

## Studies on the Paint Forming Properties of Avocado(*Persea Americana*) and African Pear (*Dacryodes Edulis*) Seed Oils.

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### ABSTRACT

Avocado(*Persea Americana*) and African Pear (*Dacryodes edulis*) seed oils were investigated for their suitability as base materials for oil paint production. Soxhlet extraction of the oils from the powdered seeds using n-hexane gave 3.63% and 10.40% yields for Avocado and African Pear respectively. Proximate analysis and chemical characterization of the seed oils were carried out using standard procedures according to the American Oil Chemist Society (AOCS) and the American Society for Testing and Materials (ASTM). The fatty acid compositions of the oils were obtained by Gas Chromatography. It showed that oleic and stearic acids are the most abundant unsaturated and saturated fatty acids respectively in both oils. Marginal differences were observed in the iodine and peroxide values of the oils. Chemical characteristics of the oils gave iodine values of 38.35mqI<sub>2</sub>/g for Avocado oil and 32.26mqI<sub>2</sub>/g for African Pear oil, both results suggestive of non-drying oils. Similarly, peroxide values of 45meq/kg and 30meq/kg were obtained for the seed oils respectively. Some chemical properties and performance characteristics of the finished paints were determined. The drying time of the paints indicates poor drying properties. The results obtained showed that Avocado and African Pear seed oils do not have the potential for normal wall paintings but may find use in artists' paintings.

**Keywords:** Avocado, African Pear, Paint, Gas Chromatography, Fatty Acid.

### I. INTRODUCTION

Human activities create a large variety of wastes which accumulate over a period of time and become toxic to the environment. Pollution and the growing volume of solid wastes are major threats to the environment and sustainable development of a nation. One of the emerging major themes in polymer science for the 21st century is the production of sustainable green polymeric materials and chemicals from renewable resources (Thakur and Singha, 2010). Seeds and fruits of plants are veritable sources of oil for domestic and industrial utility. The lipid-based raw materials for paints are vegetable oils. Many vegetable oils and some animal oils are 'drying' or 'semi-drying' and it is this property that accounts for the suitability of many oils such as linseed, tung and some fish oils as the base of paints and other coatings. Vegetable sources occupy an important position in the provision of individual raw materials for paint production. This is because they are readily renewable resources and contain high levels of unsaturated fatty acids; a well sought property for oil paint production. They are also environmental-friendly, less expensive, easy to obtain using conventional extraction techniques and produced easily in rural areas.

Although vegetable sources of raw materials are readily renewable, the utilization of wholly inedible and 'unuseful' seeds as sources of industrial raw materials will help in sustaining the

high demand for industrial raw materials and reduce the environmental pollutions usually caused by the indiscriminate dumping of such wastes (Akaranta, 1999). There are several potentially useful topical plant materials that have been left unutilized due to inadequate knowledge of their compositions. The seeds of Avocado and African Pear, exemplify such plant materials. In view of the need to find renewable sources of raw materials of quality for the paint industry, this work is a study of some seeds which are known to contain oils and are also wholly inedible. According to Ajiwe, *et al*, (1997), all seeds contain oils. With no competing food uses, attention is on Avocado and African Pear fruits, which grow in tropical and subtropical climates across the developing world. African Pear (*Dacryodes edulis*) and Avocado (*Persea Americana*) are well known plants in West Africa. The fruits are edible. The bark, leaves, stems and roots of the trees are used as local medicine for the treatment of disease (Neuwinger, 2000; Jirovetz, *et al*, 2003; Annabelle, *et al*, 2004). In Nigeria, their fruits are gathered for household use or for sale in local markets. Previous studies have shown that the seeds from these fruits contain oil which have considerable nutritional value. The fruits are rich in lipids (Kinkela and Bezar, 1993; Mbotona, *et al*, 2002). They could provide useful supplement to animal feed (Obasi and Okolie, 1993; Ajiwe, *et al*, 1997; Leaky, 1999). Research has demonstrated that Avocado and African Pear seed oils could have

industrial applications (Ikhuoria and Maliki, 2007). This study derives its importance from the environmental waste problem posed by the seeds of these fruits whenever they are in season and the inedible nature of the seeds which can be exploited. These fruits are, basically, cultivated for their fruit pulps which are edible. The seeds of these fruits are often discarded after consuming the fruit pulps probably due to a dearth of information as to the possible usefulness of the fruit seeds. Avocado pits contain polyphenolic compounds (protocatechuic acid, chlorogenic acid, syringic acid and rutin), which are very strong antioxidants (Pahua-Ramos, *et al*, 2012). The skins are also extremely rich in antioxidants. The seeds of African Pear have been found to contain a reasonable amount of oil. The composition of this oil shows that it has both domestic and industrial potentials (Gunstone and Norris, 1982; Arisa and Lazarus, 2008). Physicochemical data on the other hand suggest that the seeds of African Pear have valuable functional attributes of industrial interest (Iyawe, 2009). The seed can also be used as fodder for sheep or goats. This study is aimed at characterizing Avocado and African pear seed oils for properties which directly affect their use in paint production. It intends to reduce dependence on resin imports for oil paint production.

