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EFFECT OF STORAGE ON THE PHYSICAL AND CHEMICAL PROPERTIES OF RAPESEED *(Brassica napus)* OIL

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ABSTRACT: Biochemical evaluation of rapeseed oil was conducted to study the oil content, physical and chemical properties and stability of crude rapeseed oil. Rapeseed oil was extracted from seeds of Pactol variety grown at three different locations and for two successive seasons (2000 and 2001). The highest oil content was recorded in sample Eoynat's East, season 2001; (47.59 ± 0.18%) and the lowest oil content was found in sample Giza, season 2000; (43.35 ± 0.19%). The stability of rapeseed oil samples during storage at room temperature for 8 weeks was measured. The highest acid value was in sample Eoynat's East, season 2000; (3.33 ± 0.11 at zero time and 3.59 ± 0.09 after 8 weeks), peroxide value was in sample Eoynat's East, season 2001; (4.68 ± 0.08 at zero time and 40.37 ± 0.08 m.eq. /kg. after 8 weeks) and TBA was in sample Serw, season 2001; (20.65 ± 0.83 at zero time and 183.58 ± 1.31 after 8 weeks). The lowest acid value was in sample Serw, season 2000; (1.67 ± 0.03 at zero time and 3.15 ± 0.07 after 8 weeks), peroxide value was in sample Giza, season 2000; (3.17 ± 0.07 at zero time and 30.16 ± 0.08 m.eq. /kg. after 8 weeks) and TBA was in sample Eoynat's East, season 2000; (12.07 ± 0.80 at zero time and 170.24 ± 1.67 after 8 weeks).

Key words: Rapeseed, oil content, physical and chemical properties, stability

INTRODUCTION

Rapeseed or canola (*Brassica napus*) oil is recently among the oil crops in Egypt. The demand of lipids for human consumption or industry in Egypt is increased annuaily. The governmental policy to meet the increasing demands of relies on winter oily seed plants beside the already present summer oily crops.

Several researchers studied the oil of rapeseeds. for instance, content Adu – Peasah *et al.* (1993) found that, the ground canola seeds contains 46.9 % oil. Degenhardt *et al.* (1993) mentioned that rapeseed, varieties Eldorado and Tobin contained 42.2% and 40.9% oil respectively. Sosulski and Sosulski (1993) mentioned that, the oil percentage of Wester, Tobin and Horo cultivars of rapeseeds were 43.1, 42.2 and 44.10 %, respectively. Dunford and Temelli (1995) indicated that, the oil percentage of flaked rapeseeds was 43 %. Thobani and Diosady (1997) mentioned that, the total lipids of rapeseeds were 46.4 %. EL – Samanody (1998) found that the oil contents of different rapeseed varieties were in the range 40.30 – 44.96 %. Robertson *et al.* (2002) found that, oil content of canola was 40.5% - 46.1%.

Numerous studies were performed on the physical and chemical properties of rapeseed oil for example, Hammam (1992) found that, the specific gravity, refractive index, acid value, peroxide value, saponification value, and iodine value of rapeseed oil were 0.9132 – 0.941, 1.421 – 1.462, 0.30 – 0.33, 0.2 – 0.22, 190 – 192, and 109 – 112, respectively. Mahmoud (1995) found that, refractive index, iodine value, saponification value, acid value, and peroxide value of rapeseed oil were 1.4692 – 1.4723, 110 – 126, 186 – 193, 0.6 – 0.72 %, and 0.02 – 10 m.eq. /kg, respectively. El – Samanody (1998) found that, the refractive index, acid value, iodine value and peroxide value of different rapeseed varieties were (1.461 – 1.4644), (0.25 – 0.38), (107.8 – 116.1) and (0.27 – 0.41), respectively. McDonnell, *et al.* (1999) found that, the saponification value, acid value, and iodine value of rapeseed oil were 139.8, 2.8 and 152.5 respectively. Erhan *et al.* (2002) found that viscosity of canola was (1.3 - 4.7 mpas)

