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Evaluation of Egyptian Cottonseed, Sunflower and Canola Oils .

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Abstract:

This study was carried out to evaluate the physico-chemical properties, fatty acid composition and unsaponifiable matter of sunflower, cottonseed and canola oils. The obtained results showed a slight variation in specific gravity and refractive index between the studied oil samples. Also, the results indicated that the color of cottonseed oil was darker or higher (5.4 red and 35 yellow) than the other oil samples. In contrast, the sunflower oil recorded the lowest value of color . Canola oil was recorded the highest acid value while the lowest value was observed in sunflower seed oil. The iodine values were 122.68, 110.30 and 109.00 for sunflower, cottonseed and canola oils, respectively. The cottonseed oil recorded the highest value of saponification (194.21) while the lowest value was noticed in canola oil (185.45). The peroxide value was 0.89, 6.65 and 1.75 meq. peroxide/kg sample in sunflower, cottonseed and canola oils, respectively. The highest TBA value was recorded in canola oil (1.20 mg malonaldehyde/kg sample). In contrast, the sunflower oil showed the lowest TBA value (0.21). The obtained results revealed that the investigated oil samples had a comparable content of unsaponifiable matter. The data of fatty acid composition revealed that Canola oil contains the lowest value of the TSFA while the cottonseed oil showed the highest value of TSFA . In contrast, the cottonseed oil contained the lowest value of TUFA while the sunflower and canola oils recorded the highest value of TUFA, respectively. Unsaponifiable matters of sunflower oil were fractionated by GLC technique. It consisted mainly of hydrocarbons and sterols. The total hydrocarbons content was 23.35% . It could be arranged the hydrocarbons based on total hydrocarbon in a descending order as follows: C28, C23, C24, C16, C20, C26, C21, C30, C25, C22, C18 and C14. The total sterols was 76.65% .β-sitosterol was the major sterol fraction followed by stigmasterol and campsterol .

Introduction:

The oil industry is one of the most important food industries that needs great attention during processing, transport, handling and storage of products. The functions of oils and fats fall into two distinct parts, technically and

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nutritional. Technologically, oils and fats play various roles in foods. They are usually used in frying, cooking, salad oils and mayonnaise (Swern, 1979). In Egypt, cottonseed oil, soybean and sunflower oils are considered as a major sources of vegetable oils. Hence, they are used for several purposes, i.e. salad, cooking and frying oils. The production of vegetable oils in Egypt is not sufficient to consumption. There is a great shortage in the edible oils and large amounts are annually imported to cover the shortage in local production market. Many investigators studied the physical and chemical properties of traditional and untraditional oils 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 (Eskander, et al., 1984, Rady, et al., 1990; El-Dein, 1999; El-Sharnouby, 1999; ; Mehanni, 2006 and Mehany, 2007). The present study was aimeded to determine the physical properties, chemical characteristics , fatty acid composition and unsaponifiable matter content of sunflower, cottonseed and canola oils.

Materials and Methods

Materials:

Oils samples:

Fresh refined, bleached and deodorized sunflower oil, used in this investigation was obtained from Oil Company at 6 October city (The trade name for this type of oil is "Wasfa").

The other oil samples used in this study were cotton seed 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.

Analytical methods:

Physical properties of oils:

Specific gravity (Sp. Gr.),refractive index and color for oil samples were determined according to the AOCS official methods (1998).

Chemical characteristics of oils:

Acid value (A.V.),peroxide value,iodine value ,saponification value and thiobarbituric acid value were determined as outlined in AOCS(1998).

Fatty acid composition :

Preparation of fatty acid methyl esters:

Fatty acids of the standard and samples were converted to methyl ester according to Vogel (1975).

Identification of fatty acids:

The methyl esters of the fatty acids and standard samples were analyzed by using a GLC Rye-unicam Pro-GLC. The gas liquid chromatography equipped with a dual flam ionization detected (F.I.D.). The nitrogen (N2), hydrogen (H2) 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 m x 4 mm packed with diatomate C (100-120 mesh) and coated with 10% polyethylene glycol adipate (PEGA). The operation was carried out by programming, the initial temperature 70°C, rate temperature 8°C/min., the final temperature 190°C, the final time 35 min., the injectior temperature 250°C and the detector temperature 300°C.

The presented fatty acids were identified according to an authentic sample of fatty acids chromatographed under the same conditions. Finally, fatty acids peaks were performed by comparing the relative retention time of each peak with those of standard samples.

unsaponifable matters analysis:

Separation of the unsaponifiable matters:

The unsaponifiable matters were separated from the vegetable oil samples under investigation after saponification according to the method outlined in the AOCS (1998).

