OPEN ACCESS

GAVIN PUBLISHERS

Current Research in
Bioorganic & Organic Chemistry

Research Article

Elshiekh MMA. Curr Res Bioorg Org Chem: CRBOC-106.
DOI: 10.29011/CRBOC-106. 100006

The Effect of Ultra Violet Radiation on Sunflower Seeds and the Edibility of the Extracted Oil

Mutaz Mohamed Ahmed Elshiekh*

Department of Chemistry, Ahfad University for Women, Ahfad Center for Science and Technology, Omdurman, Sudan

***Corresponding author:** Mutaz Mohamed Ahmed Elshiekh, Department of Chemistry, Ahfad University for Women, Ahfad Center for Science and Technology, Omdurman, Sudan. Tel: +249920790284; Email: elshiekhmutaz@gmail.com

Citation: Elshiekh MMA (2018) The Effect of Ultra Violet Radiation on Sunflower Seeds and the Edibility of the Extracted Oil. Curr Res Bioorg Org Chem: CRBOC-106. DOI: 10.29011/CRBOC-106. 100006

Received Date: 21 February, 2018; **Accepted Date:** 06 April, 2018; **Published Date:** 12 April, 2018

Abstract

The work dealt with relationship between exposing the sunflower seeds to the ultra violet radiation of the sun and the oxidative spoilage of the produced oil. The standards used were the acid and peroxide values compared with the recommended codex for edible sunflower oil [1]. The main analytical technique used was The Gas Liquid Chromatography (G.L.C.). The standard fatty acids used to construct the (G.L.C.) chromatogram were the Palmitic. (16:0), Stearic (18:0), Oleic (18:1) and Linoleic (18:2) acids. Percentage areas under the peak for each of the four acids were used as a comparative quantitative analysis. Commercial sunflower seeds were subjected to the U.V. radiation of the sun. With increase the exposure time the acid value was found to increase, while the peroxide value was found to increase gradually in the beginning of the exposure, sharp increase then followed the ratio of methyl Linoleate versus methyl Oleate was found to decrease gradually with increase of the exposure period. Methyl Palmitate and methyl Stearate were affected considerably. The maximum period of time for exposure of the seeds to U.V. radiation of the sun was found to be six months beyond which the produced oil was found to be inedible. The results found were discussed and suitable conclusions were drawn.

Keywords: Acid Value; Peroxide Value and Chromatography; Rancidity; Sunflower

Introduction

Fatty Acids

Fatty acids are carboxylic acids with a long hydrocarbon chain. Fatty acids (FA) differ from one another in: Length of the hydrocarbon tails. Degree of unsaturation (double bond). Position of the double bonds in the chain

Unsaturated and Saturated Fatty Acids

Unsaturated Fatty Acids contain at least one double bond Generally unsaturated fatty acids are in the cis conformation double bonds [1].

Nomenclature of Fatty Acids

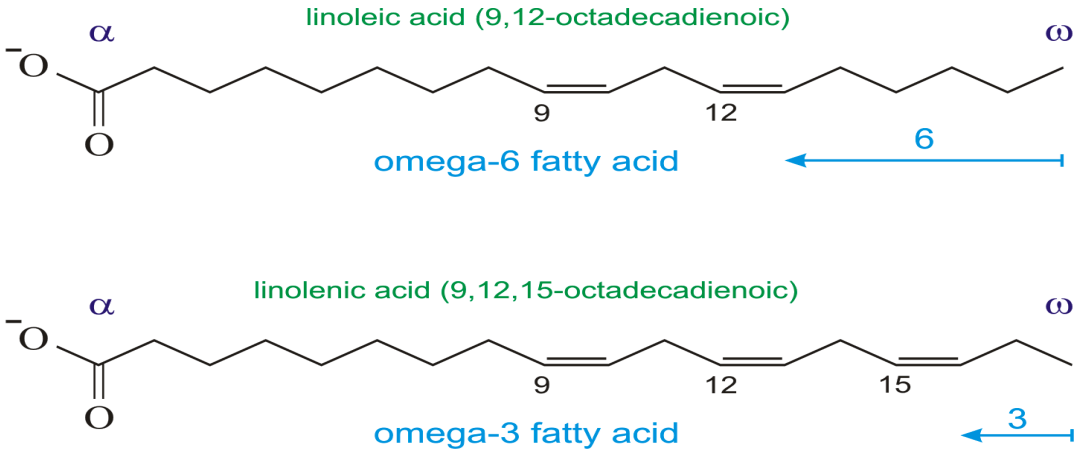
Most fatty acids have 12 to 20 carbons. Most chains have an even number of carbons (synthesized from two-carbon units). For IUPAC nomenclature carboxyl carbon is C-1. For Common nomenclature the prefixes α,β,γ,δ, ω are used . Carbon farthest from carboxyl is ω. Double bonds are generally cis. Position of double bonds indicated by Δn, where n indicates lower numbered carbon of each pair. Shorthand notation (total # carbons: # double bonds, Δ double bond positions) (Table 1). Example: (20:4Δ5,8,11,14)

