of lipids is an old and complex topic. They mentioned that peroxide value consider as measure of the peroxides content and current oxidation status only if the peroxides formed are stable and not decompose after formation. On the other hand, the most commonly used method is called the active oxygen method (AOM) promulgated by AOCS. In this method about 20 ml aliquots of fat samples aerated at 2.3 ml/s at 98 ^{o}C, and periodically analyzed for peroxide value by iodometric procedure. The time to reach a PV of 100 mequiv /kg taken to be an index of the oxidative stability. **Akoh and Moussata (2001)** mentioned that the used tert-butylhdroxyquinone (TBHQ) increased the oxidative stability of enzymatically produced canola oil based structured lipids.

Hoshina *et al.* (2004) studied the effect of triacylglycerol composition of thermal oxidative stability. They found that the thermal oxidative stability of edible oils depends on their FA composition. The relative oxidizability of FA is 8.6 for SFA, 15.9 for 18:1, 26.8 for 18:2, and 41.5 for 18:3, respectively. Thus, the variety and level of UFA in edible oil are major factors determining its thermal oxidative stability. For example, the 18:2 is a major factor determining the oxidative stability of TAG samples containing 16:0 and 18:2.

2.3.2 – Thermal stability:-

Most edible oils and fats are consumed after subjecting to heating at light temperature; during which abroad series of physical, chemical and nutritional changes take place. These changes have been of considerable concern by many workers **(Edward, 1967; Kaunitz, 1967 and Artman, 1969).** When fats and oils are used for heating operations, thermal and

oxidative deterioration of the lipid components take place, producing volatile and non volatile decomposition products. However, thermal oxidation of the fat is a phenomenon of much concern because of its effect on colour, flavour, texture and keeping quality of foods. Also, some of oxidation products have been reported to be harmful to human health **(Ohfuji and Kaneda, 1973; Khattab, *et al.* 1974; Alexander, 1978 and June, 1981).**

The extent and nature of the products which produce during heating of fats and oils are considerably affected by the composition of the fat and heating conditions; temperature, exposure to oxygen, heating period, mode of heat transfer, and metals in contact with the oil as well as initial quality of oil **(Jose and Edward, 1987 and Dobarganes and Perez-Camino, 1988).**

Leszkiewicz and Kasperek (1988) mentioned that high thermal processing of foods (frying and roasting) has been shown to damage the nutritive value of oils and fats, giving rise to the formation of such products as peroxides, oxypolymers, ringmonomers and carbonyl products. They also investigated the changes of rapeseed oil during heat processing however; the higher temperature and long heating time increase the concentrations of peroxidases. On the other hand, the level of linolenic acids decreased during the progress of heating processing. **Eskin *et al.* (1989)** studied the heating effect of low linolenic acid canola oil at frying temperature (185 ± 5^{o}C) under nitrogen and air conditions. The development of oxidation was evident of canola oil and it based on the measurement of peroxide value, Thiobarbituric acid, free fatty acids, dienals and carbonyls. On the other hand, they observed that this affects under nitrogen not only the odours but limited the oxidation in the vegetable oil.

Warner and Mounts (1993) observed the frying stability of canola, soybean and modified canola and soybean oils. They found that the free fatty acids, polar compounds and foam heights during frying were significantly less in low linolenic soybean and canola oils than the corresponding unmodified oils after 5 hr of frying. **Mehta and Swinburn (2001)** reported that the fatty acids composition of the frying oil is a key factor influencing fried food flavour and oil stability. Ideally, frying oil should have a long frying life and good organoleptic attributes, and it should be low in saturated and trans fatty acids and relatively low in PUFA.

Kiatsrichart *et al.* (2003) compared the stability of mid-oleic acid sunflower (NuSun) to commercial canola oil with a comparable iodine value during pan frying at ~ 180 ^{o}C. They found that NuSun and canola oil have similar pan-frying stabilities as there were few significant differences in the physicochemical properties of the two oils during heating. **Knothe and Dunn (2003)** stated that the reduction of highly unsaturated components likely will enhance oxidative stability more than preventing exposure to metals. They also reported the oleic and linoleic acids decreased oxidative stability with their alkyl esters.

2.4 – Effect of storage conditions and antioxidants on the characteristics and keeping quality of some vegetable oils:-

Guimaraes and Pechnik (1951) found that the peroxide value of cottonseed oil stored for 75 days at room temperature decreased, while index of unsaturation remained practically constant. Antioxidants are useful in edible fats and oils of animal and plant origin **(Hoffman, *et al.* 1954). Kapadia and Magar (1954)** found that antioxidants increased the

induction period of oils or hydrogenated fats. **Kartha (1957)** reported that the addition of antioxidants to fats in sufficient quality not only checked absorption of oxygen, but also destroyed some of the peroxides present.

Baumann (1959) stored refined cottonseed oil in drums for 28 months, he showed that the peroxide value increased in some of the oils and the stability carried out by the active oxygen method decreased. However, rancidity according to laboratory tests was not reached. There were no relation between graders judgments of the oils for "off in flavour and odour" and the tests for peroxide value and the active oxygen method fat stability test.

Romani and Valentinis (1959) reported that exposure of edible oils to air and sunlight increased the rancidity and peroxide numbers, the oxidizing effect of air progresses more rapidly than the deleterious effect of sunlight, in diffused light and in the dark the effect of air oxidation was present but less noticeable.

Lebedeva (1959) reported that 0.01 % of propyl gallate was effective against oxidative deterioration in cottonseed oil. On the other hand, **Stuckey (1959)** found that butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and propyl gallate (PG) have similar structures but different physical properties, they stabilized lipids and were quite effective in animal fats but less so in the vegetable oils.

The factors which can effect rancidity and flavour stability of fats and oils are: temperature, moisture, amount of air in contact with fat or oil, exposure to light particularly that in the ultraviolet or near ultraviolet, presence or absence of antioxidants and prooxidants, metallic ions, synergists, substances which can decompose under reaction to yield free radical and the characteristics of packing materials **(Meyer, 1960).**

Youssef, *et al.* (1961) found that the free fatty acids percentage of cottonseed oil increased gradually and reached its maximum at the end of 11 months storage period.

The storage of cottonseed oil under carbon dioxide atmosphere increased the keeping qualities of oil and excluding the light had no additional effect **(Kozin and Sitnikova, 1962).**

Ninan, *et al.* (1962) stored samples of crude, alkali-refined, and bleached cottonseed oil in closed conditions at 27 – 34 ^{o}C. for six months. They reported that the colour of crude oil increased and the colour of alkali-refined and bleached oils decreased. Small increase in free fatty acid content occurred with all samples, the colour of bleached oil prepared from alkali-refined oil decreased with increased storage time.

Griffith laboratories (1963) listed the characteristics of ideal antioxidants as follows:-

1. It should exert no harmful physiological effect (or non-toxic),
2. It should contribute no objectionable flavour , odour or colour to the fat or the foods made with the fat,
3. It should be sufficiently fat soluble,
4. It should be highly effective in retarding oxidation for long periods at low concentration,
5. It should be reasonable in cost,
6. Does not cause metal-reactive discolouration of products,
7. Packed in convenient non-returnable drums,
8. It should be readily available in adequate amount and
9. Excellent "carry-thought" stability after exposure to high baking temperature.

Garoglio (1964) reported that diffused light, inert atmosphere were the most suitable variables to improve conditions for storage of cottonseed oil.

Kulta (1964) increased the stability of cottonseed oil by using propyl gallate and ionol; these antioxidants were added in the concentrations 0.01 %, 0.02 % and 0.05 % by weight of the oil. Results indicated that the best antioxidant was 0.05 % propyl gallate but ionol was less effective.

Paquet (1967) stated that to prevent the oxidation of unsaturated fatty acids, it is necessary to binder the formation of peroxides. One way of doing this is to avoid the presence of metals. **Shiliman and Lovacher (1967**) showed that the salad oil fraction containing low amount of iron, copper and manganese was more stable to oxidation. **Flueckiger (1968)** reported that fresh oil showed weaker absorption for oxygen, but presence of heavy metal ions increased its absorption.

Abdel-Malek and Ismail (1969) investigated the effect of packing on the acidity, peroxide value and iodine value of hydrogenated cottonseed oil stored for nine months at room temperature. They concluded that oil quality was best upon using aluminum and tin cause glass containers could be used but coloured rather than transparent.

Fahmy (1969) reported that there was an increase in the free fatty acids, peroxide values and saponification values of shortenings during storage for six months at room temperature. No change in colour or melting points was observed. The same author **(Fahmy, 1969)** studied the effect of ionol, citric acid and ionol-citric acid mixture on some of the chemical and physical changes of locally shortenings during storage for six months at room temperature. Results revealed that the effect of antioxidants on the saponification values were not quite noticeable. The iodine values of the tested shortening remained unchanged throughout the six months of storage. The colour and melting points did not show any change during the period of storage.

Hashem (1969) concluded that the colour of cottonseed oil, either bleached or non-bleached, was found to improve, i.e. the colour was reduced on storage and the decrease continued as the storage advanced. The rate of colour improvement was substantially higher when the oil was stored in the light rather than when stored in the dark. The free fatty acids content and the peroxides content of the stored oil increased on prolonged storage. In addition, storage in the light caused a higher increase than storage in the dark. The iodine value, saponification number, specific gravity and the refractive index were not affected during storage either in the dark or in the light.

Harada and Komoda (1970) reported that the presence of citric acid in edible oils prevent their colouration by inactivation of the metals, i.e. iron, copper, aluminum and nickel, due to the formation of complexes. **Sawarkar (1970)** found that copper was the most active metallic pro-oxidant and particularly catalyzed peroxide decomposition while aluminum seemed to accelerate peroxide formation. **Pezinski (1971**) improved the stability of oils by removal and deactivation of metals in oils.

Sattar*, et al.* (1976) studied the sensory stability of vegetable oils (commercial refined, bleached and deodorized oils i.e. canola oil, corn, soybean and coconut) to light at 25 ^{o}C without antioxidants. The results shown that the corn oil was the most stable, while canola oil was intermediate. On the other hand, the soybean and coconut oils were the most sensitive to light.

Frankel (1984) reported the main problem of fats and oils is the oxidative deterioration. However, it causes more problems of use and storage of fats and oils. Oxidation of unsaturated fatty acids of fats and oils produce offensive odours and off-flavour. However, its limit their use and decreases the nutritional values through the formation more of secondary reaction products.

Tokarska, *et al.* (1986) investigated the storage stability of canola oil treated with different levels of tertiary butylhydroquinone (TBHQ), with and without citric acid, and canola oil without antioxidant. They found the oxidative changes in stabilized and unstabilized oils stored in amber glass bottles were much lower than oils stored in clear glass bottles. So, light was a very effective factor of off-flavour in canola oils. The same author reported that the high content of unsaturated fatty acids, especially linolenic acid, in canola oil influences its stability and keeping quality. However, these oxidative changes of unsaturated fatty acids also increase of rapid autoxidation and produce the undesirable off-flavour and off-odours during storage and heat processing.

Durance (1986) studied the storage stability of cottonseed, sunflower and canola oils containing an antioxidant mixture to fluorescncent light with an intensity of 250 ft-c (2691 lux). The results shown canola oil was less sensitive to light than cottonseed oil while sunflower oil proved to be the most stable of vegetable oils.

Warner, *et al.* (1989) tested the stability of canola, sunflower and soybean oils with and without added citrate at 100 ppm concentrate, under fluorescent light at 7535 lux (700 ft-c) at 30 ^{o}C for 8 to 16 hrs. They found that the sunflower oil proved to be the most flavours stable with or without citrate added than the other oils. At the same conditions, canola oil was more stable than soybean.

Hawrysh, *et al.* (1989) studied the flavour and odour intensities of commercially processed canola oil exposed to simulated supermarket conditions. The results shown the oxidative changes for canola oil stored in light-resistant amber bottles for 16 weeks at the same levels of canola oils stored at 4 weeks only in clear glass. On the other hand, **Rady, *et al.* (1990)** studied the stability of fresh rapeseed, cottonseed and corn oils. They found that rapeseed oil was more stable than cottonseed oil and corn

oil. **Benjelloun, *et al.* (1991)** reported that rapeseed oil contains a high amount of unsaturated fatty acids. Which, its have oxidative stability decreases rapidly particularly with increasing temperature. According to the **E.O.S. (1993)** the acceptable level regulation of common artificial regulation of antioxidants on edible oils as a follows: butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) and propylgallate (PG) were 200 mg/ kg oil, 200 mg/ kg oil and 100 mg/ kg oil, respectively. In addition, the level of mixture of them it must be not exceeding than 200 mg/ kg oil. On the other hand, the level regulations of BHA and BHT according to the European regulation were 200 mg / kg oil and 200 mg / kg oil, respectively **(Weng and Gordon, 1993 and Fox, 2001)**. Lipid oxidation was studied and established the principal factors affected which includes temperature, light and oxygen availability. In addition, non-enzymic lipid oxidation occurs by two ways of mechanisms. The first autoxidation causes when a chain reaction initiated by free radical production. The second photosensitized oxidation influence by sunlight and involves the production of singlet oxygen, however, it does not the initial production **(Davis, *et al.* 1993)**.