Yoon *et al.* (1985) mentioned that, a major cause of deterioration of lipid-containing

foodstuffs is known to be lipid oxidation. In spite of many assessments to measure the lipid oxidation in oils, no single method has been established to represent oxidative qualities of lipids because of the complexity of the reaction between lipids measured by chemical and physical methods. Among chemical methods peroxide value, TBA test, carbonyl compound, Kries test and anisidine value have been widely used. In the case of physical method, refractive index and chromatographic methods have been used to measure lipid oxidation. Podmore (1987) mentioned that palm oil has been a prominent fat oil resource for the food industry and oil blends due to several advantageous properties, such as high productively, low price, high thermal and oxidative stability and plasticity at room temperature. Teach (1993) showed that, the induction period is an expression of the stability of oils and fats towards oxidation. He found that, the stability (induction period) of palm olein, rapeseed oil and sunflower oil at 100 °C were 44.0, 11.5 and 6 hours respectively. El-Samanody (1998) found that, the stability of pure oils, palm oil, rapeseed oil and sunflower oil at 100 °C were 44.2, 49.2, 14.8 and 19.8 hours, respectively. Guillen and Cabo (2002) found that classic chemical methods for determining primary and secondary oxidation products, such as peroxide value and anisidine value, respectively were determined periodically. Changes observed in infrared data are useful indicators of edible oils oxidative stability and are closely related to changes observed in peroxide and anisidine values in the course of the oxidation of the oil samples. In the non-oxidized oil samples, the highest hydroperoxide concentration was found in safflower oil (10.9 m.eq /kg) whereas olive and rapeseed oils show similar concentrations (8.0 m. eq /kg and 9.0 respectively). In all samples peroxide value increased from the beginning of the oxidation experiment to reach a maximum value, after which a more or less pronounced decreasing of peroxide value was observed. In relation to non-oxidised oil samples the highest acid value was found for sunflower oil (3.7) followed by rapeseed oil (3.5) and olive oil (5.1), and the lowest acid value (1.1) was recorded for safflower; oil sample. The rate of acid value increase follows a general pattern in all oil

samples throughout the oxidation process.

MATERIALS AND METHODS

Materials:

Rapeseeds (*Brassica napus*), Pactol variety, were obtained from three regions, (i.e., Serw Research Station, Agriculture Research Center; Giza, Department of Oil Crops, Giza Research Station, Agriculture Research Center, Giza Department of Oil Crops, and El Eoynat's East farms of Ministry of Agriculture, in two successive seasons, 2000 and 2001.

Methods:

Rapeseed samples under investigation were cleaned from foreign matters and milled into small particles .The oil was extracted from the air-dried seeds by Soxhlet apparatus. The solvent was distilled off by rotatory evaporator at 40 – 50°C. The oil was dried over anhydrous sodium sulfate, filtered and stored at 5 °C until analysis.

Determination of oil content:

Dried samples of rapeseeds, (10g each), were extracted for 16h. in Soxhlet apparatus using petroleum ether (b.p.60-80°C). The extract was filtered. The filtrate was evaporated at 100°C. The resulting residue was heated to a constant weight. The oil content in proportion to weight of dried seeds was calculated.

The specific gravity and refractive index of oils were determined according to the method reported by A. O. A. C. (1990).

Viscosity of the oils was determined according to the method reported by Erhan *et al.* (2002).

Acid value, peroxide value, iodine value (Hanus method) and saponification value were determined according to the A. O. A. C. (1990).

Thiobarbituric acid value (TBA) value was determined according to the method of A.O.C.S. (1990).

Statistical analysis was conducted on the data of oil content, saponification, iodine, acid, peroxide and TBA values according to Snedecor (1976).

RESULTS AND DISCUSSION

Physical properties of rapeseed oil.