Number of carbons	Number of double bonds	Common name	IUPAC name	Melting point, °C	Molecular formula
12	0	Laurate	Dodecanoate	44	$CH_3(CH_2)_{10}COO^{\ominus}$
14	0	Myristate	Tetradecanoate	52	$CH_3(CH_2)_{12}COO^{\ominus}$
16	0	Palmitate	Hexadecanoate	63	$CH_3(CH_2)_{14}COO^{\ominus}$
18	0	Stearate	Octadecanoate	70	$CH_3(CH_2)_{16}COO^{\ominus}$
20	0	Arachidate	Eicosanoate	75	$CH_3(CH_2)_{18}COO^{\ominus}$
22	0	Behenate	Docosanoate	81	$CH_3(CH_2)_{20}COO^{\ominus}$
24	0	Lignocerate	Tetracosanoate	84	$CH_3(CH_2)_{22}COO^{\ominus}$
16	1	Palmitoleate	*cis*-Δ^9-Hexadecenoate	−0.5	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COO^{\ominus}$
18	1	Oleate	*cis*-Δ^9-Octadecenoate	13	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COO^{\ominus}$
18	2	Linoleate	*cis,cis*-$\Delta^{9,12}$-Octadecadienoate	−9	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COO^{\ominus}$
18	3	Linolenate	all*cis*-$\Delta^{9,12,15}$-Octadecatrienoate	−17	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COO^{\ominus}$
20	4	Arachidonate	all*cis*-$\Delta^{5,8,11,14}$-Eicosatetraenoate	−49	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COO^{\ominus}$

Table 1: Commonly used fatty acids.

Omega3 and Omega 6 fatty acids

Omega-6 fatty acids (also referred to as ω-6 fatty acids or n-6 fatty acids) are a family polyunsaturated fatty acids that have in common a final carbon-carbon double bond in the n-6 position, that is, the sixth bond, counting from the methyl end. Omega-3 fatty acids-also called ω-3 fatty acids or n-3 fatty acids are Polyunsaturated Fatty Acids (PUFAs) with a double bond (C=C) at the third carbon atom from the end of the carbon chain [2].

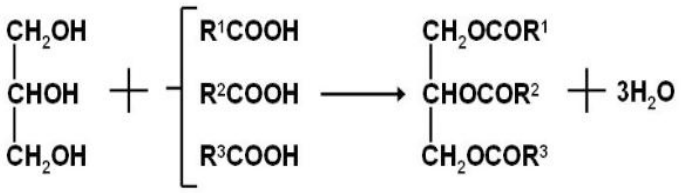


Lipids

Lipids are molecules that can be extracted from biological tissue with a nonpolar solvent. Lipids are essential components of all living organisms. Lipids are water insoluble organic compounds. They are hydrophobic (nonpolar) or amphipathic (containing both nonpolar and polar regions) [3].

Triglycerol

Fatty acids are important metabolic fuels (2-3 times the energy of proteins or carbohydrates). Fatty acids are stored as neutral lipids called Triacylglycerol (TGs). TGs are composed of 3 fatty acyl residues esterified to a glycerol (3-carbon sugar alcohol) TGs are very hydrophobic, and are stored in cells in an anhydrous form (e.g. in fat droplets).