Przybylski (1994) reported that the factors which affect the rate of oxidation of fat and oil were the degree of unsaturation of fatty acids, oxygen, light, temperature, antioxidants and prooxidants. **Neff, *et al.* (1997)** studied the oxidative stability of three rapeseed oil**s** during autoxidation and photooxidation. The results shown that the oxidative stability increased by decreasing levels of oxidizable fatty acids, increasing oleic acid content and decreasing linoleic acid at the moiety carbon 2, and decreasing levels of triacylglycerols containing linolenic and linoleic acids and increasing levels of triacylglycerols containing stearic and lauric acids in combination with oleic acid.

Oxidative stability and deterioration of oils depend on initial composition, concentration of minor compounds with antioxidant or prooxidant characteristics, degree of processing, and storage conditions. The consequence of oxidation is the development of unpleasant tastes and odours, characteristic of rancid fats and oils, as well as degradation of functional and nutritional properties. Autoxidation of unsaturated lipids is a catalytic process involving a free-radical chain reaction mechanism, with formation of hydroperoxides, and further reactions of oxidation, breakdown, and polymerization (**Crapiste, *et al.* 1999).** They also investigated the influence of storage temperature, oxygen availability, and oil composition on crude sunflower oil oxidation. Extracted oil has a higher oxidative stability during storage than pressed oil. Rate of oxidation is strongly dependent on oxygen concentration and temperature. Relatively low or no oxidation occurs at low temperatures, with limited oxygen availability, or under nitrogen atmosphere. A kinetic model for autoxidation of crude sunflower oil in terms of PV should consider both propagation and decomposition reactions. Alteration is affected by the ratio of surface area to volume of sample, indicating that the oxidative process may be limited by mass transfer phenomena as diffusion and dilution of reactants and products. Since no simple parameter provides enough information for a correct assessment of oxidation, it is necessary either to perform several analyses or to determine the composition of polar compounds in order to evaluate different stages of oxidation. In this study, good correlations between percentage of polar compounds or percentage of OTG and PV were found for the early stages of oxidation.

Goulson and Warthesen (1999) tested the oxidative stability of high oleic canola oil and conventional canola oil. The results shown that high oleic canola oil was more stable against autoxidation while conventional canola oil was more stable against photooxidation. Oxidative

reactions cause damage to lipids and proteins, thus influencing food quality. For example, oxidation of lipids results in the formation of volatile compounds that cause rancidity, oxidation of pigments (e.g, carotenoids and myoglobin) leading to colour changes, and oxidation of vitamins (e.g, A, C, and E) leading to alterations in nutritional composition. The biological tissue from which we derive foods contains several distinctively different mechanisms to control oxidation catalysts, reactive oxygen species, and free radicals. In addition, many antioxidant additives are available to increase the oxidative stability of foods. Utilization of antioxidant additives and protection of endogenous antioxidants can be effective methods to increase the quality and shelf life of foods (**Francis, 2000 and Kochhar, 2000)**.

Akoh and Moussata (2001) studied the factors affected on stability of canola oil. They found that heat, storage, assay conditions, presence, amount or absence of tocopherols and phospholipids, fatty acid types, and downstream processing. Fats, oils and lipid-based foods deteriorate through several degradation reactions during heating and storage. The main deterioration processes are oxidation reactions and the decomposition of oxidation products which result in decreased nutritional value and sensory quality. The retardation of these oxidation processes is important for food producer and induced, for all persons involved in the entire food chain from the factory to the consumer. Oxidation may be inhibited by various methods including preservation of oxygen access, use of lower temperature, inactivation of enzymes catalyzing oxidation, reduction of oxygen pressure, and the use of suitable packaging. Another method of protection against oxidation is to use specific additives which inhibit oxidation. These are correctly called oxidation inhibitors, but nowadays are mostly called antioxidants. These inhibitors represent a class of substances that vary widely in chemical structure, and have diverse

mechanisms of action. The most important mechanism is their reaction with lipid free radicals, forming inactive products **(Gordon, 2001)**. Also, in commercial deep-fat frying operations, fat is continuously exposed to air and light for extended periods at temperatures approaching 180 ^{o}C. The lipid composition of food systems cooked by deep-fat frying will potentially promote chemical changes within the frying oil. It is well established that these reactions result in significant related rapid deterioration of the frying oil that ultimately affect the functional, sensory, and nutritive values as well as the safety of fried food. For these reasons, antioxidants are added to fats, oils and foods containing fats to inhibit the development of off-flavour arising from the oxidation of unsaturated fatty acids. However, with awareness concerning the safety of synthetic antioxidants such as tertiary-butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) in food system, considerable interest in the use of natural sources of antioxidant for frying purpose has developed such as rosemary and sage.

Weng, *et al.* (2002) investigated two novel synthetic antioxidants for deep frying oils. They studied the lauryltert-butylatedhydroquinone (LTBHQ) and its oxidized compound, lauryltert-butylatedquinone (LTBQ), were synthesized from tert-butylatedhydroquinone (TBHQ) and nlauryl alcohol. They found at temperature lower than 140°C, the antioxidant activities of LTBHQ and LTBQ were lower than TBHQ. LTBHQ and LTBQ are much weaker antioxidants than TBHQ but much stronger than butylatedhydroxyanisol (BHA) and butylatedhydroxytoluene (BHT) at same concentration at 60°C in an oven. LTBHQ and LTBQ were better antioxidants for frying oils than TBHQ, BHA, and BHT, but not for bulk oil at room temperature.

Jaswir *et al.* (2002) compared between the effect of natural antioxidants and artificial materials in fats and oils during deep-fat frying.

For some quality parameters examined such as peroxide value, anisidine value, free fatty acid and polymer content, colours, viscosity, iodine value and alkaline contaminant materials, results showed that oil samples treated with the antioxidants were significantly better than control. Together with citric acid as a synergist, these natural antioxidants applied in deep-fat frying of potato chips significantly influenced appearance, taste, crispiness, odour and overall acceptability of the fried product. It was also clear that the three antioxidants had synergistic effects on the retention of fatty acid profiles of the RBD palm olein. Using response surface methodology (RSM) technique, it was found that a combination of 0.076% rosemary extract, 0.066% sage extract and 0.037% citric acid produced the optimum retention of fatty acid composition in the oil.

Boskou (2002) reported that the other substances which have been tested as alternative antioxidants for their effect on the stability of frying oils include silicone oil; secondary antioxidants such as citric acid, EDTA, tartaric acid, and ascorbyl palmitate; and polymeric antioxidants (Anoxomer) vitamins E and C, carotenoids, phenolic acids, flavonoids, sesame lignins, phytosterols, extracts from the leaves of the plants belonging to the *Lamiaceae* family, oryzanols, tea leaf extracts, phosphatides, olive oil phenols, squalene,and propolis …*etc*.

Knothe and Dunn (2003) reported that the oxidative stability was affected by the molar concentration of double bonds in fatty components. They also mentioned that oleic and linoleic acids decreased oxidative stability of commercial vegetable oil alkyl esters.

O'Brien (2004) mentioned that the antioxidants are chemical compounds that provide greater oxidative stability and longer shelf life for edible fats and oils by delaying the onset of oxidative rancidity. However, oxidation occurs in a series of steps often referred to as free radical oxidation because the initial step is the formation of a free radical on the

fatty acid portion of the fat molecule. The free radical is highly reactive and forms peroxides and hydroperoxides by reaction with oxygen. These free radicals also initiate further oxidation by propagating other free radicals. Finally, the hydroperoxides split into smaller organic compounds such as aldehydes, ketones, alcohols, and acids. These compounds provide the offensive odour and flavour characteristic of oxidized oils. Antioxidants function by inhibiting or interrupting the free-radical mechanism of glyceride autoxidation. Their ability to do this is based on their phenolic structure or the phenolic configuration within their molecular structure. Antioxidants or phenolic substances function as a free-radical acceptor, thereby terminating oxidation at the initial step. Fortunately, the antioxidant free radical that forms is stable and does not split into other compounds that provide off-flavours and odours nor does it propagate further oxidation of the glycerids.

MATERIALS AND METHODS

3- MATERIALS AND METHODS

3.1-Materials:

3.1.1 – Oil and vegetable samples:-

The two samples of some vegetable oils used in this study were cottonseed and canola oils. The first oil was obtained from Alexandria Oil & Soap Company, Alexandria – Egypt. Canola oil was purchased from the Food Science and Technology Center, Ministry of Agriculture, Giza – Egypt.

All oil samples are of refined grade and engaged in the production of various fried products such as eggplant *(Solanum melongena)*, squash *(Cucurbita pepo)* and potato *(Solanum tuberosum)*. The vegetables used in this study were obtained from the Farm of Faculty of Agriculture, Sohag, South Valley University.

3.1.2 – Frying conditions:-

Frying of eggplant, squash and potato was conducted in separate aluminum casseroles (20 cm in diameter, 15 cm in height, and 1.5 kg of oil in capacity). The process was performed intermittently two hours daily, for a total period of 12 hours at 180 ^{o}C. Oil samples after each treatment were withdrawn and kept in brown glass bottles at – 10 ^{o}C for subsequent analysis. The temperature was controlled by using an ordinary thermometer. The vegetables used were peeled manually and cut into slices before frying. The colour of fried vegetables was used to indicate the end point of frying process (**Weiss, 1970 and Iskander, 1992**). The frying conditions used in this study are shown in Table (5).

3.1.3 – Antioxidants treatment and storage conditions:

Three types of antioxidants were used in this work, namely, Butyl-hydroxy toluene (BHT), Butyl-hydroxy anisol (BHA), and Propyl gallate

(PG). They were chosen because of their effectiveness as antioxidants, relatively of low price and to their industrial utilization in fatty foods.

Both trade mark chemical names and sources of the studied antioxidants are shown in table (6). The antioxidants BHT, BHA and PG were added at the levels of 0.01 % and 0.02 % on weigh bases to the oil. Samples containing different concentrations of the antioxidants were tested for oxidation by determination of their peroxide values (PV) and Thiobarbituric acid values (TBA).The samples were packed in colourless glass containers (250 ml capacity) then stored at ambient temperature as supermarket conditions for six months.

Table (5): Frying conditions.

Kind of vegetable	Frying conditions	
	Temp. ^{o}C	Time (Min.)
Eggplant, slices (diameter 5 cm & thickness 0.5 cm)	180	4
Squash, slices (diameter 5 cm & thickness 0.5 cm)	180	4
Potato, slices (diameter 5 cm & thickness 0.5 cm)	180	4

Table (6): Trade mark chemical names sources of the studied antioxidants:-

Antioxidants		
Trivial	**Chemical names**	**Sources**
Tenox BHT	Butyl-hydroxy toluene	Esatman Kodak co. USA
Tenox BHA	Butyl-hydroxy anisol	Esatman Kodak co. USA
Tenox PG	Propyl gallate	Esatman Kodak co. USA

3.2 – Methods:

3.2.1 – Physical properties of some vegetable oils:

Refractive index (RI):

The refractive index was tested according to the method as cited in the AOCS Official method **Cc-25 (1998).** An automatic refractometer was used and the results were standardized at 25 C^o for vegetable oils.

Colour:

The colour of oil samples was measured by the colour Wesson methods using Lovibond glasses and calibrated (Lovibond and Tintometer model F. Tintometer LTD., Wiles, England). According to **Cocks and VanRede (1966)** and AOCS official methods **Cc 13- 92 (1998).** A one inch colour cell was used.

Viscosity:

The viscosity of investigated vegetable oils was detected according to the Brookfiled method (Brookfield Viscometer, Brookfield Engineering Labs Inc. MA, USA) cited in AOCS Official method **Ja 10-87(1998)** and **AOAC (2000).**

3.2.2 – Chemical characteristics of some vegetable oils:

Acid value (AV):

The acidity of the investigated samples was examined according to the method described in the AOCS official method **Cd-3d-63 (1998)** and was calculated in terms of free fatty acids percentage as oleic acid.

Iodine value (IV):

The iodine value defined as a number of grams of iodine required to saturate 100 grams of the oil sample. It was determined by the Hanus methods as described as in the AOCS official method **Cd 1-25 (1998).**

Saponification value (SV):

The saponification value was investigated as outlined in the AOCS official method **Cd3-25 (1998).** It was calculated as milligrams of KOH required to saponify one gram of oil sample.

Peroxide Value (PV):

This characteristic was tested according to the AOCS method **Cd8-53 (1998)** and **AOAC (2000).** The peroxide value was reported as milliequvalents of peroxide per kilogram sample.

Thiobarbituric acid (TBA):

The TBA value was determined as outlined in the AOCS official method **Cd 19-90 (1998).** The TBA value calculated as mg malonaldehyde / kg sample **(Girgis, (1999).**

The unsaponifiable matter:

The unsaponifiable matter was separated from the vegetable oil samples after saponification according to the method cited in the **AOCS (1998).**

3.2.3 – Fatty acids composition:

3.2.3.1 – preparation of fatty acid methyl esters:

Fatty acids of standard and samples were converted to methyl ester using etheral solution of diazo-methane. According to **Vogel (1975)** fatty acid were dissolved in 0.5 ml of anhydrous diethyl ether and methylated by drop wise addition of diazomethane solution until the yellow colour. The mixture was then left at room temperature for 15 min and the solvent was evaporated in a water bath maintained at 60 C^{o}. The methyl ester of fatty acids, were dissolved in pure chloroform and an aliquots of this solution were subjected to GLC analysis.