It is well known that physical properties of the oil are usually determined in order to assess their values. The most important physical characteristics of rapeseed oil produced from rapeseed Pactol variety cultivated in different origins in Egypt were determined and their values are recorded in Table (1). Refractive index is an important physical property and it is used for the estimation of saturation degree of the oil. The presence of a high concentration of unsaturated fatty acids in an oil lead to an increase in its refractive index. It is clear from these data that Giza, season 2001 was found to have the lowest refractive index (1.4662) and the highest value of oil produced from Eoynat's East, season 2001 which recorded (1.4687). The refractive index of other samples were Serw, season 2000; (1.4684), Serw, season 2001; (1.4682), Giza, season 2000; (1.4667) and Eoynat's East, season 2000; (1.4667). These results are in good agreement with those found by other investigators, El-Sayed (1987) and El-Samanody (1998). It is clear that the variety Giza, season 2001 have the lowest specific gravity (0.8956) and the highest value was recorded for Eoynat's East variety, season 2001 (0.9072) as shown in Table (1). The specific gravity values of other samples were Serw, season 2000; (0.9029), Serw, season 2001; (0.8986), Giza, season 2000; (0.9026) and Eoynat's East, season 2000; (0.8966). These results agreed with those reported by Gulbaran Tulbentci (1986) and Hammam (1992). The viscosity values of rapeseed oil under investigation are ranged from (Giza, season 2001) 3.96 mpas to (Eoynat's East, season 2001) 5.15 mpas as shown in Table (1). This property is mainly due to the long chain of their glyceride molecules. These results agreed with those reported by Erhan *et al.* (2002); (1.3 – 4.7 mpas). The viscosity, generally, slightly decreases with increase of the oil degree of unsaturation and with decrease in fatty acid molecular weights.

Chemical properties of rapeseed oil:

The chemical properties of the oil extracted from rapeseeds "Pactol variety" under study are shown in Table (2). The oil acid value determination is one of the best measurements of seed damage

and the acid value normally refers to the degree of hydrolysis or the free acidity of oil. The highest value of acid value was recorded in the variety Pactol Eoynat's East, season 2000 which was (3.33 ± 0.11), while the lowest value for variety Serw, season 2000 (1.67 ± 0.03). The results of the oil acidity is in good agreement with the findings of Diosady *et al.* (1982), Gulbaran Tulbentci (1986), McDonnell *et al.* (1999) and Guillen and Cabo (2002). The peroxide values in Table (2) show that the samples Giza, season 2000 and Eoynat's East, season 2000 were characterized by low peroxide values (3.17 ± 0.07 and 3.18 ± 0.06m.eq. /kg respectively). Meanwhile the variety Eoynat's East, season 2001 recorded the highest peroxide value which was (4.68 ± 0.08 m.eq. /kg). In this context, the long storage period of seeds induce high peroxide value in the seed oil, especially under unsuitable storage conditions. These data of the peroxide value are in agreement with those obtained by El Sayed (1987) and Mahmoud (1995).

The saponification value as clear from data in Table (2) varied according to the oil sample. The highest saponification was value recorded in sample Eoynat's East, season 2000 (187.52 ± 0.94) and the lowest value was (172.19± 1.36) found in Giza, season 2001. Other oil samples were Serw, season 2000; (180.94 ± 0.59), Serw, season 2001; (173.77± 0.97), Giza, season 2000; (177.77± 0.84) and Eoynat's East, season 2001; (187.12 ± 0.98). These data are similar to that found by Gulbaran Tulbentci (1986), El – Sayed (1987) and Mahmoud (1995). The iodine value indicates in general the degree of oil unsaturation. The iodine value of oil extracted from rapeseeds under investigation showed that the lowest iodine value was recorded in the sample Serw, season 2000; (92.02 ± 0.89) while the highest value recorded in the sample Eoynat's East, season 2001; (103.48 ± 0.56). Whilst, the iodine values for other samples were Serw, season 2001; 98.28 ± 0.81, Giza, season 2000; 102.05 ± 0.64, Giza, season 2001; 96.46 ± 0.24 and Eoynat's East, season 2000; 99.62 ± 0.27 These data were in agreement with those obtained by Gulbaran Tulbentci (1986); Hammam (1992) and El-Samanody (1998).