Triglycerol + three fatty acids → a triglyceride + three waters

Sunflower Oil

Sunflower oil is the non-volatile oil compressed from the seeds of sunflower (Helianthus annuls). Sunflower oil is commonly used in food as a frying oil, and in cosmetic formulations as an emollient. The world's largest sunflower oil producers now are Ukraine, Russia and Argentina.

Analysis of the Oil and Fats

Generally carried out on the oil sample these are test for unsaturation (iodine number), average molecular weight of the acid components of the oil (saponification value), average acid content of the sample (acid value) and average oxygen content of the sample (peroxide vale) in addition to a fully lipid analysis which is conducted through various forms of chromatography and spectroscopy.

Rancidity of the Oil

Rancidity is the obnoxious flavor and odor due the exposure of the fat to light, air, heat or moisture for long period of time. Rancidity of the oil is either hydrolytic or oxidative. Hydrolytic spoilage is due hydrolysis of the fat with the liberation of the volatile fatty acids whereas oxidative spoilage is due to oxidation of the unsaturated fatty acid fragment of the ester to produce aldehyde, ketone or acids [4].

Oxidative Spoilage of the Oil

Oxidative of olefinic compounds by atmospheric oxygen is important in the development rancidity and off - flavor of the edible fat. This process needs activation; the first isolable oxidative products are hydro peroxides which undergo further reaction to furnish more extensively oxidized derivatives of the original alkene followed by fission of the carbon chain and formation of high molecular weight polymers [5].

Anti-Oxidation

The best naturally occurring antioxidants are the lard prop lies and the citric acid respectively, α- tocopherol alone if used as antioxidant, increase the rancidity of the oil, mixture of antioxidants were found to be effective in Inhibiting oxidation. Prepared antioxidants were also determined, examples are Propyl Gallate (PG), Butylated Hydroxyl Anisole (BHA), Ascorbyl Palmitate (AP) and Tertiary Butyl Hydro Quinone (TBHQ).AP was found to be the most effective one PG and TBHQ were effective in inhibiting oxidation degradation for long periods of storage, however The antioxidant activity of dichloromethane extract from ginger was evaluated during 6 months of storage of refined sunflower oil at 25 and 45 C [6] (Table 2).

Character	Draft codex
Refractive density	0.918 -0.923
Refractive index	1.407-1.460
Saponification value	188-194
Acid number KOH/g	4 max
Iodine value Waj"S	110-143
Perioxide value mL equivalent/ Kg	10 max
UNsaponification matter g/kg	15 max
G.L.C. range of fatty acid composition	
14:0	< 0.5
16:0	5 - 10
16:1	< 1
18:0	1 - 10
18:1	14 - 65
18:2	20 - 75
18:3	< 0.7
20:0	< 1.5
20:1	< 0.5
22:0	< 1.5
24:0	< 0.5
24:1	< 0.5

Table 2: Characteristics and recommended codex of edible sunflower oil [7].

Methods

Sunflower seeds obtained from Arab company for plant oil (Khartoum) were subjected to the U.V. radiation of the sun adapting

storage conditions of the seeds in the oil producing companies or mills, a sample of 60 g of the seeds were extracted and analyzed for acid value and peroxide value in addition to the G.L.C. analysis of the methyl ester of the oil. This step was repeated at a time interval of 90 days. The maximum period of time beyond which the value for acid and peroxide value become out of the range of the recommended codex values for edible oil and fats was found. G.L.C. Analysis for the methyl ester of the extracted oil was applied before and after exposure to the U.V. radiation for a maximum period of time after which the oil become inedible.

Extraction of the Oil

The seeds (60 g) were crushed and extracted using a soxthlet apparatus with a n- hexane as a solvent. The homogenous solution was filtered through a fluted filter paper (what man no.1) and the solvent removed in vacue at 37°C, the residual oil was then analyzed.