3.2.3.2 – Identification of fatty acids:

The methyl esters of the fatty acids and standard samples were analyzed by using a GLC. Pye-Unicam Pro-GLC. Gas liquid chromatography equipped with a dual flame Ionization detected (F.I.D.). The nitrogen (N_2), hydrogen (H_2) and air flow rates were 30, 33 and 330 ml/min., respectively. The chart speed was 0.4 cm/min. The used column was SP- 2300-fatty acids which has dimensions 1.5 x 4 mm. The operation was carried out by programming; the Initial Temperature 70C^o, rate temperature 8C^o /min, the final temperature 190C^o, the final time 35C^o/ min, the injector temperature 250C^o and the detector temperature 300C^o. Finally, Fatty acids peaks were performed by comparing the relative retention time of each peak with those of standard samples.

RESULTS AND DISSCUTION

4 – RESULTS AND DISCUSSION

4 .1 – Physical and chemical characteristics of cottonseed and canola oils:

The physical and chemical characteristics of fats and oils play an important role in either industry or nutrition. So, some of them give a good idea about the quality of these oils. The acid value, saponification value and iodine value are usually used to give a good idea about its constituents. Physical and chemical properties of cottonseed and canola oils were determined and the obtained results are shown in table (7). On the basis of the viscosity of cottonseed and canola oils, the data obtained in table (7) indicated that there is a difference in the viscosity of the studied oils. The viscosity of cottonseed and canola oils were 44.80 and 57.00 mPa·sec, respectively. Generally, viscosity tends to increase slightly with increasing degree of saturation and increasing chain length. These results are in harmony with **Swern (1979) and Hui (1996).** Refractive index is of the important physical parameters which used in the identification of fats and oils; it could be used for the estimation of the degree of saturation of oils. The data presented in table (7) reported the following refractive index values at 25 ^{o}C: 1.4685 and 1.4691 for cottonseed and canola oils, respectively. Since, the refractive index depends largely upon the degree of unsaturation of oil and the average molecular weight of the glycerids as well. These finding are in general agreement with those reported by **Craig (1977)**; **Swern (1979); Hui, (1996); Francis (2000), Ibrahim (2000) and O'Brien (2004).**

As for Colour of investigated cottonseed and canola oils, it was found to be 6.8 and 6.6, respectively in the red scale while yellow scale is fixed at 35 in one inch cell. These results obtained herein are in general accordance with **Swern (1979)** who mentioned that the good cottonseed oil may readily be refined to a colour on the Lovibond scale of 35:0 yellow and 4.0 to 7.0 red. On the other hand, the colour values obtained in table (7) were higher than **E.O.S. (1993) and (1997).** These differences could be attributed to the presence of large amount of gums and natural pigments which passes from oil bearing material into oil during extraction process as well as due to the secondary pigments whose presence is due to the treatment conditions of the bearing material it was subjected. In addition, the oil seed stored for prolonged periods under unfavorable temperature and moisture conditions and exposed to air oxidation yields darker coloured oils than fresh seeds. Dark colour may also, be caused by high cooking temperature, partially by oxidation of the oil, and partially by colour bodies extracted by the hot oil from the seed and seed coat. Such results are in agreement with those secured by **Weiss (1970); Van Oss (1975) and Abdo (1999).**

In addition, **June (1981)** mentioned that the increase in the colour intensity of oil samples during heat treatment could be attributed to the formation of fatty acid polymers which accumulate as a result of triglycerides hydrolysis under effect of high temperature. In contrast, the decrease in the colour intensity can be due to the possible decomposition or oxidation of some the colour pigments or colouring substances to colourless compounds **(Ninan, *et al.* 1962; El-Wakeil, *et al.* 1973 and Abdo 1999).**

It is a well know fact that the colour development in an oil is very much associated with oxidation that could be take place due to exposure to

air, presence of pro-oxidatant, improper processing and mishandling **(Johari, 1996).** In this direction, **Kathleen (1998)** reported that in requirements for good quality processed fats and oils, the oils should meet quality standard for physical properties such as moisture and colour.

Table (7): Physical and chemical characteristics of cottonseed and canola oils

Characteristics*	Type of oil	
	Cottonseed	Canola
Viscosity (mPa. Sec/ 25 ^{o}C)	44.80	57.00
Refractive index 25 ^{o}C	1.4685	1.4691
Lovibond colour (Y/R) one in. cell	35/6.8	35/6.6
Acid value A.V. (mg. KOH/ g oil)	0.18	0.53
Iodine value (Hanus), I.V. (g iodine saturate /100 g oil)	103.00	111.15
Saponification value S.V. (mg. KOH saponify / g oil)	198.45	191.80
Unsaponifiable matter (%)	1.07	1.42
Peroxide value P.V. (meq. Peroxide / kg oil)	9.40	1.82
Thiobarbituric acid T.B.A. (mg malonaldehyde /kg sample)	0.78	1.42

*** Each figure given in this table is a mean of three determinations.**

On the basis of acid value, the data in table (7) indicated that the acid value of cottonseed and canola oils were 0.18 and 0.53 mg KOH/g oil, respectively. The differences in acid value may be due to the conditions during ripening of the seeds and conditions of harvesting and storage as well

as conditions during processing, *e.g.* extraction, neutralization, bleaching, deodorization and winterization. Similar results were obtained by **Ibrahim (2000).**

Concerning the iodine value, the data obtained in table (7) indicated that the iodine value of cottonseed and canola oils were 103.00 and 111.15, respectively. This is to be expected since the high iodine value could be attributed to the higher content of linoleic and linolenic. Generally, it can be observed that the variation in iodine value could be attributed to the variation in polyunsaturated fatty acid contents. These results are in accordance with those reported by **Weiss (1970); Van Oss (1975); Swern, (1979); Vaisey-Genser, *et al.* (1979); E.O.S. (1993); Hui, (1996); E.O.S. (1997); El-Sharnouby (1999b); Rodenbush, *et al.* (1999); Ibrahim (2000); Codex (2004) and O'Brien (2004).**

As for the saponification value, the results in table (7) revealed that the cottonseed oil gave the highest saponification value (198.45) while, the lowest value was recorded in canola oil (191.80). These differences could be attributed to the formation of new fatty acids that differ in their molecular weight. In general, the high saponification value indicates lower molecular fatty acids. These results are in harmony with those reported by **Weiss (1970); Van Oss (1975); Swern (1979); E.O.S. (1993); Hui, (1996); E.O.S. (1997); El-Sharnouby (1999b); Ibrahim (2000); Codex (2004) and O'Brien (2004).**

The unsaponifiable matter (includes hydrocarbons, sterols, vitamins and pigments compounds) usually plays an important role in the oil stability. It is obvious from table (7) that the oils under investigation had comparable contents of unsaponifiable matter (1.07 % and 1.42 % for cottonseed and

canola oils, respectively). These findings are in the same line with those recorded by **Swern, (1979); E.O.S. (1993); Hui, (1996); E.O.S. (1997), Ibrahim (2000); Codex (2004) and O'Brien (2004).**

Oxidative rancidity is the principal problem in fats and oils. Two determinations, peroxide value (as indicator of primary oxidation) and thiobarbituric acid (as indicator of secondary oxidation) are employed in this study to determine the extent of oxidation caused in the investigated oils.
Data in table (7) indicated that the peroxide value was 9.40 and 1.82 meq. peroxide / kg sample in cottonseed and canola oils, respectively. The results indicated also that the peroxide values of oil samples used in this study either cottonseed oil or canola oil were below the permissible limits of 10 milliequvalent of peroxide/ kg sample **E.O.S. (1993; 1997) and Codex (2004).**

Concerning the aldehyde development as shown by the thiobarbituric acid (T.B.A.) which is considered as a more reliable indicator of oxidative rancidity **(Jacobson, 1967)** the results presented in table (7) showed that the T.B.A. values varies with the kind of oils. It can be observed from the results in table (7) that the T.B.A. value in canola oil was higher (1.42 mg. malnaldehyde / kg sample than in cottonseed oil 0.78). This variation in T.B.A. value may be due to the differences in chemical constituents of oil samples. These results are in coinciding with those reported by **Iskander (1992).**

4 .2 – Fatty acid composition of cottonseed and canola oils:

The results presented in table (8) show the fatty acid analysis of cottonseed and canola oils. The data obtained by gas liquid chromatography (G.L.C.) analysis pointed out that canola oil was rich in unsaturated fatty

acid (TUFA) which represented 91.07 % of total fatty acids. The most amounts of unsaturated fatty acids were found as oleic (56.54 %) and linoleic (25.81 %). In addition, the data given in table (8) indicated that the amount of linolenic in canola oil was 6.80 %. Meanwhile, the saturation fraction of fatty acids was recorded about 8.93 %. The major saturated fatty acid was found as palmitic acid ($\mathbf{C_{16:0}}$) which it comprise 5.82 % of the total fatty acids. The other saturated fatty acids ($\mathbf{C_{10:0}}$, $\mathbf{C_{12:0}}$, $\mathbf{C_{14:0}}$, $\mathbf{C_{18:0}}$ and $\mathbf{C_{20:0}}$) were detected in the studied samples.

Furthermore, it could be observed from the data tabulated in table (8) that there are three fatty acids represent the major content of the two oil samples under investigation, namely palmitic ($\mathbf{C_{16:0}}$), oleic ($\mathbf{C_{18:1}}$), linoleic ($\mathbf{C_{18:2}}$) and linolenic ($\mathbf{C_{18:3}}$) The highest percentage of palmitic acid present in cottonseed oil (23.20 %). Meanwhile, canola oil contained much lower amounts of palmitic acid (5.82 %). The obtained data also indicated the same differences in the amount of stearic acid in the investigated oils, as the range was 2.05 % to 2.15 %. Similar, results were reported by **E.O.S. (1993); Neff, *et al.* (1994a); Daun, *et al.* (1994); Hawrysh, *et al.* (1995); Mohamed (1995); Taha, (1996); E.O.S. (1997); Francis (2000); Ibrahim (2000); Codex (2004) and O'Brien (2004).**

Table (8): Fatty acid composition of cottonseed and canola oils (wt. % of total fatty acids)

Fatty acids %	Cottonseed oil	Canola oil
Saturated fatty acids (SFA)		
Capric $C_{10:0}$	**0.13**	**0.10**
Lauric $C_{12:0}$	**0.35**	**0.04**
Myristic $C_{14:0}$	**0.70**	**0.20**
Palmitic $C_{16:0}$	**23.20**	**5.82**
Stearic $C_{18:0}$	**2.15**	**2.05**
Arachidic $C_{20:0}$	**-**	**0.72**
Total SFA	**26.53**	**8.93**
Unsaturated fatty acids (UFA)		
Monounsaturated fatty acids (MUFA)		
Palmitoleic $C_{16:1}$	**1.46**	**-**
Oleic $C_{18:1}$	**25.06**	**56.54**
Gadoleic $C_{20:1}$	**-**	**1.72**
Erucic $C_{22:1}$	**-**	**0.20**
Total MUFA	**26.52**	**58.46**
Polyunsaturated fatty acids (PUFA)		
Linoleic $C_{18:2n-6}$	**46.85**	**25.81**
Linolenic $C_{18:3n-3}$	**00.10**	**6.80**
Total PUFA	**46.95**	**32.61**
Total UFA	**73.47**	**91.07**
TUFA : TSFA	**2.77**	**10.20**
$C_{18:2}$: $C_{18:1}$	**1.87**	**0.46**

On the other hand, the data obtained in table (8) also indicated that canola oil had the highest amounts of total unsaturated fatty acids (91.07 %) followed by those found in cottonseed oil (73.47 %). The data indicated that

the majority of oleic acid was found in canola oil (56.54 %) compared with lower amounts of cottonseed oil (25.06 %). However, polyunsaturated fatty acid (linoleic acid) was the predominant unsaturated fatty acids in cottonseed oil (46.85 %). Besides, canola oil contained much lower amount of linoleic acid (25.81 %). In contrast, data in table (8) declared that the highest value of linolenic acid (6.80 %) was found in canola oil in comparison with lowest value (0.1 %) in cottonseed oil. The percentage of gadoleic ($C_{20:1}$) and erucic ($C_{22:1}$) of canola oil were 1.72 and 0.20 %, respectively, whereas, these fatty acids were not found in cottonseed oil. The results obtained herein are in general agreement with those obtained by **Gunstone, *et al*. (1986); E.O.S. (1993); Mohamed, (1995); Taha, (1996); E.O.S. (1997); Hashem, *et al.* (1997); El-Sharnouby (1999b); Francis (2000); Ibrahim (2000); Codex (2004) and O'Brien (2004).**

Mc-Gandy and Egsted (1975) as well as **Vergroesen and Gottenbos (1975)** reported that the diet which has a high content of linoleic acid and low content of saturated fatty acids play an important role in preventing or inhibition of atherosclerotic disease by lowering the blood cholesterol effect. In addition, **FAO/WHO (1977)** reported that the high content of linoleic acid not only lowers blood cholesterol concentration but also the tendency of the platelets was significantly decreased. On the other hand, **Haumann (1998)** reported that the saturated fatty acids with 16 or fewer carbon atoms raise serum cholesterol levels. In contrast, dietary, stearic acid, on 18 carbon atom saturated fat, does not effect. So, he thinks that this may be related to stearic acid which has a relatively high melting point.