Oil content

Data in Table (3) show the oil content of rapeseed "Pactol variety" samples. The highest oil content was in sample Eoynat's East, season 2001; (47.59 ± 0.18%) and the lowest oil content was in sample Giza, season 2000; (43.35 ± 0.19%). While the oil content of other samples were Serw, season 2000; (46.16± 0.1%), Serw, season 2001; (44.44 ± 0.19%), Giza, season 2001; (46.44± 0.13%) and Eoynat's East, season 2000; (46.54 ± 0.13%). These results agreed with that obtained by Zadernowski and Sosulski (1978); (42-43.7%), Daun and Biely (1980); (40-43%), Embong and Jelen (1980); (46.2 - 46.3 %), Kondra *et al.* (1991); (43.7 - 43.8 %), Degenhardt *et al.* (1993); (40.9 - 42.2 %), Dunford and Temelli (1995); (43 %), Thobani and Diosady (1997); (46.4 %), El – Samanody (1998); (40.30 – 44.96%) and Robertson *et al.* (2002); (40.5 - 46.1%).

Effect of the Storage period on rapeseed oil stability

The oil samples were submitted to oxidative conditions under a constant airflow, in darkness at room temperature. Periodically, their peroxide value (PV), acid value (AV) and thiobarbituric acid value (TBA) were determined.

The changes in acid values of rapeseed oils during storage for 8 weeks at room temperature are shown in Table (4) and Figure (1). There was slow increase in the acid value with storage period from zero time to final time, The initial and final acid values for the various oil samples were Serw, season 2000; (1.67 – 3.15), Serw, season 2001; (1.75 – 3.29), Giza, season 2000; (2.65 – 3.57), Giza, season 2001; (2.18 – 3.86), Eoynat's East, season 2000; (3.33 – 3.59) and Eoynat's East, season 2001; (2.89 – 5.69). The increase in acid value is due to hydrolysis produced by microorganisms and moulds or by hydrolytic factors such as the lipases, commonly present. The highest AV was in Eoynat's East, season 2000; 3.33 ± 0.11and Eoynat's East, season 2001; 2.89 ± 0.10. The lowest AV was in Serw, season 2000; 1.67 ± 0.03and Serw, season 2001; 1.75 ± 0.06 samples. These values were nearly, similar to that found by Tulbentci (1986); (1.4 – 1.5) and Guillen and Cabo (2002); (3.5). Some authors indicated that these values are comparable only within

each oil type because initial AV varies among oil sources. Figure (1) shows that at the beginning of the storage period there was very small increase in AV, as in the case of Serw, season 2000 and Serw, season 2001 samples, to small values in Giza, season 2000 and Giza, season 2001 samples, or to significant values in Eoynat's East, season 2000 and Eoynat's East, season 2001 samples. After this there was a second stage where an increase in AV in all samples, especially in Eoynat's East, season 2000 and Eoynat's East, season 2001 samples.

The changes in peroxide value of rapeseed oils during storage for 8 weeks at room temperature are shown in Table (5) and Figure (2). The rate of hydroperoxide formation increased with the time. There was non-linear relationship between the peroxide value and storage period. There was a gradual increase in the PV of all oils from zero time to final time. The PV at the start and end of the storage period were Serw, season 2000; (4.19 – 32.33), Serw, season 2001; (4.10 - 40.70), Giza, season 2000; (3.17 –30.16), Giza, season 2001; (3.34 – 30.06), Eoynat's East, season 2000; (3.18 – 38.86) and Eoynat's East, season 2001; (4.68 to 40.37). At the beginning of the storage period, the highest hydroperoxide concentration was found in Eoynat's East, season 2001; (4.68 ± 0.08 m. eq. / kg), and the lowest hydroperoxide concentration was in Giza, season 2000; (3.17 ± 0.07 m. eq. / kg). These results were in agreement with that obtained by El-Sayed (1987), Mahmoud (1995) and Guillen and Cabo (2002). It is worth noting that the initial PV had no relationship to the rate at which these oil samples were degraded.

It is worth mentioning that Figure (2) shows, two different stages for hydroperoxide formation, i.e., during the first 14 days PV there was very slow increase in PV while 3 weeks till 8 weeks a pronounced increase in PV was observed.

The changes in the TBA values of rapeseed oils during storage for 8 weeks at room temperature are shown in Table (6) and Figure (3). There was a non-linear relationship between the TBA values and storage period. There was a very small increment in TBA value from zero time to 3rd week of storage. In all samples, TBA value was remarkably increased from the 3rd week of the oxidation experiment to one has to deduce that there was a

concomitant increase between PV and TBA during storage.