Peroxide Value

2g of the oil was dissolved in 12ml of $CHCl_3$, 18 ml of glacial acetic acid was added together with 0.5 ml of saturated solution of KI. The flask was quickly stoppered and shaken for 1 minute and kept away from light for exactly 15 minutes. 30 ml of distilled water was then added and the liberated iodine was then titrated with a standardized solution (0.002 N) of $Na_2S_2O_3$ using a starch as an indicator. The peroxide value was then estimated as ml equivalent of active oxygen per kilogram of the oil [8]. Duplicate determinations were carried out together with a blank test. Peroxide value = {(V sample - V blank) x N x 1000}/ wt of the sample.

Acid Value

2g of the oil was dissolved in 50 ml of 1:1; V/V of ethanol (95%) and diethyl ether. 2ml of phenolphthalein indicator was added, this solution was titrated with KOH (0.1 M). Acid value = titration volume x 5.61/ wt of the sample [9].

Methylation of Free Acids and Oil

7.00 ml of BF_3 etherate solution was transferred into a 25 ml volumetric flask and the solution was completed by the addition of dry methanol. 0.2 g of the oil was refluxed with (5-7) ml of this solution at 80 ^{O}C for 1 hour. This solution was transferred into a separator funnel, 5 ml of saturated NaCl solution was added, the flask then rinsed with n-hexane (2x 10 ml) and added to the separator funnel contents whilst shaking vigorously in order to extract the methyl ester, the solvent was then removed. The methyl esters were kept in a refrigerator at 0^{O}C for further analysis.

Gas Liquid Chromatography (G.L.C.)

Preparation of Standard Chromatogram

Standard chromatogram was based on four different fatty acids palmitic and srearic as saturated fatty acids, oleic and linoleic as unsaturated fatty acids. Their methyl esters were injected separately and their retention times were determined, equal amount of the fatty acids then mixed and esterified (3.4), the methyl esters of the mixture were then injected and their retention times were compared with the pure methyl esters of the acids above. The conditions of the G.L.C. analyses (injection and column temperature, N2 flow rate … etc) were kept constant throughout [10].

G.L.C. Analyses of Methyl Esters of the Sunflower Oil Sample

A sample of the oil was injected in a G.L.C. under identical conditions of the standard chromatogram. Different methyl esters of the acids were identified comparing the Retention Time (R.T.) in the mixture with those in standard chromatogram as well as calculating the areas under the peaks. Changes accompanied exposure of the seeds to the U.V. radiation of the sun estimated by comparing the areas under the peaks of the fatty acids before and after exposure periods (Table 3).

Number	Parameter	Condition
1.	Column	Glass column: length :1.5 ml meter Internal diameter : 4 ml meter
	Support	Chromos orb Q, Mish range : 80- 100
	Liquid phase	10% carbowax
	Temperature	Injection: 200°C Oven : 165°C
	Detector	Flame ionization detector FIT (250°C)
	Recorder	Chart speed : 300 mm / h
	Carrier gas	N2 flow rate : 40 ml / min

Table 3: Gas liquid chromatographic conditions for the separation of fatty acids methyl esters.

Results

Table 4.1: Variation of acid, peroxide values with time of exposure of 60 g of the seeds to the U.V. radiation of the sun.

Time of exposure in mouths	acid value mg KOH/g oil	Peroxide value ml equivalent/Kg oil
0	2.9	4.00
3	3.4	7.00
6	3.9	8.00
9	4.45	110.00
12	4.95	143

Figure 4.1: Variation of acid value with time of exposure to the U.V. radiation of the sun.