The results recorded in table (8) showed also an inverse relationship between oleic acid content and linoleic acid content. The present findings are in the trend with those recorded by **Abdo (1999).**

Generally, from the above mentioned results it can be concluded that canola seed oil contained large amount of unsaturated fatty acids especially oleic acid and considerable amount of linoleic and linolenic acids as compared with other investigated oils. Therefore, canola oil can be used in food purpose side to side with other common plant oils. Similarly results and conclusion were obtained by **Abdo (1999); El-Sharnouby (1999b); Ibrahim (2000) and O'Brien (2004).**

4 .3 – Effect of frying on physical and chemical properties as well as fatty acid composition of some vegetable oils:

Frying is still a popular cooking method in home and in many restaurants. Even with the emphasis on low fat diets, people are still found of fried foods because of their crispy texture and desirable fried food flavour. Oxidation, hydrolysis, polymerization and cracking are a various chemical reactions occur during the frying process. These reactions affected on the physical and chemical characteristics of vegetable oils.

The effects of frying on the physical and chemical characteristics of canola and cottonseed oils as well as changes in fatty acid composition are summarized in tables 9 – 18.

4.3.1 – Viscosity:-

The viscosity of frying oils increased as a consequence of oxidation and polymerization reaction **(Gutierrez, *et al.* 1988)**. The amount of oil that

coats the fried products has an important role on its oil-uptake (**Alim and Morton, 1974; Guillaumin, 1988** and **Yaghmur, *et al.* 2001).**

The viscosity of the oil is directly correlated to the coating kinetics and adsorbing amounts (**Guillaumin, 1988** and **Pinthus & Saguy, 1994).** The viscosity of the studied oils was Newtonian. Data presented in table (9) demonstrate the effect of frying time, kind of vegetable as well as type of oil on the viscosity development of canola and cottonseed oils. It could be noticed that the viscosity increased gradually as frying time of the oil increased. The rate of increasing depends on the kind of vegetables used in frying as well as the type of oil. The oxidation process and polymerization of canola oil was accompanied by viscosity increased (57 to 114.8 mPa.s), while cottonseed oil viscosity remained relatively low (44.8 to 82 mPa.s). On the other hand, it was observed that the viscosity of oil samples that remained after frying eggplant in cottonseed oil for 12.00 hours was higher (82.00 mPa.s) than that of potatoes (74.00 mPa.s) and squash (71.9 mPa.s). In addition, it was noticed that potatoes slices were found to affect the viscosity of canola oil samples more markedly than other vegetables. These variations may be attributed to the differences in chemical composition of the studied vegetables as well as type of oil. Such findings agree with **Iskander (1992).** Generally, the results indicated that there is an approximately linear relationship between log viscosity and temperature. However the viscosity increased on prolonged heating due to the formation of dimeric and oligomeric fatty acid group.

Table (9): Changes in the viscosity* of canola and cottonseed oils during frying of some vegetables at 180 ^{o}C for 4 minutes.

Frying Time (Hours)	Frying oils of different vegetables					
	Canola oil			Cottonseed oil		
	EG.**	PO.**	SQ.**	EG.	PO.	SQ.
0.00	57.0	57.0	57.0	44.8	44.8	44.8
2.00	61.9	58.9	60.2	57.3	53.0	56.0
4.00	73.1	68.0	64.0	61.1	64.7	67.1
6.00	79.0	86.0	71.0	65.0	68.0	69.0
8.00	91.0	93.0	88.0	69.0	71.0	70.8
10.00	90.2	107.7	97.6	74.1	72.0	68.2
12.00	101.7	114.8	99.1	82.0	74.0	71.9

Where: * Viscosity calculated as mPa.sec at 25 ^{o}C.
**** EG = Eggplant, PO = Potatoes, SQ = Squash.**

4.3.2- Refractive index (R.I.):

Refractive index of the oil samples either fresh or intermittently fried oil, under this investigation, was measured and the obtained results are shown in table (10). The observed results indicated that the refractive index of the studied oil samples decreased gradually with increase in frying time. The rates of decreasing depend on the kind of vegetables used in frying as well as oil brand. In the case of frying with cottonseed oil, the fried oil sample of squash was recorded the lowest value of refractive index (1.4673) after 12 hours of frying. The refractive indexes of the other oil samples for the same period of frying were 1.4673 and 1.4676 for potatoes and squash, respectively. On the other hand, the lowest value of the refractive index (1.4666) was observed with squash oil sample after 12 of frying using canola

oil. In contrast, the fried oil sample of eggplant was recorded the lowest decrease of the refractive index (1.4667) after the same period of frying in canola oil. **Guillaumin (1971)** reported that heating lipids caused chemical modification such as isomerization of unsaturated fatty acids from action of both heat and atmosphere oxygen on the present fatty acids and glycerids. More recently, **Aziz (1982)** and **Mohamed (1988)** reported that the decrease in refractive index of the refined and deodorized sunflower seed oils during intermittent heating at 180 ^{o}C was attributed to the polymerization which could have occurred during heating at high temperature. The results obtained here in are in general accordance with **Vaisey-Genser, *et al.* (1979); Frankel, *et al.* (1984); El-Sharnouby (1999a); Ibrahim (2000)** and **Rossell (2001).**

Table (10): Changes in the refractive index* (R.I.) of canola oil and cottonseed oils during frying of some vegetables at 180 ^{o}C for 4 minutes.

Frying Time (Hours.)	Frying oils of different vegetables					
	Canola oil			Cottonseed oil		
	EG.**	PO.**	SQ.**	EG.	PO.	SQ.
0.00	1.4685	1.4685	1.4685	1.4691	1.4691	1.4691
2.00	1.4681	1.4682	1.4683	1.4690	1.4689	1.4690
4.00	1.4680	1.4679	1.4681	1.4687	1.4687	1.4689
6.00	1.4677	1.4676	1.4678	1.4683	1.4685	1.4684
8.00	1.4675	1.4673	1.4675	1.4682	1.4682	1.4680
10.00	1.4672	1.4669	1.4672	1.4680	1.4678	1.4680
12.00	1.4667	1.4668	1.4666	1.4677	1.4676	1.4673

Where: * Determined at 25 ^{o}C by Automatic Refractometer.
**** EG = Eggplant, PO = Potatoes, SQ = Squash.**

4.3.3- Colour:

Concerning the effect of frying eggplant, potatoes and squash on the colour intensity of cottonseed and canola oils, the results presented in table (11) revealed that the colour intensity was increased during frying but, the extent of increase was affected by the kind of vegetables used in frying, oil brand and frying time. Such results agree with those reported by **Helen (1982); Iskander, *et al.* (1985b)**; **Abdel aal and Karara (1986); Iskander, (1992); Saguy, *et al.* (1996)** and **Yaghmur, *et al.* (2001).**

The increase in the colour intensity of oil samples during heat treatment could be attributed to the formation of fatty acid polymers which accumulate as a result of triglycerides hydrolysis under the effect of high temperature **(June, 1981 and Ota, 1981).** Furthermore, **White (1991)** and **Saguy, *et al.* (1996)** reported that the increase in colour index is probably due to oxidation typically resulting in the generation of hydroperoxides, conjugated dienoic acids, epoxides, hydroxides and ketones. These compounds could undergo further oxidation, and fission into smaller fragments or may remain in the triglyceride molecule and cross-link with each other, leading to dimeric and higher polymeric triglycerides. Oils and fats can also produce dimeric acids, and form polymers of higher molecular weight, causing a darker colour and a deposit of yellow or brown pigments **(Blumenthal, 1991).** Additional cause for a colour change in deep-fat frying might be presence of pigments in the commercial oils together with the solublization of browning pigments from the vegetable during the frying **(White, 1991 and Melton, *et al.*1994).**

Generally, it can be observed from the results in table (11) that the highest increase in colour intensity was recorded in cottonseed and canola oil samples remaining after 12 hours of frying eggplant (red 11.5 and blue

3.7 in cottonseed oil while red was 11.7 and blue 5.0 in canola oil). In contrast, the lowest value of increase in colour intensity was obtained in cottonseed and canola oil samples remaining after 12 hours of frying potatoes: this variation could be attributed to the browning pigments from the foods which were dissolved into frying oils. This agrees with the finding of **Fritsch (1981).** Also, the results in table (11) indicated that the rate of change for canola oil was higher than that for cottonseed oil after 12 hours of frying.

Table (11): Changes in colour intensity* of canola and cottonseed oils during frying of some vegetables at 180 ^{o}C for 4 minutes.

Frying Time (Hours)	Frying oils of different vegetables											
	Canola oil						Cottonseed oil					
	EG.**		PO.**		SQ.**		EG.		PO.		SQ.	
	R***	B***	R	B	R	B	R	B	R	B	R	B
0.00	7.6	0.0	7.6	0.0	7.6	0.0	7.8	0.0	7.8	0.0	7.8	0.0
2.00	9.3	3.2	8.0	2.1	7.8	2.4	8.1	2.3	8.0	1.1	8.2	2.2
4.00	9.8	3.6	8.7	2.7	8.9	2.8	10.2	2.7	8.4	2.2	8.7	2.6
6.00	10.1	4.0	9.2	3.0	9.9	3.1	10.7	2.9	9.5	2.7	9.6	2.8
8.00	11.2	4.2	10.1	3.2	10.8	3.4	10.9	3.0	9.7	2.9	10.3	3.0
10.00	11.6	4.7	10.9	3.4	11.0	3.7	11.3	3.1	10.2	3.0	10.6	3.2
12.00	11.7	5.0	11.2	3.5	11.3	3.8	11.5	3.7	10.9	3.2	11.1	3.6

Where: * Colour was determined by the Lovibond Tintometer, using a one inch cell colour and yellow = 35,
**** EG = Eggplant, PO = Potatoes, SQ = Squash,**
***** R = Red and B = Blue.**

4.3.4 – Lipoltic rancidity:-

Acid value (A.V.) was used to assess frying oil degradation and is related to fried food quality **(Fritch, 1981; Melton *et al.,* 1994).** During frying, acid value increases due to progressive hydrolytic reactions **(Fritch, 1981; Melton *et al.,* 1994).** Acid value could be used as an indicator to show whether the hydrolysis process is in control **(Saguy *et al.,* 1996**). High acid value is not accepted in any commercial product because of the strong off-flavour caused by the degradation products (volatile and nonvolatile compounds) of the free fatty acids during deep fat frying (**Melton *et al.,* 1994; Yaghmur *et al.,* 2001).**

Data presented in table (12) demonstrate the effect of frying time, kind of vegetable as well as type of oil on the acid value development of canola and cottonseed oils. It could be noticed that the A.V. increased gradually as frying time of the oil increased, the rate of increase depending on the kind of vegetables used in frying as well as type of oil. The gradual increase in A.V. could be attributed to the effect of heat treatment which can cause hydrolysis of triglycerides. Such results are in reasonable agreement with those reported by **Swern, (1979); June, (1981); Moharam** and **Osman, (1982); Iskander *et al.,* (1985b); Augustin *et al.,* (1988)** and **Rossel (2001).**

Furthermore, the data in table (12) indicated that among the frying oils examined in our study, the change in A.V. for canola oil was the highest followed by cottonseed oil. Acid value of canola oil was increased from 0.53 to 1.38, 1.07 and 0.98 after 12 hours of heating and frying of eggplant, potatoes and squash, respectively. In addition, the acid value of cottonseed

oil was increased from 0.18 to 1.12, 1.04 and 0.94 after heating and frying of eggplant, potatoes and squash, respectively for the same period of frying.

Table (12): Changes in acid value* (A.V.) of canola oil and cottonseed oils during frying of some vegetables at 180 ^{o}C for 4 minutes.

Frying Time (Hours)	Frying oils of different vegetables					
	Canola oil			Cottonseed oil		
	EG.**	PO.**	SQ.**	EG.	PO.	SQ.
0.00	0.53	0.53	0.53	0.18	0.18	0.18
2.00	0.58	0.57	0.55	0.23	0.21	0.25
4.00	0.63	0.60	0.60	0.37	0.41	0.43
6.00	0.79	0.72	0.69	0.48	0.52	0.47
8.00	0.83	0.79	0.74	0.71	0.68	0.65
10.00	0.88	0.82	0.80	0.88	0.91	0.87
12.00	1.38	1.07	0.98	1.12	1.04	0.94

Where: * Calculated as mg KOH/g. oil sample.
**** EG = Eggplant, PO = Potatoes, SQ = Squash.**

On the basis of acid value it can be observed from the results in table (12) that the eggplant slices were found to affect the acidity of oil samples more markedly than potato and squash samples. These variations may be attributed to the differences in the chemical composition of the studied vegetables and the accelerating effect of moisture content of vegetables on glycerids splitting and free fatty acid formation **(Weiss, 1970; Swern; 1979 and Iskander, 1992).**

Generally, the results revealed that the acidity development confirm the finding of **Fritsch (1981)** and **Iskander *et al.*, (1985a)** that lipolytic rancidity is not a major problem in fats and oils hence they reported that the amount of free fatty produced by hydrolysis during frying operation is too small to affect the quality of the food. The adverse effects are due to oxidation. Because the determination of F.F.A. by titration does not differentiate between acids formed by oxidation and those formed by hydrolysis, the increase in F.F.A. is a poor measure of frying of deterioration.