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Table (1): Physical properties of rapeseed oil produced from Pactol variety cultivated in Egypt

Variety	Refractive index at 25 °C	Viscosity at 25 °C / mpas	Specific gravity at 25°C, g / Cm^3
Serw, season 2000	1.4684	4.69	0.9029
Serw, season 2001	1.4682	4.10	0.8986
Giza, season 2000	1.4667	4.27	0.9026
Giza, season 2001	1.4662	3.96	0.8956
Eoynat's East, season 2000	1.4667	4.09	0.8966
Eoynat's East, season 2001	1.4687	5.15	0.9072

Table (2): Chemical properties of rapeseed oil produced from Pactol varieties cultivated in Egypt

Variety	Acid value	Peroxide value	Saponification value	Iodine value
Serw, season 2000	1.67 ± 0.03	4.19 ± 0.05	180.94 ± 0.59	92.02 ± 0.89
Serw, season 2001	1.75 ± 0.06	4.10 ± 0.07	173.77 ± 0.97	98.28 ± 0.81
Giza, season 2000	2.65 ± 0.07	3.17 ± 0.07	177.77 ± 0.84	102.05 ± 0.64
Giza, season 2001	2.18 ± 0.07	3.34 ± 0.06	172.19 ± 1.36	96.46 ± 0.24
Eoynat's East, season 2000	3.33 ± 0.11	3.18 ± 0.06	187.52 ± 0.94	99.62 ± 0.27
Eoynat's East, season 2001	2.89 ± 0.10	4.68 ± 0.08	187.12 ± 0.98	103.48 ± 0.56

Table (3): Oil content of rapeseeds produced from Pactol variety cultivated in Egypt

Variety	Oil content (%)
Serw, season 2000	46.16 ± 0.1
Serw, season 2001	44.44 ± 0.19
Giza, season 2000	43.35 ± 0.19
Giza, season 2001	46.44 ± 0.13
Eoynat's East, season 2000	46.54 ± 0.13
Eoynat's East, season 2001	47.59 ± 0.18

Table (4): - Acid value (AV) of rapeseed oil during storage period

Variety	Storage period (week)					
	Zero	1	2	3	5	8
Serw, season 2000	1.67 ± 0.03	2.24 ± 0.18**	2.32 ± 0.17**	2.35 ± 0.09**	2.93 ± 0.07**	3.15 ± 0.07**
Serw, season 2001	1.75 ± 0.06	2.36 ± 0.1**	2.62 ± 0.15**	2.69 ± 0.08**	2.77± 0.08**	3.29 ± 0.22**
Giza, season 2000	2.65 ± 0.07	3.16 ± 0.11**	3.23 ± 0.13**	3.32 ± 0.12**	3.52 ± 0.07**	3.57 ± 0.12**
Giza, season 2001	2.18 ± 0.07	2.88 ± 0.13**	3.02 ± 0.07**	3.13 ± 0.07**	3.23 ± 0.06**	3.86 ± 0.07**
Eoynat's East, season 2000	3.33 ± 0.11	4.76± 0.05**	4.95± 0.11**	5.31 ± 0.07**	5.42 ± 0.07**	5.59 ± 0.09**
Eoynat's East, season 2001	2.89 ± 0.10	4.62 ± 0.08**	4.83 ± 0.06**	5.01` ± 0.07**	5.21± 0.08**	5.69 ± 0.06**