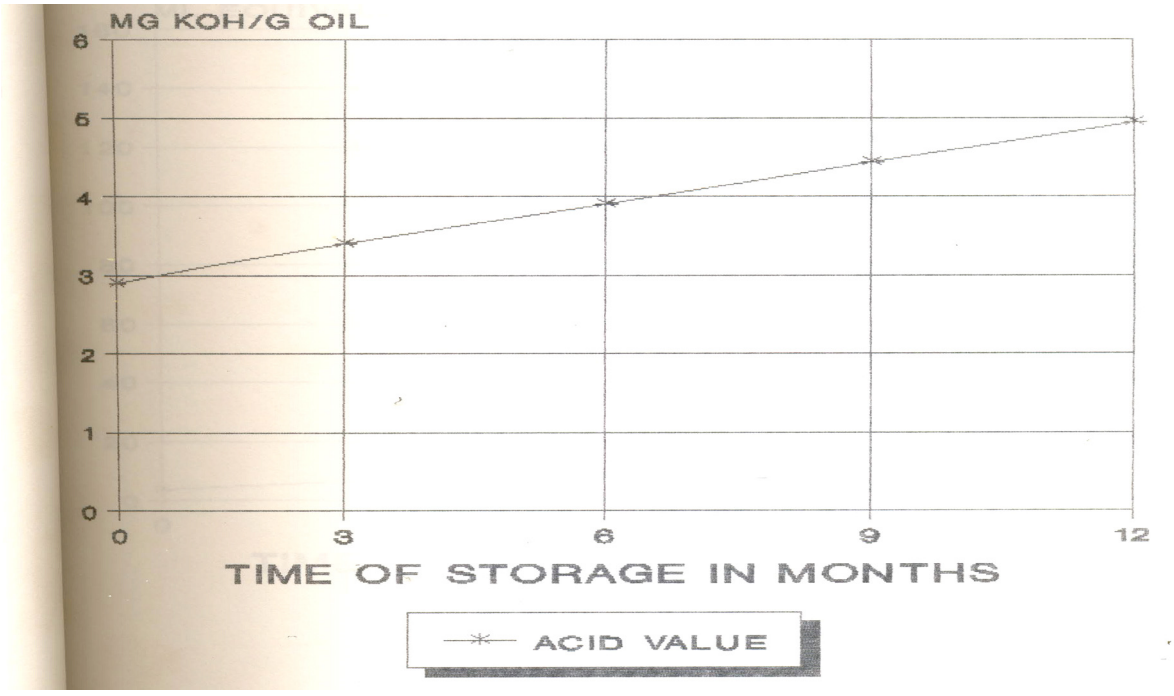


Figure 4.2: Variation of peroxide value with time of exposure to the U.V. radiation of the sun.

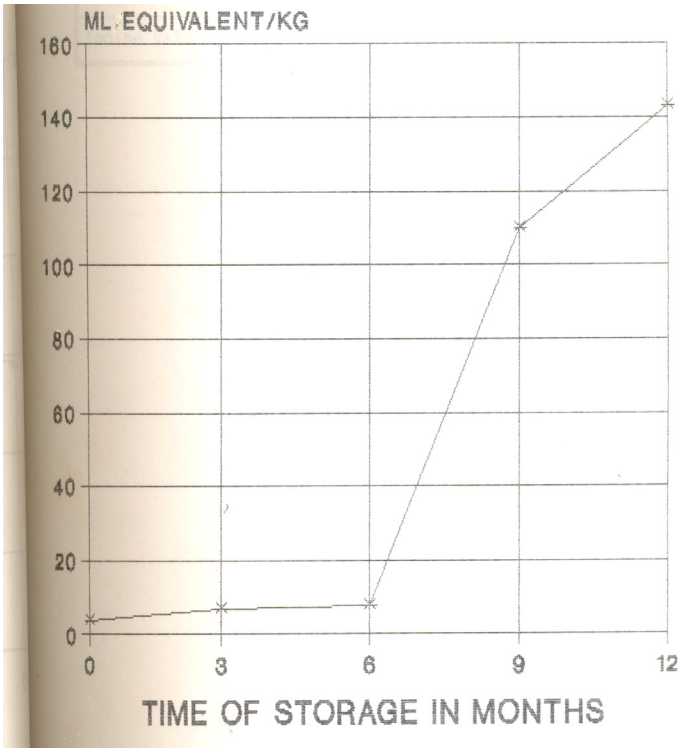


Figure 4.3: The four fatty acids standard chromatogram.