4.3.5 – Oxidative rancidity:-

Oxidative rancidity is the principal problem in fats and oils. Two determinations, peroxide value (as indicator of primary oxidation) and thiobarbituric acid (as indicator of secondary oxidation) are employed in this study to determine the extent of autoxidation and thermal in canola and cottonseed oils caused by heating during frying eggplant, potatoes and squash under experimental conditions.

The peroxide value (P.V.) is related to the hydroperoxides, the primary oxidation products, which are unstable under frying conditions and readily decompose into mixtures of mainly volatile aldehyde compounds. The oxidation product concentrations, expressed in P.V., may increase after the sample in with drawn from the fryer, thus P.V. may not indicate the actual extent of oil deterioration **(Fritch, 1981; Melton *et al.*, 1994** and **Yaghmur, *et al.*, 2001).**

Data given in table (13) showed the changes that took place in peroxide value (P.V.) and thiobarbituric acid value (T.B.A.) of canola and cottonseed oils due to heating during frying some vegetables. Generally, it

was noticed that P.V. increased gradually in all oil samples (either canola or cottonseed) due to frying at 180 ^{o}C. Further increase occurred in P.V. as heating or frying time proceeded till 10 hours then decreased. The rate of change in P.V. value increase or decrease depending on the kind of vegetable used in frying as well as the type of oil. The data in table (13) clearly show a difference between the two oils. While cottonseed oil showed a rapid increase in P.V. from 9.40 to 16.20, 15.70 and 14.20 meq. peroxide/Kg after 12 hours of frying eggplant, potatoes and squash, respectively. For the canola oil, the results in the same table showed a slight increase in the P.V. value from 1.82 to 1.99, 2.10 and 1.89 meq. peroxide/Kg after 12 hours of frying eggplant, potatoes and squash, respectively.

The gradual increase in the P.V. could be attributed to the accelerating effect at high temperature in the presence of oxygen on thermal oxidation and peroxide formation. Similar trend was reported by **June (1981); Gunstone** and **Norris (1983); Lorusso *et al.,* (1983); Iskander, (1991,** and **1992);** and **Yaghmur *et al.,* (2001).** On the other hand, the decrease of P.V. after 12 hours of heating during frying (table 13) can be explained on the basis that at high temperatures, the rate of decomposition of peroxides and hydroperoxides is higher than the rate of their formation. These results are in agreement with the findings of **Lea (1982); Moharram** and **Osman (1982); Iskander *et al.,* (1985b); Taha *et al.,* (1988); Iskander, (1992); Neff *et al.,* (1994a); Malcolmson *et al.,* (1996)** and **Mehta & Swinburn (2001).**

Table (13) Changes of peroxide value (P.V.) and thiobarbituric acid value (T.B.A.) of canola oil and cottonseed oils during frying of some vegetables at 180°C for 4 minutes.

Frying Time (Hours)	Type of vegetable					
	Eggplant	Potatoes	Squash	Eggplant	Potatoes	Squash
	P.V.*					
	Canola oil			Cottonseed oil		
0.00	1.82	1.82	1.82	9.40	9.40	9.40
2.00	1.89	1.87	1.86	13.20	12.60	12.20
4.00	2.14	2.10	1.98	13.80	12.90	12.70
6.00	2.25	2.23	2.29	15.75	15.80	14.90
8.00	3.20	3.25	3.33	17.00	16.10	15.50
10.00	3.55	3.51	3.62	18.80	17.90	16.90
12.00	1.99	2.10	1.89	16.20	15.70	14.20
TBA**						
0.00	1.42	1.42	1.42	0.78	0.78	0.78
2.00	1.56	1.53	1.55	1.23	1.11	1.29
4.00	1.92	1.67	1.79	1.75	1.59	1.67
6.00	2.08	2.10	2.14	2.01	1.93	2.15
8.00	2.23	2.36	2.48	2.27	3.85	3.27
10.00	2.78	2.91	3.01	3.19	3.98	3.61
12.00	3.63	3.47	3.59	4.31	4.19	4.05

Where: * PV = peroxide value as meq. peroxide /Kg. sample
****TBA = thiobarbituric acid value as mg. malonaldehyde /Kg sample and measured at wavelength 532 nm.**

Concerning the aldehyde development as shown by the thiobarbituric acid (T.B.A.) which is considered as a more reliable indicator of oxidative rancidity (**Jacobson, 1967 and Ganguli & Jain, 1973**), the results presented in table (13) showed that the T.B.A. values varies with the kind of vegetable used in frying , the nature of oil undergoing the heat treatment and the frying period. Generally, it was noticed that the T.B.A. value increased gradually as heating or frying time increased in all samples. This increase in T.B.A. value due to increase in absorption at 532 nμ could reflect increases in shorter chain dienals and malonaldehydes which are not as pleasant in flavour (**Jacobson, 1967).**

On the other hand, the oil samples remaining after 12 hours of frying eggplant (table 13) showed the highest increase in T.B.A. values than oil samples of potatoes and squash. This variation may be due to the differences in chemical constitutes of vegetable samples used in frying. **Iskander, (1992),** obtained similar results**.** Results in table (13) also revealed that although the initial value of T.B.A. was lower in cottonseed oil samples (0.78 mg. malonaldehyde/Kg) than canola oil ones (1.42) it was noteworthy that the increase in T.B.A. value was higher in cottonseed oil than canola oil samples at the end period of frying. This variation might be due to the difference in glycerids structure, which depends on the oil source.

4.3.6 – Degree of unsaturation:-

Data given in table (14) illustrate the changes that took place in the degree of unsaturation, as shown by change in iodine value (I.V.), of canola and cottonseed oils used in frying eggplant, potatoes and squash. It could be noticed that the I.V. decreased gradually in all oil samples during heat

treatment. Further decline occurred as heating of frying time increased. The extent of decrease in I.V. was affected by kind of vegetable, frying time as well as the oil brand used as frying medium. The decrease of I.V. during frying could be attributed to the formation of fatty acids which differ in their degree of unsaturation or to the distribution of double bonds. Such results are in reasonable agreement with those reported by **Edward (1967); Ota, (1981); Moharrm** and **Osman (1982); Iskander *et al.,* (1985b); Abdel-aal** and **Karara (1986)** and **Augustin *et al.,* (1988).** Other workers **(Johnson and Kummerow, 1957; Melnick *et al.,* 1958; Swern, 1979** and **June, 1981)** reported that the formation of fatty acids polymers during thermal oxidation of oil will have an effect on decreasing iodine value. In addition, results in table (14) also indicated that the highest decrease in I.V. was observed in oil samples remaining after 12 hours of frying squash. This variation may be due to the differences in chemical composition of vegetables used in frying processes. These results are in accordance with those reported by **El-Sharnouby (1999b)** and **Ibrahaim (2000)**

Table (14): Changes in iodine value* (I.V.) of canola oil and cottonseed oils during frying of some vegetables at 180 ^{o}C for 4 minutes.

Frying Time (Hours)	Frying oils of different vegetables					
	Canola oil			Cottonseed oil		
	EG.**	PO.**	SQ.**	EG.	PO.	SQ.
0.00	111.15	111.15	111.15	103.00	103.00	103.00
2.00	110.50	110.00	109.00	101.00	102.00	99.00
4.00	107.00	107.00	108.00	99.20	98.00	97.00
6.00	106.30	106.70	107.70	97.70	96.30	95.10
8.00	106.00	105.00	104.90	96.00	95.50	94.00
10.00	105.90	104.80	104.40	95.80	95.30	93.70
12.00	105.00	104.70	104.10	94.10	93.00	92.50

Where:* Iodine value was reported as number of grams of iodine required to saturate 100 grams of oil.
**** EG = Eggplant, PO = Potatoes, SQ = Squash.**

4.3.7 – Saponification value (S.V.):-

The changes in saponification value of canola and cottonseed oils during frying of some vegetables at 180 ^{o}C for 12 hours are shown in table (15). The data indicated that the saponification value (S.V.) increased gradually in all oil samples as heating or frying time increased. The rate of increase in S.V. was affected by frying time, kind of vegetable and oil brand used in frying process. The increase in S.V. during frying could be attributed to the formation of new fatty acids which have a lower molecular weight, usually due to presence of lower fatty acids. Such results agree with those

reported by **Williams (1966); Moharram** and **Osman (1982) and Ibrahaim (2000).**

Data in table (15) indicated also that the oil sample remaining after 12 hours of frying eggplant recorded the highest increase in S.V. (197.7.0 and 201.45 for canola and cottonseed oils, respectively). In contrast, the oil sample remaining after frying squash for the same period of frying showed the lowest increase in S.V. (197.00 and 201.15 for canola and cottonseed oil samples, respectively). This is to be expected since it may be attributed to the differences in chemical composition of vegetable samples used in frying. These results are in the same trend with those reported by **El-Sharnouby (1999b)** and **Ibrahaim (2000).**

Table (15): Changes in saponification value* (S.V.) of canola oil and cottonseed oils during frying of some vegetables at 180 ^{o}C for 4 minutes.

Frying Time (Hours)	Frying oils of different vegetables					
	Canola oil			Cottonseed oil		
	EG.**	PO.**	SQ.**	EG.	PO.	SQ.
0.00	191.80	191.80	191.80	198.45	198.45	198.45
2.00	193.00	193.70	192.00	198.95	198.75	199.05
4.00	194.00	194.20	192.80	199.20	199.50	199.60
6.00	196.00	195.00	194.00	199.75	199.80	200.10
8.00	197.00	196.50	195.00	200.20	200.25	200.55
10.00	197.45	196.90	195.80	200.55	200.75	201.00
12.00	197.70	197.00	196.50	201.45	201.20	201.15

Where: * Saponification value calculated as mg. KOH require to saponify one gram of oil sample.
**** EG = Eggplant, PO = Potatoes and SQ = Squash.**

4.3.8 – Unsaponifiable matter:-

These compounds usually exert an effect on the stability of vegetable oils **(Williams, 1966; Swern, 1979** and **Hui, 1996).** Data given in table (16) illustrate the changes in unsaponifiable matter percentage of canola and cottonseed oils during frying eggplant, potatoes and squash. Generally, it can be observed that the unsaponifiable matter percentage decreased gradually in all oil samples during frying. The rate of decreasing depends on kind of vegetable, oil brand used in frying and frying time. The decreasing in unsaponifiable matter during heat treatment might be due to the effect of heating and oxidation. Also, the results in table (16) showed that the oil samples remaining after 12 hours of frying potatoes was recorded the highest decrease in unsaponifiable matter percentage than other vegetables. In contrast, the oil samples remaining after 12 hours of frying eggplant showed the lowest decrease in the percentage of unsaponifiable matter.

4.3.9 – Fatty acid composition:-

Data given in tables (17) and (18) showed the change in fatty acid composition of cottonseed and canola oils due to heating at 180 ^{o}C during frying some vegetables for 6 and 12 hours. The results obtained revealed that heating caused a gradual increase in $C_{10:0}$, $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$ and TSFA with increasing frying time. In contrast, a gradual decline was observed in $C_{18:1}$, $C_{20:1}$, TMUFA, $C_{18:2n-6}$, $C_{18:3n-3}$, TPUFA, TUFA as well as ratios of TUFA : TSFA and $C_{18:2}$: $C_{18:1}$. Similar trend was reported by **Lorusso *et al.,* (1983); Leszkiewicz** and **Kasperek, (1988)** and **Iskander, (1992).** The rate of either increase or decrease was dependent on the type of oil, frying time as well type of vegetable used in frying. The decrease in

$C_{18:2n-6}$, $C_{18:3n-3}$ and TUFA could be attributed to the autoxidation and thermal oxidation, hence the change in the degree of unsaturation. These results are in accordance with those reported by **Swern, (1979); Leszkiewicz** and **Kasperek, (1988)** and **Hui, (1996).**

Table (16): Changes in unsaponifiable matter percentage of canola oil and cottonseed oils during frying of some vegetables at 180 ^{o}C for 4 minutes.

Frying Time (Hours)	Frying oils of different vegetables					
	Canola oil			Cottonseed oil		
	EG.*	PO.*	SQ.*	EG.	PO.	SQ.
0.00	1.42	1.42	1.42	1.07	1.07	1.07
2.00	1.29	1.23	1.31	0.93	0.95	1.02
4.00	1.19	1.17	1.21	0.91	0.88	0.86
6.00	1.12	1.11	1.14	0.88	0.80	0.79
8.00	1.07	1.02	1.08	0.80	0.78	0.75
10.00	1.02	0.98	1.01	0.77	0.69	0.68
12.00	0.98	0.91	0.97	0.59	0.55	0.58

Where: * EG = Eggplant, PO = Potatoes and SQ = Squash.

Table (17): Changes in fatty acid composition* of cottonseed oil during frying of some vegetables at 180 °C for 4 minutes.