Identification of the unsaponifiable matter components by gas liquid chromatography:

The unsaponifiable matters (hydrocarbons and sterols) were identified by using a Hewlett Packard gas chromatography model 5890 equipped with a flame ionization detector in the presence of nitrogen as carrier gas. The separation was carried out at 100-280°C (temperature rate 5°C/min) followed by 20 min. at 280°C. The column used for separation was 25 x 0.2 mL.D. fused silica capillary column coated with dimethyl silicaon fluid. The injector and detector temperatures were 250 and 300°C, respectively. The sample size was 1 µL. The authentic samples of hydrocarbons and sterols were also injected under the same conditions and the relative retention times (R.R.T) were calculated. The peaks were identified by comparing their retention times with those of stand and under the same conditions. Retention times were determined by using Hewlet Packared 3392 integrator.

Results and Discussion

Physical properties and chemical characteristics of sunflower, cotton seed and canola oils:

The physical and chemical characteristics of oils and fats play an important role and established its capability of application in either nutrition or industry. So, some: of them give a good idea about the quality of these products. Some of physical and chemical properties of sunflower, cottonseed and canola oils were determined and the obtained results are shown in Table (1). It can be observed from the results that the specific gravity at 25°C of the studied oil samples were 0.9173, 0.9159 and 0.9101 in sunflower, cottonseed and canola oils, respectively. The change in Sp. Gr. is depending on the chain length, the degree of unsaturation and the temperature. The present findings are in

the same line with those reported by Swern (1979), TNSA (1988), Hui (1996), EOSQC (1997), AOCS (1998), Fadia (2004), O'Brien (2004), EOSQC (2005),Mehany (2007) and Mahanni (2010).

The refractive index (R.I.) of fats and oils is an important characteristic because of the ease and speed with which it can be determined precisely, the small quantity of sample needed, and its relationship, to structure. It is useful for identification purposes and for establishing purity and also for observing the progress of reactions, such as catalytic hydrogenation and isomerization (Swern 1979 ; Hui 1996 and O'Brien 2004). As shown in Table (1) the results revealed that the refractive index of the studied oil samples can be arranged in the following descending order: sunflower oil (1.4735 at 25°C), cottonseed oil (1.4689 at 25°C) and canola oils (1.4680 at 25°C). Such differences in R.I. levels might be mainly due to the variation in the length of the hydrocarbon chain and the number of double bonds. These results obtained herein are in a general accordance with Weiss (1970); Eskander (1974); Van Oss (1975); Habib (1986); AOSC (1998); Francis (2000); Ibrahim (2000); Fadia (2004) and Mehanni (2006). In this direction, Hui (1996) mentioned that the R.I. of fats and fatty acids increased with increasing the length of the hydrocarbon chain. Also, it was increased with the number of double bonds and with increase in conjugation.

As for color (another indicator of quality) of the investigated sunflower, cottonseed and canola oils, it was found to be 3.5, 5.4 and 5.2, respectively in the red scale while yellow scale is fixed at 35.00 in one inch cell. These results obtained herein are in a general accordance with Swern (1979) who mentioned that the good cottonseed oil may readily be refined to a color on the Lovibond scale of 35.00 yellow and 4.0 to 7.0 red. These differences in color intensity 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 period under unfavorable temperature and moisture conditions and exposed to air oxidation yield darken colored oils than fresh seeds. Dark color may also be caused by high cooking temperature, partially by oxidation of the oil, and partially by color bodies extracted by the hot oil from the seed and seed coat. Such results are in agreement with those secured by Rich (1967); Weiss (1970); Gega and Dodbiba (1971); Swern (1979); Eskandar and Banu (1982); Abdo (1999) and Mehanni (2006 & 2010).

It is a well know fact that the color development in an oil is

very much associated with oxidation that could be take place due to exposure to air, presence of pro-oxidant, improper processing and mishandling (Johari, 1996). In this direction, Kathleen (1998) reported that in requirement for good quality processed fats and oils, the oils should meet quality standard for physical properties such as moisture and color.