## II. MATERIALS AND METHODS

**Sample Collection and Preparation:** Avocado and African Pear fruits were purchased from Mile 3 market in Port Harcourt, Nigeria. The pulps of the fruits were removed by cutting with a knife, the seeds were cleaned by washing with distilled water and oven dried to constant weight in a JP Selecta hot air at 100°C for 10 hours. The dried seeds were then milled with a corona traditional mill (1.00mm particle size) prior to solvent extraction.

**Oil Extraction:** Oils of the Avocado and African Pear fruits were extracted from the milled powders with n-hexane in a soxhlet extractor. 985g and 1000g of Avocado and African Pear seed meals were introduced respectively into the extraction unit of the soxhlet extractor. A round-bottomed flask containing the solvent was placed in a water bath at a temperature of 65°C. The extraction process was considered to be complete when the arm through which the solvent passed down to the flask became colourless. After extraction, the oil – hexane mixtures were concentrated by distilling off the solvent in order to obtain the oils. The recovered oils were further heated in the oven to ensure the complete removal of last traces of hexane from the oils.

**Oil Yield:** The seed meals were weighed before extraction. After extraction, the oils were weighed. The % yield was determined using the formula:

weight of oil/weight of sample x100

**Evaluation of the seed oils:** Analytical methods specified by the American Oil Chemists' Society for characterizing composition, structure and stability of fats and oils were employed. The fatty acid composition, iodine value, and acid value of the seed oils were determined in line with AOCS standards. Gas chromatography was used to determine the fatty acid compositions of the oils. The oil samples were reacted with methanol in the presence of BF<sub>3</sub> as catalyst to form the methyl esters. The fatty acid methyl esters were analysed using HP5890 SERIES 11, GC fitted with a flame ionisation detector and an ATLAS software data processor. Helium gas was used as the carrier gas. For the peroxide values of the oils: 2g each of the oils were weighed into 2 x 100ml Erlenmeyer flasks. 12ml of acetic acid-chloroform solution was added with the aid of a graduated cylinder. The flasks were swirled until the samples were completely dissolved. With a 1ml Mohr pipette, 0.2ml of saturated potassium iodide solution was added and swirled for exactly one minute. Then 12ml of distilled water was added immediately using a graduated cylinder. The solutions were titrated with 0.1N sodium thiosulphate solution. Titration was continued until the blue grey colour disappeared in the (upper) layer. The volume of titrant used was then recorded and a blank determination of the reagents was conducted and the peroxide value for each oil was calculated. For the acid value: 5g each of the oil samples were weighed into 2 x 250ml conical flasks and 50ml of neutralized ethanol solution was added. The solutions were mixed by swirling until the oils were dissolved. The solutions were titrated with 0.1N KOH solution using phenolphthalein indicator until a pink colour was obtained. The volume of titrant used was recorded and a blank titration was conducted. The acid value of each oil was calculated and recorded.

**Paint Preparation:** Prepared alkyd resins were formulated into white gloss paints without the use of driers. This was to accurately determine the drying rate of the oils. The alkyd resins and part of the solvent were premixed in a clean vessel. The pigment, TiO<sub>2</sub> was then added and mixed to uniform consistency. Talc powder was finally added while stirring vigorously. The viscosity of the mixture was adjusted by the addition of more solvent.

### Evaluation of Paint Films

**Preparation of Test Panels:** Aluminium panels measuring 3.5cm x 10cm were wiped with a clean cotton cloth dipped in ethanol and allowed to dry in air. Paint samples were applied on the panels with a

paint brush to obtain uniform coats. The panels were then left to air-dry.

**Drying Time:**The touch method was used to determine the drying performances of the paints. The films were monitored to determine the extent of drying. The drying performances of the paints were recorded.

**Adhesion:**Baked films of both paints were cut by cross hatching and the flakes were cleaned off the

substances using a brush. A scotch tape was adhered on to the film of each substrate and peeled off quickly at an angle of 180°. The results were recorded. The film resistance tests were carried out in alkalis, acids, distilled water and organic solvents respectively using standard methods specified by the American Society for Testing and Materials (ASTM, 1985).

### III. RESULTS AND DISCUSSION

**Result:**

**Oil Yield:**

1. Avocado Seed Oil: % Oil yield = 3.63%
2. African Pear Seed oil: %Oil yield = 10.40%

**Discussion:**A percentage oil yield of 3.63% was obtained after extraction from the Avocado seed meal.10.40% of oil was recovered from the African

Pear seed. This is high in comparison with that of the avocado seed. The higher yield may be attributed to genetic factors. Arisa and Lazarus (2008) reported a value of 50% for the African Pear seed oil. The difference in oil content could be attributed to differing climatic conditions, stage of ripening/development of the fruit at the time of harvest and growth conditions.