Identified Fatty acids %	Fried oil samples									
	Ctrl**	0.0 hr.			6 hr.			12 hr.		
		EG.**	PO.**	SQ.**	EG.	PO.	SQ.	EG.	PO.	SQ.
SFA										
Capric $C_{10:0}$	0.13	0.17	0.21	0.27	0.93	0.81	0.94	1.41	1.61	1.35
Lauric $C_{12:0}$	0.35	0.53	0.54	0.65	1.23	1.13	1.23	2.01	2.03	2.17
Myristic $C_{14:0}$	0.70	1.00	0.99	1.17	2.41	2.61	2.65	4.13	4.00	4.19
Palmitic $C_{16:0}$	23.20	23.86	24.08	24.15	25.50	25.11	25.21	26.70	26.20	26.21
Stearic $C_{18:0}$	2.15	2.87	2.61	2.58	3.11	3.50	3.41	3.61	3.77	3.41
Arachidic $C_{20:0}$	-	0.17	0.13	0.20	1.43	1.55	1.37	1.23	1.11	1.14
Total SFA	26.53	28.60	28.56	29.02	34.61	34.71	34.81	39.09	38.72	38.47
UFA										
MUFA										
Palmitoleic $C_{16:1}$	1.46	1.27	1.23	1.37	0.98	0.89	0.98	0.19	0.16	0.21
Oleic $C_{18:1}$	25.06	24.85	24.81	24.11	21.37	21.11	21.87	20.48	20.01	19.81
Gadoleic $C_{20:1}$	-	0.13	0.19	0.17	0.07	0.13	0.19	0.11	-	0.09
Erucic $C_{22:1}$	-	-	-	-	-	-	-	-	-	-
Total MUFA	26.52	26.25	26.23	25.65	22.42	22.13	23.04	20.78	20.17	20.11
PUFA										
Linoleic $C_{18:2n-6}$	46.85	45.13	45.11	45.23	42.91	43.10	42.11	40.11	41.09	41.02
Linolenic $C_{18:3n-3}$	00.10	0.02	0.10	0.10	0.06	0.06	0.04	0.02	0.02	0.40
Total PUFA	46.95	45.15	45.21	45.33	42.97	43.16	42.15	40.13	41.11	41.42
Total UFA	73.47	71.40	71.44	70.98	65.39	65.29	65.19	60.91	61.28	61.53
TUFA:TSFA	2.77	2.50	2.50	2.45	1.89	1.88	1.87	1.56	1.58	1.60
$C_{18:2}$: $C_{18:1}$	1.87	1.82	1.82	1.88	2.00	2.04	1.93	1.96	2.05	2.07

Where: * wt. % of total fatty acids.
**** EG=Eggplant, PO=Potato, SQ=Squash and Ctrl =control (fresh sample).**

Table (18): Changes in fatty acid composition* of canola oil during frying of some vegetables at 180 °C for 4 minutes.

Identified Fatty acids, %	Fried oil samples									
	Ctrl.**	0.0 hr.			6 hr.			12 hr.		
		EG.**	PO.**	SQ.**	EG.	PO.	SQ.	EG.	PO.	SQ.
SFA										
Capric $C_{10:0}$	0.10	0.14	0.37	0.36	0.41	0.27	0.32	0.59	0.51	0.71
Lauric $C_{12:0}$	0.04	0.17	0.38	0.43	0.29	0.34	0.47	0.70	0.59	0.67
Myristic $C_{14:0}$	0.20	0.29	0.56	0.63	1.22	1.38	1.43	1.91	1.88	1.79
Palmitic $C_{16:0}$	5.82	6.91	6.99	6.89	6.86	7.10	7.37	8.27	8.91	8.71
Stearic $C_{18:0}$	2.05	3.19	4.43	4.29	4.11	4.62	4.57	5.91	5.93	5.98
Arachidic $C_{20:0}$	0.72	0.99	0.97	1.13	1.61	1.77	1.98	2.27	2.13	2.34
Total SFA	8.93	11.69	13.70	13.73	14.50	15.48	16.14	19.65	19.95	20.20
UFA										
MUFA										
Palmitoleic $C_{16:1}$	-	0.09	0.11	0.19	0.37	0.41	0.55	0.69	0.71	0.89
Oleic $C_{18:1}$	56.54	55.30	54.17	54.53	54.13	54.00	53.87	52.95	52.70	52.83
Gadoleic $C_{20:1}$	1.72	1.34	0.98	1.27	1.19	0.71	0.87	0.59	0.61	0.60
Erucic $C_{22:1}$	0.20	0.37	0.44	0.29	0.41	0.37	0.33	0.27	0.21	0.19
Total MUFA	58.46	57.10	55.70	56.28	56.10	55.49	55.62	54.50	54.23	54.51
PUFA										
Linoleic $C_{18:2n-6}$	25.81	25.33	24.87	24.09	23.69	23.50	23.71	22.20	22.10	21.70
Linolenic $C_{18:3n-3}$	6.80	5.88	5.73	5.90	5.71	5.53	4.53	3.65	3.72	3.59
Total PUFA	32.61	31.21	30.60	29.99	29.40	29.03	28.24	25.85	25.82	25.29
Total UFA	91.07	88.31	86.30	86.27	85.50	84.52	83.86	80.35	80.05	79.80
TUFA:TSFA	10.20	7.55	6.30	6.28	5.90	5.46	5.20	4.09	4.01	3.95
$C_{18:2}$: $C_{18:1}$	0.46	0.46	0.46	0.44	0.44	0.44	0.44	0.42	0.42	0.41

Where: * wt. % of total fatty acids.

**** EG=Eggplant, PO=Potato, SQ=Squash and Ctrl =control (fresh sample).**

4.4 – Effect of storage period and antioxidants on physical and chemical properties and fatty acid composition of some vegetable oils:-

4.4.1 – Physical properties:-

Data in tables (19) and (20) summarizes the changes that took place in the physical properties of cottonseed and canola oils during storage at room temperature for six months. In addition, the results in the same tables showed the effect of some antioxidants. From these data, the following changes could be observed:-

(a) The viscosity increased gradually in all oil samples during storage. However, the rate of increase was dependent on the oil brand, storage period, and type of antioxidants as well as antioxidants concentration. The highest increase in the viscosity was recorded in the control sample after six months of storage in either cottonseed oil (51.70 mPa.sec.) or canola oil (75.80 mPa.sec). On the contrary, the lowest increase in the viscosity was found in oil samples stored for three months and treated with 0.02 % of either B.H.A. or B.H.T. Generally, viscosity tends to increase with increasing degree of saturation and increasing chain length. These results are in general accordance with **Swern (1979)** and **Hui (1996).**

(b) As for as the unsaponifiable matter of the stored oil samples, the results obtained in tables (19) and (20) showed a slightly decrease in the unsaponifiable matter content during storage. This probably indicates that no major changes occurred during storage in oil composition that might affect the unsaponifiable matter content.

(c) Concerning the refractive index of the stored oil samples in relation to storage period and antioxidants, treatment it could be noticed from

data obtained in tables (19) and (20) that the refractive index of oil samples was decreased gradually as storage period increased. The rate of decrease was dependent on the storage period, type of antioxidant used as well as antioxidants concentration. The decrease in the refractive index of the studied oil samples during storage could be explained on the basis of the double bonds saturation of the fatty acids during the production of hydroperoxides and intermediate compounds. These results are in accordance with those reported by **Swern (1979); Gunstone** and **Norris (1983)** and **Hui (1996).**

(d) On the basis of the colour intensity change of the studied oil samples during storage at room temperature for six months, the results presented in tables (19) and (20) revealed that the colour intensity was increased during storage. The extent of increase was affected by the storage period; oil brand, type and concentration of antioxidants. These results are in coincide with those obtained by **Helen (1982); Iskander, *et al.* (1985b); Saguy, *et al.* (1996)** and **Yaghmur, *et al.* (2001).** The increase in colour intensity of the oil samples during storage could be attributed to the formation of fatty acid polymers which accumulate a result of triglycerides hydrolysis during storage (**June, 1981** and **Ota, 1981**). On the other hand, **White (1991)** and **Saguy, *et al.* (1996)** reported that the increase in colour index is probably due to oxidation typically resulting in the generation of hydroperoxides, conjugated dienoic acids, epoxides, hydroxides and keteones. Oils and fats can also produce dimeric acids, and form polymers of higher molecular weight, causing a darker colour and a deposit of yellow or brown pigments **(Blumenthal, 1991).**

Table (19): Effect of storage and antioxidants on the physical properties* of cottonseed oil.

Antioxidants		Storage Period (months)	Viscosity (mPa.Sec.) at 25°C	Unsaponif-iable matter (%)	Refractive Index at 25°C	Colour***	
Type**	Concentration (%)					R	B
Control	0.00	0	44.80	1.07	1.4685	6.8	0.0
		3	48.20	1.07	1.4683	7.3	1.0
		6	51.70	1.06	1.4676	8.7	2.7
BHA	0.01	3	45.70	1.06	1.4684	7.7	1.6
		6	47.00	1.05	1.4683	8.9	0.8
	0.02	3	45.00	1.05	1.4685	7.1	1.8
		6	46.20	1.05	1.4683	9.4	0.0
BHT	0.01	3	45.60	1.06	1.4680	7.6	3.2
		6	46.70	1.05	1.4679	9.3	3.6
	0.02	3	45.00	1.06	1.4684	8.1	2.0
		6	46.30	1.06	1.4680	8.9	1.4
PG	0.01	3	46.00	1.06	1.4680	7.9	0.2
		6	47.10	1.05	1.4679	9.1	0.9
	0.02	3	45.30	1.06	1.4681	8.7	0.0
		6	47.00	1.06	1.4684	9.3	0.0

Where: * Each figure given in this table is mean of three determinations.
****B.H.A Butlated hydroxyl anisole.**
B.H.T. Butlated hydroxyl toluene.
P.G. Propyl gallate.
*****Colour was determined by lovibond Tintometer, using a one inch cell colour and yellow = 35, R = Red and B = Blue.**

Table (20): Effect of storage and antioxidants on the physical properties* of canola oil.

Antioxidants		Storage Period (months)	Viscosity (mPa.Sec.) at 25°C	Unsaponif-iable matter (%)	Refractive Index at 25°C	Colour***	
Type**	Concentration (%)					R	B
Control	0.00	0	57.00	1.42	1.4691	6.6	0.0
		3	63.90	1.41	1.4680	8.3	2.1
		6	75.80	1.40	1.4682	8.8	4.7
BHA	0.01	3	61.10	1.41	1.4681	8.1	1.3
		6	67.30	1.40	1.4671	8.6	2.7
	0.02	3	59.80	1.42	1.4679	8.4	1.1
		6	65.40	1.41	1.4677	9.2	0.0
BHT	0.01	3	60.70	1.41	1.4677	8.7	3.0
		6	64.10	1.40	1.4674	8.9	4.4
	0.02	3	59.00	1.42	1.4677	8.7	2.5
		6	63.00	1.41	1.4673	9.1	4.1
PG	0.01	3	62.20	1.41	1.4673	7.9	1.7
		6	69.10	1.40	1.4671	8.4	2.1
	0.02	3	62.90	1.41	1.4677	7.4	2.3
		6	70.10	1.40	1.4676	8.8	4.7

Where: * Each figure given in this table is mean of three determinations.
****B.H.A Butlated hydroxyl anisole.**
B.H.T. Butlated hydroxyl toluene.
P.G. Propyl gallate.
*****Colour was determined by lovibond Tintometer, using a one inch cell colour and yellow = 35, R = Red and B = Blue.**

4.4.2 – Chemical characteristics:-

4.4.2.1 – Acid value:-

Concerning the acidity of the stored cottonseed and canola oil samples, the results in tables (21) and (22) show that the acid value increased gradually in all oil samples during storage. However, the rate of increase was dependent on the storage time, oil brand, type and concentration of antioxidant used. Generally, it can be observed from the results in tables (21) and (22) that the control oil samples stored for six months had the highest increase in acid value either in cottonseed oil (0.46) or in canola oil (0.98) followed by control oil samples stored for three months. The lowest increase in acid value was found in oil samples stored for three months and treated with 0.02 % B.H.A. (0.27 and 0.55 in cottonseed and canola oil samples, respectively). Results in table (21) and (22) also, revealed that the oil samples treated with the concentration 0.01 % of antioxidants showed a little higher increase in acid value than oil samples treated with 0.02 %. The slight gradual increase in the acidity could be attributed to the hydrolysis of some phosphatides and triglycerides into glycerol and free fatty acids. These results are in coincide with those reported by **Swern, (1979); June, (1981); Moharam** and **Osman, (1982); Iskander, *et al.* (1985b); Augustin, *et al.* (1988)** and **Rossell, (2001).** In addition, **Aziz (1982)** reported that oils were considered to be unsuitable for edible purposes when their acid number increased to values greater than 2.0. Although the acid value is an index of hydrolytic rancidity, it was measured as acids contribute to the development of off-flavours and off-odours in the product **(Noor** and **Augustin, 1984).**

4.4.2.2 – Peroxide value (P.V.) and thiobarbituric acid (T.B.A.):