On the basis of acid value of the investigated oil samples, the results obtained in Table (1) noted that the highest acid value (mg KOH/g oil sample) was recorded in canola oil (0.49) while, the lowest acid value was observed in sunflower seed oil (0.05). In addition, the acid value of cottonseed oil was 0.14. These results are in harmony with EOSQC (1997 and 2005); Codex (2004) and Mehany (2007). The variation in acid value could be attributed to the differences in the degree of hydrolysis of some phosphatides and triglycerides and the liberation of free fatty acids. In addition, to the formation of free fatty acids during oxidation as a result of cleavage and oxidation of double bonds. Also, the differences in acid value may be due to the conditions during ripening of the oil 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 Swern (1979); Eskandar and Banu (1982); Hui (1996); Ibrahim (2000); Fadia (2004); Mehanni (2006) and Mehany (2007).

Table (1): Physical properties and chemical characteristics of sunflower, cottonseed and canola oils.

Characteristic*	Type of oil		
	Sunflower	Cottonseed	Canola
Specific gravity at 25/25°C (Sp. Gr.)	0.9173	0.9159	0.9101
Refractive index at 25°C (R.I.)	1.4735	1.4689	1.4680
Color: lovibond (Y/R), one inch cell	35/3.5	35/5.4	35./5.2
Acid value A.V. (as mg KOH/g oil)	0.05	0.14	0.49
Iodine value I.V. (hanus) (g. iodine saturate/100 g oil)	122.68	110.30	109.65
Saponification value (S.V.) (mg. KOH saponify g. of oil)	190.33	194.21	185.45
Peroxide value (P.V.) (meq. Peroxide/ kg oil)	0.89	6.65	1.75
Thiobarbituric acid (T.B.A.) (mg. malonaldehyde/kg sample)	0.21	0.68	1.20
Unsaponifiable matter (%)	1.03	1.07	0.93

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

Concerning the iodine value (I.V.), the data obtained in Table (1) indicated that the iodine values of sunflower, cottonseed and

canola oil samples were 122.68, 110.30 and 109.65, 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); EOSQC (1997 and 2005); Ibrahim (2000); Codex (2004); Mehany (2007) and Mehanni (2010).

As for the saponification value (mg KOH saponify g. oil), the results in Table (1) revealed that the cottonseed oil recorded the highest saponification value (194.21) while, the lowest value was observed in canola oil (185.45). These differences in S.V. 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 Van Oss (1975); Egan et al (1981); Eskandar and Banu (1982); TNSA (1988); EOSQC (1997 and 2005); AOCS (1998); Codex (2004); Ethel, et al. (2004) and Mehany (2007).

Oxidative rancidity is the principal problem in fats and oils. Two determination: 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 (1) indicated that the peroxide value (P.V.) was 0.89, 6.65 and 1.75 meq. Peroxide/kg sample in sunflower, cottonseed and canola seed oils, respectively. The results indicated also that the P.V. of oil samples used in this study were below the permissible limits of 10 milliequivalent of peroxide/kg sample EOSQC (1997 and 2005) and Codex (2004).

Concerning the aldehyde development as shown by the thiobarbituric acid (TBA) which is considered as a more reliable indicator of oxidative rancidity (Jacobson, 1967 and Hui, 1996) the results presented in Table (1) showed that the TBA values varies with the kind of oil. It can be observed from the results obtained in Table (1) that the highest TBA value was recorded in canola oil (1.20 mg. malonaldehyde/kg sample). In contrast, the sunflower seed oil showed the lowest TBA value (0.21). This variation in TBA value may be to the differences in chemical constituents of oil sample. These results are in coinciding with those reported by Egan et al (1981), Iskander (1992); Hui (1996) 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 the results in Table (1) that the oil samples under investigation had comparable

content of unsaponifiable matter (1.03%, 1.07% and 0.93%) for sunflower, cottonseed and canola oils, respectively). These finding are in the same line with those recorded by Itoh, et al. (1973); Van Oss (1975); TNSA (1988); EOSQC (1997 & 2005); AOCS (1998); Codex (2004); O'Brien (2004) and Mehanni (2007).