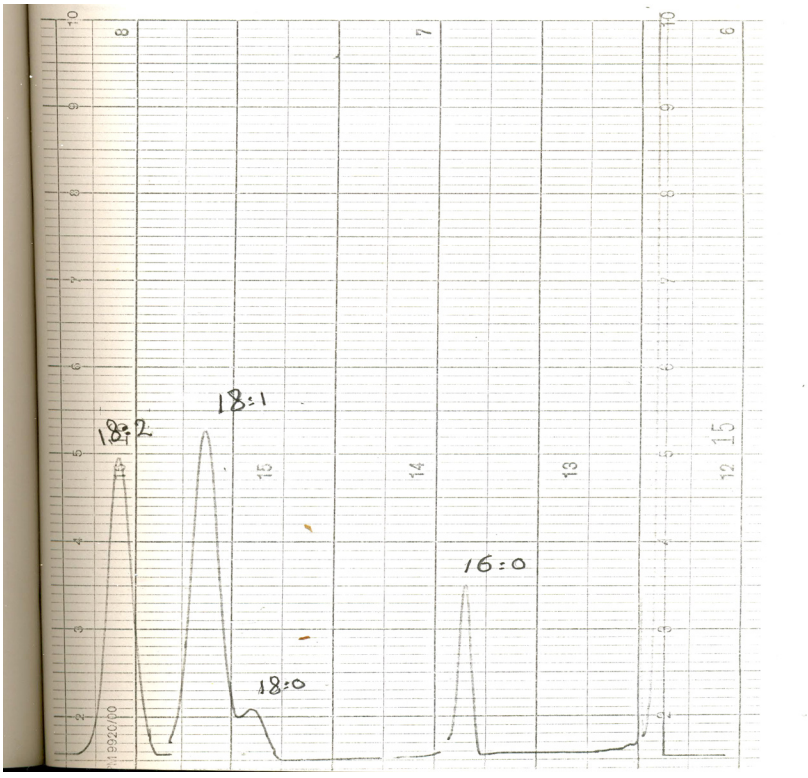


Table 4.2: Retention time range of the four standard fatty acids.

The Acid	Retention time in (CM)
Palmitic acid 16:0	4
Stearic acid 18:0	7.8 - 7.9
Oleic Acid 18:1	8.5 - 9.00
Linoleic acid 18:2	9.6 - 10.2

Figure 4.4: G.L.C chromatogram for the methyl ester of the extracted sunflower oil before exposure to the U.V. radiation of the sun.