The data presented in tables (21) and (22) showed the changes that took place in peroxide value (P.V.) and thiobarbituric acid value (T.B.A.) of cottonseed and canola oils due to storage for six months at room temperature. Generally, it was noticed that the P.V. and T.B.A. values were increased gradually in all oil samples during storage; the rate of increased was higher in the oil samples stored for three months. Also, the rate of increased in P.V. and T.B.A values were higher in oil samples (either cottonseed or canola) treated with 0.01 % concentration of antioxidants than those treated with 0.02 % concentration. In addition, the control oil samples stored for six months had the highest increased in P.V. and T.B.A values. The gradual increased in the P.V. could be attributed to the accelerating effect of storage temperature in the presence of oxygen on oxidation and peroxide formation. The presented findings are in the same line with those reported by **June (1981); Lorusso, *et al.* (1983); Iskander, (1986)** and **Yaghmur, *et al.* (2001).** In addition, the increase in TBA value due to increasing in absorption at 532 nm could reflect increases in shorter chain dienals and malonaldehydes, which are not as pleasant in flavour **(Jacobson, 1967).** On the other hand, the spoilage of either cottonseed oil or canola oil was considered to have occurred when the peroxide value surpassed 10 meq /Kg. according to **Codex (2004).**

4.4.2.3 – Iodine value (I.V.):

The data of this investigation in tables (21) and (22) revealed that the iodine value (I.V.) of all oil samples was decreased during storage. However, the rate of decrease was dependent on the oil brand, storage period, antioxidant type and concentration. The highest decrease in iodine

value was recorded in control oil samples stored for either three or six months. This may be due to the absent of antioxidants. Also, it can be observed from the results in tables (21) and (22) that the rate of decrease in iodine value of the oil samples treated with 0.01 % concentration of antioxidants was higher than those oil samples treated with 0.02 % either stored for three or six months. The decrease in iodine value of oil samples during storage could be explained on the basis of the double bonds saturation of the fatty acids during the production of hydroperoxides and intermediate compounds. These results are in accordance with those reported by **Swern, (1979); Gunstone** and **Norris (1983); Frankel, *et al.* (1984); Iskander, *et al.* (1986); Przybyski, (1994); Hawrysh, (1998)** and **Rossell, (2001).**

4.4.2.3 – Saponification value (S.V.):

The changes in the saponification value of cottonseed and canola oils during storage at room temperature for six months are shown in tables (21) and (22). Generally, it can be observed from the results that the S.V. increased gradually in all oil samples as storage period increased. The rate of increase in S.V. was affected by storage time, type of oil, type and concentration of antioxidants. The highest increase in S.V. was recorded in control oil samples stored for six months. These results are in general agreement with those reported by **Williams (1966); Moharram** and **Osman (1982)** and **Ibrahim (2000)** who mentioned that the saponification value of oil increased during storage. High saponification values indicate a lower molecular weight, usually due to presence of lower fatty acids **(Swern, 1979** and **Hui, 1996).**

Table (21): Effect of storage and antioxidants on chemical characteristics of cottonseed oil.

Antioxidants		Storage period (months)	Chemical characteristics*				
Type **	Concentration (%)		A.V.	P.V.	I.V.	T.B.A.	S.V.
Control	0.00	0	0.18	9.40	103.00	0.78	198.45
		3	0.38	10.80	96.20	1.21	208.55
		6	0.46	18.80	83.70	1.47	213.45
BHA	0.01	3	0.31	9.40	101.20	0.87	200.15
		6	0.37	12.60	100.30	1.03	201.65
	0.02	3	0.27	9.18	102.00	0.87	199.45
		6	0.33	10.78	101.15	0.98	201.25
BHT	0.01	3	0.31	9.62	100.90	0.85	199.45
		6	0.36	12.10	98.55	0.97	202.45
	0.02	3	0.28	9.46	101.20	0.93	199.45
		6	0.34	11.26	99.35	0.98	201.45
PG	0.01	3	0.34	9.45	99.00	1.01	201.45
		6	0.38	12.69	98.30	1.07	203.65
	0.02	3	0.33	9.23	99.80	0.98	200.65
		6	0.36	11.97	98.75	1.13	202.55

Where: * A.V = Acid value (mg. KOH / g. oil),
P.V. = Peroxide value (meq. peroxide / Kg. oil),
I.V. = Iodine value (g. iodine saturate 100 g. oil),
T.B.A. = Thiobarbituric acid (mg. malonaldehyde / Kg. oil),
S.V. = Saponification value (mg. KOH saponify gram oil).
**** B.H.A Butlated hydroxyl anisole,**
B.H.T. Butlated hydroxyl toluene,
P.G. Propyl gallate.

Table (22): Effect of storage and antioxidants on chemical characteristics of canola oil.

Antioxidants		Storage period (months)	Chemical characteristics*				
Type **	Concentration (%)		A.V.	P.V.	I.V.	T.B.A.	S.V.
Control	0.00	0	0.53	1.82	111.15	1.42	191.80
		3	0.73	2.55	104.20	1.62	198.70
		6	0.98	2.97	101.20	2.16	202.00
BHA	0.01	3	0.57	1.99	109.35	1.44	194.50
		6	0.64	2.70	108.20	1.46	194.80
	0.02	3	0.55	1.97	109.70	1.46	193.30
		6	0.59	2.10	109.00	1.65	195.80
BHT	0.01	3	0.59	1.99	109.45	1.56	193.30
		6	0.66	2.65	108.50	1.92	194.80
	0.02	3	0.58	1.88	109.85	1.52	193.80
		6	0.61	2.30	108.75	1.82	195.80
PG	0.01	3	0.60	2.10	109.35	1.60	194.80
		6	0.66	2.90	108.85	2.02	197.30
	0.02	3	0.59	2.00	109.65	1.57	194.00
		6	0.58	2.70	109.00	1.98	195.80

Where: * A.V = Acid value (mg. KOH / g. oil),
P.V. = Peroxide value (meq. peroxide / Kg. oil),
I.V. = Iodine value (g. iodine saturate 100 g. oil),
T.B.A. = Thiobarbituric acid (mg. malonaldehyde / Kg. oil),
S.V. = Saponification value (mg. KOH saponify gram oil).
**** B.H.A Butlated hydroxyl anisole,**
B.H.T. Butlated hydroxyl toluene,
P.G. Propyl gallate.

4.4.3 – Fatty acid composition:

The data presented in tables (23) and (24) showed the change that took place in fatty acid composition of cottonseed and canola oils due to storage for six months at room temperature. In general, it can be observed from the results of the gas liquid chromatography in tables (23) and (24) that the values of C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, TSFA and ratio of $C_{18:2}$: $C_{18:1}$ were increased with increasing the storage period in all concentrations of antioxidants. In contrast, the values of $C_{16:1}$, $C_{18:1}$,$C_{20:1}$, $C_{22:1}$, TMFA, $C_{18:\ 2n-6}$, $C_{18:3n-3}$, TPUFA, TUFA and ratio of TUFA : TSFA were decreased. The rate of change (either increase or decrease) was dependent on the oil brand, antioxidant type and concentration. The decrease in unsaturated fatty acids either polyunsaturated fatty acids ($C_{18:\ 2n-6}$ and $C_{18:3n-3}$) or monounsaturated fatty acids could be attributed to the oxidation and hence the change in the degree of unsaturation. Also, in the present work it was noticed that the decrease in the linoleic and linolenic acid content was accompanied by the decrease in the iodine value (table 14). These results are in accordance with those reported by **Swern, (1979); Iskander, *et al.* (1986); Leszkiewicz and Kasperek, (1988); Hui, (1996)** and **Ibrahim, (2000).**

From the above results, it can be concluded that the storage of cottonseed and canola oils for long period at room conditions undoubtedly resulted in undesirable changes in their physical and chemical properties. Furthermore, it reduced the nutritive value of the stored oils through the reduction of their unsaturated fatty acid contents. Similar results were obtained by **Iskander, *et al.* (1986)** and **Ibrahim, (2000).** Furthermore, **Frankel, *et al.* (1984)** reported that the main problem of fats and oils is the

oxidative deterioration. However, it causes more problems of use and storage of fats and oils. Oxidation of unsaturated fatty acids of fats and oils produce offensive odours and off-flavour. However, its limit their use and decreases the nutritional quality through the formation more of secondary reaction products.

Table (23): Effect of storage at room temperature for six months and antioxidants treatment on fatty acid composition of cottonseed oil.

Fatty acids (wt. % of total fatty acids)	Ctrl.	Antioxidants type and concentration					
		B.H.A.		B.H.T.		P.G.	
		0.01%	0.02%	0.01%	0.02%	0.01%	0.02%
Saturated fatty acids (SFA)							
Capric $C_{10:0}$	0.13	0.20	0.18	0.38	0.22	0.39	0.38
Lauric $C_{12:0}$	0.35	0.43	0.40	0.65	0.50	0.68	0.60
Myristic $C_{14:0}$	0.70	0.95	0.90	1.30	1.05	1.40	1.25
Palmitic $C_{16:0}$	23.20	24.24	24.10	25.05	24.71	25.17	24.73
Stearic $C_{18:0}$	2.15	3.20	2.51	3.47	3.29	3.50	3.40
Arachidic $C_{20:0}$	-	-	-	-	-	-	-
Total SFA	**26.53**	**29.02**	**28.09**	**30.85**	**29.77**	**31.14**	**30.36**
Unsaturated fatty acid (UFA)							
MUFA							
Palmitoleic $C_{16:1}$	1.46	1.40	1.25	1.10	1.00	1.00	1.00
Oleic $C_{18:1}$	25.06	23.33	24.51	22.20	23.63	22.11	23.14
Gadoleic $C_{20:1}$	-	-	-	-	-	-	-
Erucic $C_{22:1}$	-	-	-	-	-	-	-
Total MUFA	26.52	24.73	25.76	23.30	24.63	23.11	24.14
PUFA							
Linoleic $C_{18:2n-6}$	46.85	46.15	46.05	45.85	45.60	45.75	45.50
Linolenic $C_{18:3n-3}$	00.10	00.10	00.10	00.00	00.00	00.00	00.00
Total PUFA	46.95	46.25	46.15	45.85	45.60	45.75	45.50
TUFA	**73.47**	**70.98**	**71.91**	**69.15**	**70.23**	**68.86**	**69.64**
TUFA: TSFA	**2.77**	**2.45**	**2.56**	**2.24**	**2.36**	**2.21**	**2.29**
$C_{18:2}$: $C_{18:1}$	**1.87**	**1.98**	**1.88**	**2.07**	**1.93**	**2.07**	**1.97**

Table (24): Effect of storage at room temperature for six months and antioxidants treatment on fatty acid composition of canola oil.

Fatty acids (wt. % of total fatty acids)	Ctrl.	Antioxidants type and concentration					
		B.H.A.		B.H.T.		P.G.	
		0.01%	0.02%	0.01%	0.02%	0.01%	0.02%
Saturated fatty acids (SFA)							
Capric $C_{10:0}$	0.10	0.15	0.10	0.20	0.17	0.16	0.14
Lauric $C_{12:0}$	0.04	0.10	0.05	0.15	0.10	0.10	0.10
Myristic $C_{14:0}$	0.20	0.54	0.43	0.51	0.45	0.45	0.39
Palmitic $C_{16:0}$	5.82	6.84	6.10	6.40	6.30	6.29	6.15
Stearic $C_{18:0}$	2.05	3.18	3.15	3.25	3.20	3.20	3.15
Arachidic $C_{20:0}$	0.72	0.90	0.85	0.95	0.90	0.90	0.85
Total SFA	**8.93**	**11.71**	**10.68**	**11.46**	**11.12**	**11.10**	**10.78**
Unsaturated fatty acid (UFA)							
MUFA							
Palmitoleic $C_{16:1}$	-	-	-	-	-	-	-
Oleic $C_{18:1}$	56.54	54.29	55.57	54.74	55.08	55.05	55.47
Gadoleic $C_{20:1}$	1.72	1.60	1.55	1.50	1.50	1.50	1.50
Erucic $C_{22:1}$	0.20	0.20	0.15	0.15	0.15	0.15	0.15
Total MUFA	58.46	56.09	57.27	56.39	56.73	56.70	57.12
PUFA							
Linoleic $C_{18:2n-6}$	25.81	25.75	25.65	25.70	25.75	25.75	25.70
Linolenic $C_{18:3n-3}$	6.80	6.45	6.40	6.45	6.40	6.45	6.40
Total PUFA	32.61	32.20	32.05	32.15	32.15	32.20	32.10
TUFA	**91.07**	**88.29**	**89.32**	**88.54**	**88.88**	**88.90**	**89.22**
TUFA: TSFA	**10.20**	**7.54**	**8.36**	**7.73**	**7.99**	**8.00**	**8.28**
$C_{18:2}$: $C_{18:1}$	**0.46**	**0.47**	**0.46**	**0.47**	**0.47**	**0.47**	**0.46**

SUMMARY AND CONCULTIONS

5- SUMMARY AND CONCLUSIONS

There is a big gap between the production and consumption of vegetable oils in Egypt, where 90 % of consumed quantities is imported from the outside. Thus, the researchers and producers try to find substituted vegetable oils such as canola oil. Canola crop is distingued by its high content of oil. Also, it is a winter crop, not conflicting with crop rotation and short growing season crop.