- Fatty acid composition:

The results presented in Table (2) showed the fatty acid composition of sunflower, cottonseed and canola oils. The data obtained by gas liquid chromatography (G.L.C.) analysis pointed out that the major fatty acids were oleic and linoleic which represented 29.60-58.87 and 26.50-51.50%, respectively, followed by palmitic acid (4.40-16.05%), stearic acid (1.55-5.19%), arachidic acid (0.25-0.54%), behenic acid (0.15-0.52%) and linolenic acid which it ranged between 0.25 and 6.15%. In addition, the data given in Table (2) indicated that the total amount of saturated fatty acids (TSFA) was ranged between 6.59% in canola oil and 20.08% in cottonseed oil while, the total amount of unsaturated fatty acids (TUFA) ranged from 79.92% (in cottonseed oil) to 93.41% (in cauola oil. These results obtained herein are in general accordance with those reported by Cummins et al. (1967); Fedeli et al. (1971); Morrison and Robertson (1978); Morrison (1983); Purdy (1985); Sridhar et al. (1991); EOSQC (1997 and 2005); AOCS (1998); Lampi et al. (1999); Francis (2000); Ibrahim (2000); Codex (2004); O'Brien (2004); Mehany (2007) and Mehanni (2010).

Generally, it can be concluded from the results obtained in Table (2) that the canola oil contains the highest percentage of oleic acid (58.87%), while the sunflower and cottonseed oils contains 30.19 and 29.60%, respectively.

- The sunflower seed oil contained the highest percentage of C18:2 (51.50%) while the canola oil contains the lowest value (26.50%).
- There were little differences in the amount of palmitic acid and stearic acid between the investigated oil samples.Small percentages of arachidic, behenic and linolenic acids were peresent in the examined oils.
- Canola oil contained the lowest value of the TSFA (6.59%). In contrast, the cottonseed oil showed the highest percentage (20.08%). On the other hand, the cottonseed oil contains the lowest value of TUFA (79.92) while, the canola oil contained the highest percentage (93.41%).

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 linoleic acid and low content of saturated fatty acids play an important role in preventing or inhibition of atheroscle- rotic 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) showed 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 (2) showed also, a linear relation between iodine value and linoleic acid content. At the same time, it was observed an invers relationship between oleic content and linoleic acid content such results and conclusions agree with those reported by Spencer et al. (1976); Eskandar and Banu (1982) and Mehany (2007).

Table (2): Fatty acid composition of sunflower, cottonseed and canola oils (wt. % of total fatty acids).

Fatty acids %		Type of oil		
		Sunflower	Cottonseed	Canola
Saturated fatty acids (SFA)				
Myristic	$C_{14:0}$	0.40	0.83	0.15
Palmitic	$C_{16:0}$	10.45	16.05	4.40
Stearic	$C_{18:0}$	5.19	2.60	1.55
Arachidic	$C_{20:0}$	0.54	0.25	0.34
Behenic	$C_{22:0}$	0.52	0.35	0.15
Total saturated fatty acids (TSFA)		**17.10**	**20.08**	**6.59**
Unsaturated fatty acids (UFA)				
Monounsaturated fatty acids (MUFA)				
Palmitoleic	$C_{16:1}$	00.39	1.25	0.30
Oleic	$C_{18:1}$	30.19	29.60	58.87
Gadoleic	$C_{20:1}$	00.25	0.14	1.44
Erucic	$C_{22:1}$	---	0.10	0.15
Total MUFA		**30.83**	**31.09**	**60.76**
Polyunsaturated fatty acids (PUFA)				
Linoleic	$C_{18:2}$	51.50	48.58	26.50
Linolenic	$C_{18:3}$	00.57	00.25	6.15
Total PUFA		**52.07**	**48.83**	**32.65**
Total unsaturated fatty acids (TUFA)		**82.90**	**79.92**	**93.41**
TUFA : TSFA		**4.85**	**3.98**	**14.17**
$C_{18:2} : C_{18:1}$		**1.71**	**1.84**	**0.45**

Unsaponifiable matters of sunflower oil:

The results present in Table (3) illustrate the GLC analytical results of unsaponifiable matters of sunflower seed oil. From the tabulated data it could be observed that the known unsaponifiable matters consisted mainly of hydrocarbons and sterols. It was noticed that the total hydrocarbons content represent 23.35% of the total unsaponifiable matter. It could be arranged the hydrocarbons based on total hydrocarbon in a descending order as follows: C28, C23, C24, C16, C20, C26, C21, C30, C25, C22, C18 and C14.

Data present in Table (3) showed that the total sterols of the unsaponifiable matters of sunflower oil was 76.65% of the total unsaponifiable matters. The β-sitosterol was the major sterol fraction of total sterol followed by stigmasterol and campsterol. The percentage of β-sitosterol was 52.83% while the values of stigmasterol and campesterol were 14.87 and 8.95% of the total unsaponifiable matters, respectively. These results are in the same line with those recorded by Itoh et al. (1973), Swern (1979) and Hui (1996) who mentioned that the vegetable oil sterols are known collectively as phytosterols. Two of the most common phytosterols are β-sitosterol and stigmasterol. These results also, are in accordance with those reported by Vlahakis and Hazebroek (2000); Fadia (2004) and Mehany (2007).