** Significant at 0.01

Table (5): - Peroxide value (PV) of rapeseed oil during storage period

Variety	Storage period (week)					
	Zero	1	2	3	5	8
Serw, season 2000	4.19 ± 0.05	8.42 ± 0.07**	12.42 ±0.06**	19.08 ± 0.07**	25.39 ± 0.06**	32.33 ± 0.06**
Serw, season 2001	4.10 ± 0.07	13.36 ± 0.05**	18.59±0.07**	25.14 ± 0.06**	30.19 ± 0.07**	40.70 ± 0.07**
Giza, season 2000	3.17 ± 0.07	10.11 ± 0.09**	15.23 ±0.08**	20.79 ± 0.08**	22.86 ± 0.08**	30.16 ± 0.08**
Giza, season 2001	3.34 ± 0.06	10.13 ± 0.07**	15.24± 0.08**	18.17 ± 0.08**	22.08 ± 0.08**	30.06 ± 0.07**
Eoynat's East, season 2000	3.18 ± 0.06	12.57 ± 0.07**	18.81 ±0.06**	21.77 ± 0.07**	31.43 ± 0.08**	38.86 ± 0.09**
Eoynat's East, season 2001	4.68 ± 0.08	12.81 ± 0.08**	19.07 ±0.07**	23.19 ± 0.08**	32.14 ± 0.09**	40.37 ± 0.08**

* Significant at 0.05
** Significant at 0.01

Table (6): - Thiobarbituric acid value (TBA) of rapeseed oil during storage period

Variety	Storage period (week)					
	Zero	1	2	3	5	8
Serw, season 2000	16.23 ± 0.10	53.84 ± 1.45**	54.40 ± 1.17**	64.03 ± 1.20**	130.16 ± 2.24**	166.67 ± 1.54**
Serw, season 2001	20.65 ± 0.83	55.59 ± 1.57**	56.79 ± 1.79*	83.07 ± 1.45**	121.65 ± 1.97**	183.58 ± 1.31**
Giza, season 2000	14.07 ± 0.55	53.19 ± 1.28**	56.79 ± 1.50**	64.04 ± 2.14**	144.38 ± 2.40**	179.4 ± 2.18**
Giza, season 2001	12.63 ± 0.83	46.81 ± 1.63**	50.77 ± 1.64**	65.16 ± 2.13**	134.85 ± 2.93**	176.49 ± 1.08**
Eoynat's East, season 2000	12.07 ± 0.80	38.29 ± 1.17**	46.22 ± 1.61**	50.52 ± 1.75**	115.86 ± 1.53**	170.24 ± 1.67**
Eoynat's East, season 2001	14.01 ± 1.22	63.24 ± 1.81**	68.80 ± 1.26**	75.24 ± 1.60**	143.72 ± 1.30**	185.6 ± 1.19**