This study was carried out as a comparing study between cottonseed oil and canola oil to evaluate:

- **A.** The physical and chemical characteristics of the studied oils.
- **B.** Fatty acid composition.
- **C.** Effect of frying (at 180 ^{o}C for 12 hours) on physical and chemical characteristics as well as fatty acid composition.
- **D.** Effect of storage period and antioxidants on physical and chemical characteristics as well as fatty acid composition.

The results obtained can be summarized as follow: -

A- The physical and chemical characteristics of cottonseed and canola oils:

The physical and chemical properties of cottonseed oil were 44.80, 1.4685, 35/6.8, 0.18, 103.00, 198.45, 1.07, 9.40 and 0.78 for viscosity (m.Pa.sec./25^{o}C), refractive index, colour, acid value, iodine value, saponification value, unsaponifiable matter (%), peroxide value and thiobarbituric acid, respectively. The physical and chemical properties of canola oil were 57.00, 1.4691, 35/6.6, 0.53, 111.15, 191.80, 1.42, 1.82 and 1.42 for viscosity (m.Pa.sec./25 ^{o}C), refractive index, colour, acid

value, iodine value, saponification value, unsaponifiable matter (%), peroxide value and thiobarbituric acid, respectively.

B-Fatty acid composition of cottonseed and canola oils:

The major fatty acid content of oil samples under investigation, namely palmitic ($C_{16:0}$), oleic ($C_{18:1}$) and linoleic ($C_{18:2}$). The highest percentage of palmitic acid was recorded in cottonseed oil (23.20 %). Meanwhile, canola oil contained much lower amounts of palmitic acid (5.82 %). Also, the amount of stearic acid in the investigated oils was ranged between 2.05 % and 2.15 %. Canola oil had the highest amounts of total unsaturated fatty acids (91.07 %) followed by those found in cottonseed oil (73.47 %). The data indicated that the majority of oleic acid was found in canola oil (56.54 %) compared with lower amounts in cottonseed oil (25.06 %). However, polyunsaturated fatty acids in cottonseed oil (46.85 %). Besides, canola oil contained much lower amount of linoleic acid (25.81 %). The highest value of linolenic acid (6.80 %) was found in canola oil in comparison with the lowest value (0.1 %) in cottonseed oil. The percentage of gadoleic ($C_{20:1}$) and erucic ($C_{22:1}$) of canola oil were 1.72 and 0.20 %, respectively, whereas, these fatty acids were not detected in cottonseed oil. Generally, canola seed oil contained large amount of unsaturated fatty acids especially oleic acid and considerable amount of linoleic and linolenic acids as compared other investigated oils. Therefore, canola oil can be used in food purpose side to side with other common plant oils.

C-Effect of frying (at 180 ^{o}C for 12 hours) on physical and chemical characteristics as well as fatty acid composition:

1-The viscosity increased gradually as frying time of the oil increased. The rate of increasing depends on the kind of vegetables used in frying as well as the type of oil.

2-The colour intensity was increased during frying but, the extent of increase was affected by the kind of vegetables used in frying, oil brand and frying time. The highest increase in colour intensity was recorded in cottonseed and canola oil samples remaining after 12 hours of frying eggplant (red 11.5 and blue 3.7 in cottonseed oil while red and blue were 11.7 and 5.0, respectively, in canola oil). In contrast, the lowest value of increase in colour intensity was obtained in cottonseed and canola oil samples remaining after 12 hours of frying potatoes: this variation could be attributed to the browning pigments from the foods which were dissolved into frying oils.

3-The decrease in refractive index of the refined and deodorized oils during intermittent heating at 180 ^{o}C was attributed to the polymerization which could have occurred during heating at high temperature. In addition, the refractive index of the studied oil samples decreased gradually with increase in frying time. The rates of increasing depend on the kind of vegetables used in frying as well as oil brand.

4-The differences in acid value (A.V.) may be due to the conditions during ripening of the seeds and conditions of harvesting and storage as well as conditions during processing. Furthermore, the change in A.V. for canola oil was the highest followed by cottonseed oil. On the basis of acid value, the eggplant slices were found to affect the acidity of oil samples more markedly than potato and squash samples.

5-The iodine value (I.V.) decreased gradually in all oil samples during heat treatment. The extent of decrease in I.V. was affected by kind of vegetable, frying time as well as the oil brand used as frying medium. The decrease of I.V. during frying could be attributed to the formation of fatty acids which differ in their degree of unsaturation or to the distribution of double bonds. In addition, the highest decrease in I.V.

was observed in oil samples remaining after 12 hours of frying squash. This variation may be due to the differences in chemical composition of vegetables used in frying processes.

6-The saponification value (S.V.) increased gradually in all oil samples as heating or frying time increased. The rate of increase in S.V. was affected by frying time, kind of vegetable and oil brand used in frying process. The oil sample remaining after 12 hours of frying eggplant recorded the highest increase in S.V. In contrast, the oil sample remaining after frying squash for the same period of frying showed the lowest increase in S.V.

7-The unsaponifiable matter percentage decreased gradually in all oil samples during frying. Also, the oil samples remaining after 12 hours of frying potatoes was recorded the highest decrease in unsaponifiable matter percentage than other vegetables. In contrast, the oil samples remaining after 12 hours of frying eggplant showed the lowest decrease in the percentage of unsaponifiable matter.

8-The peroxide value (P.V.) and thiobarbituric acid (T.B.A.) are employed in this study to determine the extent of oxidation caused in the investigated oils. This variation in either P.V. or T.B.A. values may be due to the differences in chemical constituents of oil samples**.** Generally, the P.V. increased gradually in all oil samples (either canola or cottonseed) due to frying at 180 ^{o}C. The data clearly show a difference between the two oils. While cottonseed oil showed a rapid increase in P.V. from 9.40 to 16.20, 15.70 and 14.20 meq. peroxide/Kg after 12 hours of frying eggplant, potatoes and squash, respectively. For the canola oil, the results showed a slight increase in the P.V. value from 1.82 to 1.99, 2.10 and 1.89 meq. peroxide/Kg after 12 hours of frying eggplant, potatoes and squash, respectively. Also, the T.B.A. value increased gradually as heating or frying time

increased in all samples. The oil samples remaining after 12 hours of frying eggplant showed the highest increase in T.B.A. values than oil samples of potatoes and squash. This variation might be due to the difference in glycerids structure which depends on the oil source.

9-Concerning the effect of frying on the fatty acid composition of cottonseed and canola oils, the obtained results indicated that the heating temperature during frying caused a gradual increase in $C_{10:0}$, $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{18:0}$, TSFA and ratio of $C_{18:2}$: $C_{18:1}$ with increasing frying time. In contrast, a gradual decline was observed in $C_{16:1}$, $C_{18:1}$, $C_{20:1}$, $C_{22:1}$, TMUFA, $C_{18:2n-6}$, $C_{18:3n-3}$, TPUFA, TUFA as well as ratio of TUFA: TSFA.

D-Effect of storage period and antioxidants on physical and chemical characteristics as well as fatty acid composition:

1-The viscosity increased gradually in all oil samples during storage. The highest increase in the viscosity was recorded in the control sample after six months of storage either in cottonseed oil (51.70 mPa.sec.) or canola oil (75.80 mPa.sec.). On the other contrary, the lowest increase in the viscosity was found in oil samples stored for three months and treated with 0.02 % of either B.H.A. or B.H.T.

2-The unsaponifiable matter of the stored oil samples a slightly decrease in the unsaponifiable matter content during storage.

3-The refractive index of oil samples was decreased gradually as storage period increased. However, the decrease in the refractive index of the studied oil samples during storage could be explained on the basis of the double bonds saturation of the fatty acids during the production of hydroperoxides and intermediate compounds.

4-The colour intensity was increased during storage. The extent of increase was affected by the storage period; oil brand, type and

concentration of antioxidants. The increase in colour intensity of the oil samples during storage could be attributed to the formation of fatty acid polymers which accumulate as a result of triglycerides hydrolysis during storage. The increase in colour index is probably due to oxidation typically resulting in the generation of hydroperoxides, conjugated dienoic acids, epoxides, hydroxides and keteones. Oils and fats can also produce dimeric acids, and form polymers of higher molecular weight, causing a darker colour and a deposit of yellow or brown pigments.

5-The acid value increased gradually in all oil samples during storage. The control oil samples stored for six months had the highest increase in acid value either in cottonseed oil (0.46) or in canola oil (0.98) followed by control oil samples stored for three months. The lowest increase in acid value was found in oil samples stored for three months and treated with 0.02 % B.H.A. (0.27 and 0.55 in cottonseed and canola oil samples, respectively). The oil samples treated with the concentration 0.01 % of antioxidants showed a little higher increase in acid value than oil samples treated with 0.02 %. The slight gradual increase in the acidity could be attributed to the hydrolysis of some phosphatides and triglycerides into glycerol and free fatty acids. Although the acid value is an index of hydrolytic rancidity, it was measured as acids contribute to the development of off-flavours and off-odours in the product.

6-The P.V. and T.B.A. values were increased gradually in all oil samples during storage; the rate of increase was higher in the oil samples stored for three months. Also, the rate of increase in P.V. and T.B.A values were higher in oil samples (either cottonseed or canola) treated with 0.01 % concentration of antioxidants than those treated with 0.02 % concentration. In addition, the control oil samples stored for six

months had the highest increased in P.V. and T.B.A values. The gradual increase in the P.V. value could be attributed to the accelerating effect of storage temperature in the presence of oxygen on oxidation and peroxide formation. The increase in TBA value due to increasing in absorption at 532 nm could reflect increases in shorter chain dienals and malonaldehydes which are not as pleasant in flavour.

7-The iodine value (I.V.) of all oil samples was decreased during storage. The highest decrease in iodine value was recorded in control oil samples stored for either three or six months. The rate of decrease in iodine value of the oil samples treated with 0.01 % concentration of antioxidants was higher than those oil samples treated with 0.02 % either stored for three or six months.

8-The S.V. increased gradually in all oil samples as storage period increased. The rate of increase in S.V. was affected by storage time, type of oil, type and concentration of antioxidants. The highest increase in S.V. was recorded in control oil samples stored for six months.

9-The values of fatty acids; C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, TSFA and ratio of $C_{18:2}$: $C_{18:1}$ were increased with increasing the storage period in all oil samples. In contrast, the values of $C_{16:1}$, $C_{18:1}$, $C_{20:1}$, $C_{22:1}$, TMFA, $C_{18:2n-6}$, $C_{18:3n-3}$, TPUFA, TUFA and ratio of TUFA: TSFA were decreased. The rate of changes was dependent on the oil brand, antioxidant type and concentration. The decrease in unsaturated fatty acids either polyunsaturated fatty acids ($C_{18:2n-6}$ and $C_{18:3n-3}$) or monounsaturated fatty acids could be attributed to the oxidation and hence the change in the degree of unsaturation. Finally, the storage of cottonseed and canola oils for long period at room conditions causes undesirable changes in their physical and chemical properties.

Furthermore, it reduced the nutritive value of the stored oils through the reduction of their unsaturated fatty acid contents.

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ARABIC SUMMARY

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كلية الزراعة
قسم علوم الاغذية

دراسات كيميائية و تكنولوجية على بعض الزيوت النباتية

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أبوالحمد السيد مهنى

(ǴƜØdƦă ȳzŸȝ) ǴƐȝäøÂöä ȳzŸĬöä ż âzƜøzöÀÒƋ
(ČĚĚĐ) r̂zƐèŭ ǴĬƞÀDZ – Ǵøȝäø Âöä ǴƐŸõ

للحصول على درجة الماجستير فى العلوم الزراعية
(علـوم الاغــذيـــة)

8äÅìŭ ǨƠ

أ.د/ منير حنا إسكندر
ǴƜØdɟă ȳzŸȝ ǰÊę ÈƐøø ş æÀǫèŭ
ÀƐĄţă ǴĤƞÀDZ – Ǵȝäø Âöä ǴƐŸõ

أ.د/ أحمد محمود همام
ȟÀÀǫţă ǴƜØdɟă ȳzŸȝ æÀǫèŭ
ÀƐĄţă ǴĬƞÀDZ – Ǵȝäø Âöä ǴƐŸõ

د/ محمد عبد الحميد سرور
ǴƐəäØ8öä ğÅȝÀAÔöä Æȝ ÀÊƞ æÀǫèŭ
ʔåäzöä ā zADZ ǴĬƞÀDZ –Ǵȝäø Âöä ǴƐŸõ

čċċđ

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ĞGŒGΣä ɔɳ̧Ü

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₡ƶɳ̧Æę Ȧţ ÀʌÆÖQöä ş ȷȦƶÀĦöä ş ÀȮÎöä ŌʌÂDZ ǰT ȳÆęÜ ş ȝȓäƶǫţä ŌŧĦöä äØŁ ƧÆŁÜ

ȯäƶù ŁǪĦDzì ş äKȝõ ŁǩȦƶÜ ĞŧŒę ğäæ ğäåȦìøÜ ş ǴəȦÔφ ş ğȦƮŒDZƶǩ ɒɳ̧

.ĞèäøÆöä

أبو الحمد السيد مهنى