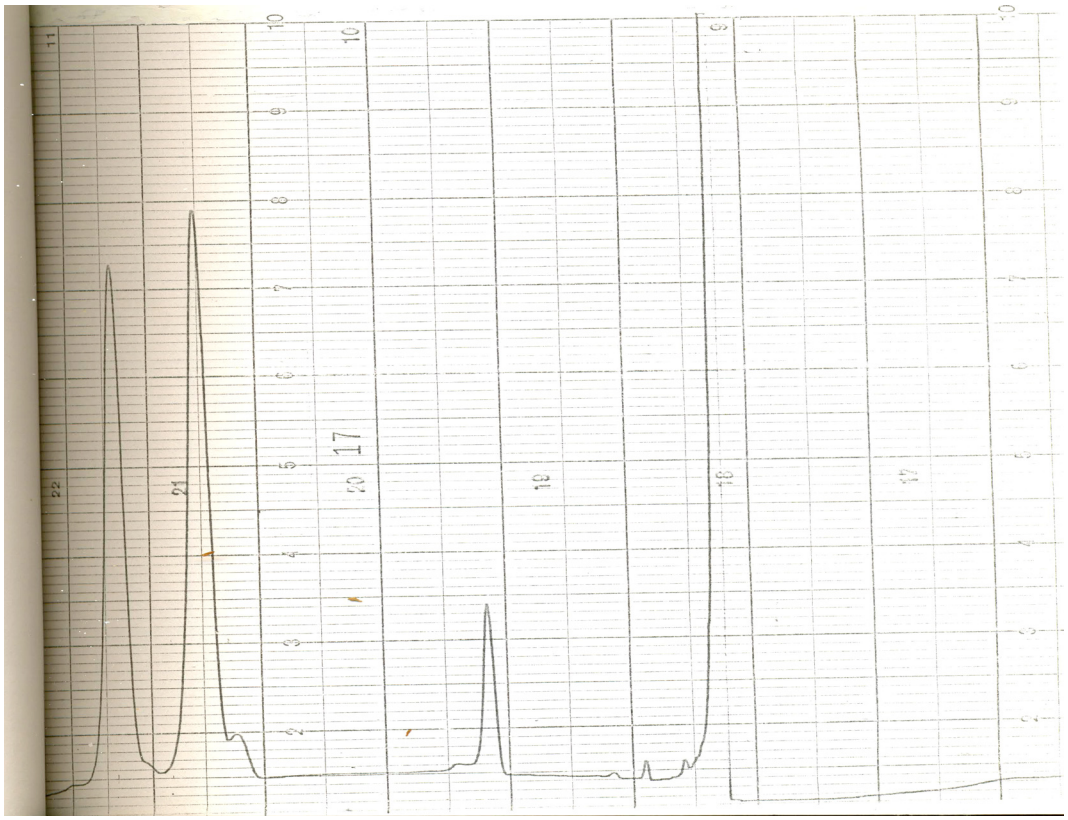
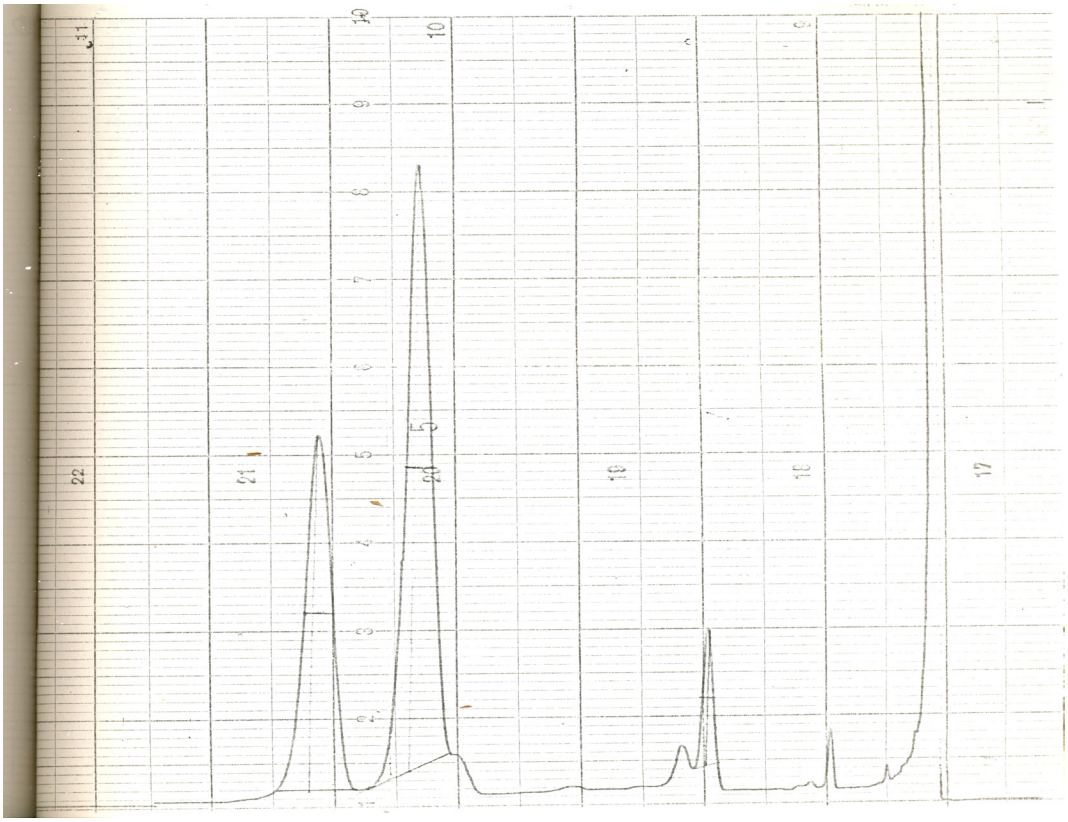


Figure 4.5: G.L.C chromatogram for the methyl ester of the extracted sunflower oil after exposure to the U.V. radiation of the sun for six months.