* Significant at 0.05
** Significant at 0.01

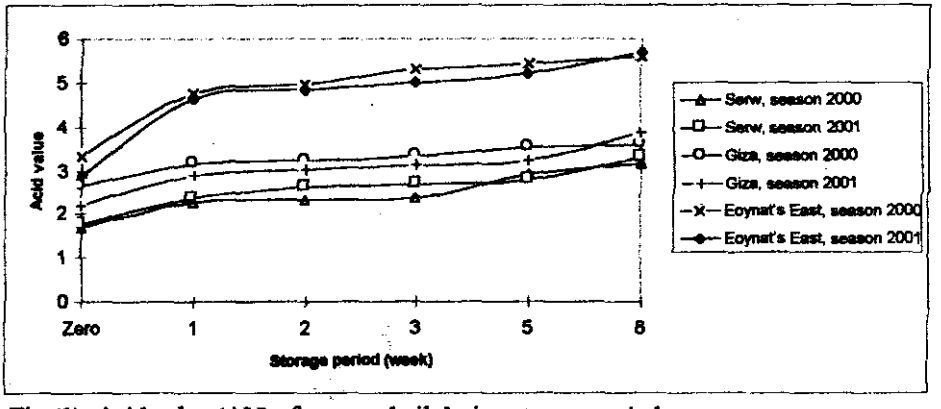

Fig (1): Acid value (AV) of rapeseed oil during storage period

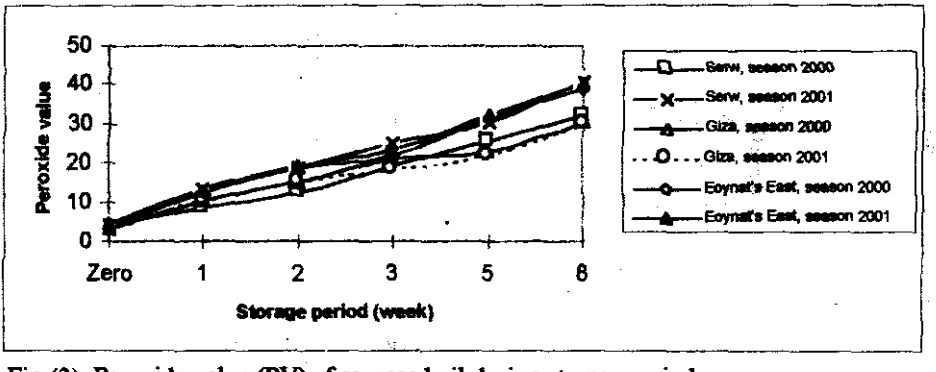

Fig (2): Peroxide value (PV) of rapeseed oil during storage period

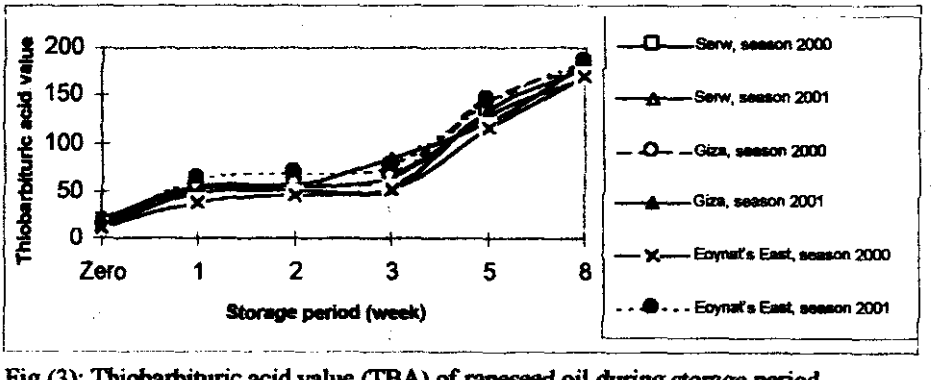

Fig (3): Thiobarbituric acid value (TBA) of rapeseed oil during storage period

تأثير التخزين علي الخواص الطبيعية والكيميائية لزيت بذرة الشلجم

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أجريت هذه الدراسة على زيت بذرة الشلجم صنف باكتول تمت زراعته في ثلاث مناطق مختلفة محطة السرو ، محطة الجيزة وشرق العوينات خلال موسمي الزراعة ٢٠٠٠، ٢٠٠١ وذلك لدراسة الخواص الطبيعية والكيميائية للزيت وكذلك على درجة ثبات الزيت أثناء التخزين لمدة شهرين. وكان أعلى محتوى زيت لصنف شرق العوينات موسم ٢٠٠١ (٤٧,٥٩ ± ٠,١٨%) وأقل قيمة لصنف جيزة موسم٢٠٠٠ (٤٣,٣٥ ± ٠,١٩%) وأظهرت النتائج الخاصة بدراسة تأثير فترة التخزين على ثبات الزيت حيث كان أعلى قيمة في رقم الحمض لصنف شرق العوينات موسم ٢٠٠٠ (٣,٣٣ ± ٠,١١ -٣,٥٩ ± ٠,٠٩) وأقل قيمة لرقم الحمض في صنف سرو موسم ٢٠٠٠ (١,٦٧ ± ٠,٠٣ -٣,١٥ ± ٠,٠٧) وأعلى قيمة لرقم البروكسيد لصنف شرق العوينات موسم ٢٠٠١ (٤,٦٨ ± ٠,٠٨ ٤٠,٣٧ ± ٠,٠٨ ملليمكافئ/كجم) وأقل قيمة لرقم البيروكسيد لصنف جيزة موسم٢٠٠٠ (٣,١٧ ± ٠,٠٧ -٣٠,١٦ ± ٠,٠٨ ملليمكافئ/كجم) وكانت أعلى قيمة لرقم الثيوباربيتيوريك لصنف سرو موسم ٢٠٠١ (٢٠,٦٥ ± ٠,٨٣ -١٨٣,٥٨ ± ١,٣١) وأقل قيمة لثيوباربيتيوريك لصنف شرق العوينات موسم ٢٠٠٠ (١٢,٠٧ ± ٠,٨ - ١٧٠,٢٤ ± ١,٦٧).