Table (3): Unsaponifiable matters content (hydrocarbons and sterols) of sunflower seed oil (% of the total unsaponifiable matters).

Fractions		Unsaponifiable matter%
A- Hydrocarbons		
n-Tetradecane	C_{14}	0.34
n-Hexadecane	C_{16}	2.15
n-Octadecane	C_{18}	0.54
n-Eicosane	C_{20}	1.93
n-Uncosane	C_{21}	1.51
n-Docosane	C_{22}	1.05
n-Tricosane	C_{23}	4.46
n-Tetracosane	C_{24}	2.16
n-Pentacosane	C_{25}	1.07
n-Hexacosane	C_{26}	1.81
n-Octacosane	C_{28}	5.08
n-Triacontane	C30	1.25
Total hydrocarbons		**23.35**
B-sterols		
Campsterol		8.95
Stigmasterol		14.87
β-sitosterol		52.83
Total sterols		**76.65**

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تقييم زيوت بذرة القطن ودوار الشمس والكانولا المصرية

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تهدف هذه الدراسة لعمل مقارنة لبعض الخواص الطبيعية والكيماوية وتركيب الأحماض الدهنية والمواد الغير قابلة للتصبن لزيوت عباد الشمس وبذرة القطن والكانولا.أظهرت نتائج دراسة الخواص الطبيعية وجوداختلاف بسيط فى الوزن النوعي ومعامل الانكسار للزيوت تحت الدراسة،أما بالنسبة للون فقد أوضحت النتائج أن زيت بذره القطن كان أكثر دكانة (5.4 أحمر، 35 أصفر) ، بينما سجل زيت عباد الشمس أقل قيمة لونية.كما أظهرت نتائج دراسة الخواص الكيماوية تسجيل أعلى قيمة للحموضة لعينات زيت الكانولا ،بينما سجلت أقل قيمة للحموضة لزيت بذرة عباد الشمس.و أظهرت نتائج الرقم اليودى للزيوت تحت الدراسة أن الرقم اليودي لزيت عباد الشمس(122.68)، يليه زيت بذرة القطن (110.30) ،ثم زيت الكانولا (109.00) ، بينما سجلت النتائج أعلى رقم تصبن لزيت بذرة القطن بينما سجل زيت الكانولا أقل رقم تصبن . و كانت نتائج رقم البيروكسيد ارتفاعه فى زيت بذرة القطن ثم الكانولا ثم زيت عباد الشمس على الترتيب،بينما سجلت النتائج أعلى أرقام لحامض الثيوبريتيوريك .T.B.A لزيت الكانولا،و أقل رقم لزيت عباد الشمس. أوضحت النتائج المتحصل عليها أن الزيوت تحت الدراسة أعطت أرقام متقاربة للمواد الغير قابلة للتصبن (الهيدروكربونات، الاستيرولات، الفيتامينات والصبغات).أظهرت نتائج تقدير الأحماض الدهنية أن زيت الكانولا يحتوى على أقل نسبة من الأحماض الدهنية المشبعة الكلية بينما سجل زيت بذرة القطن أعلى تركيز للأحماض الدهنية المشبعة الكلية وعلى العكس من ذلك سجل زيت بذرة القطن أقل تركيز للأحماض الدهنية الغير مشبعة الكلية بينما سجل زيت عباد الشمس والكانولا تركيزات أعلى على الترتيب،وكان الحامض السائد هو حامض الأوليك فى زيت الكانولا، حامض اللينوليك فى زيت عباد الشمس وزيت بذرة القطن.وبينت نتائج تقدير المواد الغير قابلة للتصبن أن الهيدروكربونات والاستيرولات المكون الرئيسى للمواد الغير قابلة لتصبن بزيت عباد الشمس،و تمثل الهيدروكبرونات (23.35%) من المواد الغير قابلة للتصبن ويمكن ترتيبها تنازلياً كالآتي: C18, C22, C25, C30, C21, C26, C20, C16, C24, C23, C28وأخيراً C14،بينما تمثل الاستيرولات الكلية (76.65%) من المواد الغير قابلة للتصبن ويعتبر البيتا سيتو استيرول أعلى المكونات يليه استيجما استيرول ثم الكامب ستيرول.