Time of exposure in months	%Area 16:0 stearic	%area 18:2 palmitic	% area 18:1 oleic	%area 18:2 linoleic	% area 18:2/ 18:
0 - Months	9.60	0.23	48.36	42.00	0.87
6 - Months	9.60	0.23	48.36	38.32	0.79

Table 4.3: variation of the % area under the peak of the stearic, palmitic, oleic and linoleic methyl ester with respect to time of exposure to the U.V. radiation of the sun.

Discussion

The main issue of this work is to establish proper storage conditions for longest period of time for sunflower seeds without any deterioration in the organoleptic properties and/or the edibility of the produced oil. The seeds were subjected to the U.V. radiation of the sun adopting storage conditions usually maintained in industry, changes accompanying the acid value, peroxide value for the extracted oil were determined and compared with the recommended codex for edible sunflower oil. Concerning the acid value, it is found that there is a gradual increase with increase the storage time (from the 1st month to the 12th) when the seeds were subjected to the radiation of the sun (Table 4.1). On oxidation of unsaturated, epoxides result, these are reactive intermediates i.e. there are further cleavages of the carbon chain and ring opening to form aldehydes, which are intern easily oxidized to acids and per acids. This explains the increase

of the acid value versus the time of storage under the sun (figure 4.1). Concerning the peroxide value, there is a gradual increase in the peroxide value versus the period of storage under the U.V. radiation of the sun in the 1st six months (Table 4.1) , followed by sharp increase (figure 4.2) .This may be explained in terms of enzymatic action of an oxidizing enzymes and / or through analysis of biologically bound Fe , Zn, Cu and Mn .On exposing the seeds to the U.V. radiation for different periods of time ,change in the percentage of each of the four fatty acids was detected. This percentage is estimated by calculating the percentage area under the peak for each of the four fatty acids separately. The ratio, percentage linoleic / oleic is used to estimate this change. This ratio decreased with increase of the exposure period (0.87 before exposure, 0.79 after exposure for 6 months), this can be explained in terms of the number of double bonds found in each acid, linoleic consists of two double bonds in the carbon chain thus it is susceptible to oxidation rather than Oleic which consists of only one double bond (Table 4.3).

Conclusion

The data so obtained were compared with the recommended codex for edible sunflower oil from which we conclude that storing sunflower seeds under the U.V. radiation of the sun for a period of time of six months will produce an oil of a considerable diversity from the recommended codex standards, then such oil is then considered to be inedible.

References

1. https://en.wikipedia.org/wiki/Unsaturated_fat.
2. Mayo Clinic (2012) Omega-3 fatty acids, fish oil, alpha-linolenic acid.
3. Alfred Thomas (2002) Fats and Fatty Oils. Ullmann's Encyclopedia of Industrial Chemistry Weinheim: Wiley-VCH.
4. YC Lee, SW Oh, J Chang, IH Kim (2004) Chemical composition and oxidative stability of safflower oil prepared from safflower seed roasted with different temperatures. Food chemistry 81: 1-6.
5. Aluyor EO, Ori-Jesu M (2008) The Use of Antioxidants in Vegetable Oils- Review. African Journal of Biotechnology 7: 4836-4842.
6. Zia□ur□Rehman , AM Salariya, Farzana Habib (2003) Antioxidant activity of ginger extract in sunflower oil. Journal of the Science of Food 83: 624-629.
7. https://mvo.nl/media/voedselveiligheid/codex_standard_named_vegetable_oils.pdf
8. Chakrabarty MM (2003) Chemistry and technology of oil and fats, 752 . Allied Publishers Pvt. Ltd.
9. HEJ, Sir Avvin Pelovello (2011) Biochemistry 34.1: 35493.
10. Hui-QinWu, Xiao-LanHuang, Xiao-ShanLin, FangHuang, Zhi-XinZhu, et al. (2007) Gas Chromatographic Retention Time Rule and Mass Spectrometric Fragmentation Rule of Fatty Acids and Its Application in Food. Chinese Journal of Analytical Chemistry 35: 998-1003.