**Results:**

**Table 1:** % Fatty Acid Compositions of Avocado and African Pear Seed Oils

Fatty Acid	Avocado Seed Oil (%)	African Pear Seed Oil (%)
<b>Saturated Fatty Acids</b>		
(i)Palmitic Acid	18.6	38.56
(ii)Stearic Acid	0.97	2.81
(iii)Palmitoleic Acid	7.4	-
<b>Unsaturated Fatty Acids</b>		
(i)Oleic Acid	62.69	32.62
(ii)Linoleic Acid	10	27.30
(iii)Linolenic	0.52	1.25

**Note:** The oil compositions may not add up to 100% due to the presence of minor fatty acids.

**Discussion:** The fatty acid composition of the avocado seed oil gave the total concentration of saturated fatty acids as 26.97% and that of the unsaturated fatty acids as 73.21% with oleic acid being the predominant fatty acid and palmitic, the predominant saturated fatty acid as shown in table 1, and figures 1 and 2. Pushkar,*et al*, (2001), reported the concentration of C<sub>18.1</sub>, C<sub>18.2</sub>, and C<sub>18.3</sub> fatty acids in the Fuerte Cultivar seed oil of the avocado fruit as 17.41%, 38.89%, and 6.58% respectively. However, the concentrations of these fatty acids in the seed oil of the Fuerte Cultivar of the avocado pear in this study (62.69%, 10% and 0.52% respectively) were different from the cited report. This quantitative difference is justifiable in view of the difference in their geographical origins of the fruits and factors such as maturity and harvest practices. The total concentration of saturated fatty acids in African Pear Seed oil was 41.37% while that of the unsaturated fatty acids

was about 61.17%. In this instance, oleic acid is the major unsaturated fatty acid. Both oils are composed of the same type of unsaturated fatty acids, but had their compositions differ quantitatively. African Pear seed oil also had its major saturated fatty acid as palmitic acid but did not contain palmitoleic acid. The fact that both seed oils are rich in oleic acid means that the oils are most probably non-drying oils even though they contain more than 50% unsaturated fatty acids. This is so because the participation of monounsaturated oleic acid in the drying of an oil is limited as oils with more polyunsaturated fatty acids than monounsaturated acids are more susceptible to oxidation and drying and as a rule, only linoleic, linolenic, ricinoleic and  $\alpha$ -eleostearic acids are constituents of drying oils. Oils that are rich in oleic acid like Avocado and African Pear seed oils display greater oxidative stability than those containing more polyunsaturated fatty acids.

**Results:**

**Table 2:** Physico-chemical Properties of Avocado and African Pear Seed Oils

Property	Avocado Seed Oil	African Pear Seed Oil
Iodine value (mqI <sub>2</sub> /g)	38.35	32.26
Acid value (mgKOH/g)	3.01	6.17
Peroxide value of fresh oil (meq/kg)	45	30
Peroxide value of oil after 20 hours (meq/kg)	62	60
Active Oxygen Method(AOM) no. of hours(hrs)	32	33
Colour	Reddish brown	Greenish brown

**Discussion:Iodine Value:** The iodine value of the avocado seed oil is given as 38.35mqI<sub>2</sub> /g, as in table 2. A higher iodine value, 69.4mqI<sub>2</sub>/g for the seed oil was reported by Pushkaret al, (2001). Both values though differing greatly are suggestive of non-drying oils. African Pear oil had an iodine value of 32.26mqI<sub>2</sub>/g. This is in close agreement with the value (32.40mqI<sub>2</sub> /g) reported by Arisa and Lazarus (2008). The variation in iodine values of the Avocado and African Pear seed oils reflects the difference in the degree of unsaturation of the seed oils. The higher iodine value of the Avocado seed oil is due to its slightly higher concentration of unsaturated fatty acids. The low iodine values of both oils imply very low reactivity oxygen uptake and further makes the oils classifiable as non-drying oils. Thus, both oils will be suitable for use as plasticizers or as lubricants.

**Acid Value:** The acid value of the Avocado Seed oil was 3.01mgKOH/g (table 2). Pushkaret al (2001) reported a value of 2.06mgKOH/g for the crude oil. Rachimoella,et al,(2009) gave the acid value of the Avocado seed oil as 5.2mgKOH/g. However, no information was given as regards the state of the oil at the time of analysis. 6.17mgKOH/g was obtained as the acid value of the African Pear seed oil. This is in close agreement with the value (5.61mgKOH/g) reported by Ajayi and Adesanwo (2009). According to Arisa and Lazarus (2008), the acid value of the African Pear seed oil was determined as 9.6mgKOH/g. An acid value of 4mgKOH is recommended by Codex-Alimentarius (1993) for edible oils. This value indicates low levels of hydrolytic and lipolytic activities in the oil. Williams, (1996) reported that low acid values for oils are useful in the manufacture of paints and varnishes. The acidity level of both oils is explained as arising from the thermal degradation of the polyester chains during heating to concentrate the miscella (solvent-oil) mixture. The thermal degradation products of polyester are a function of temperature and oxygen content of the atmosphere. The principal decomposition products (acetaldehyde, water,

carbon oxides and the acid and anhydride end groups) and the kinetics of degradation suggest a random chain scission (Cullis and Hirschler, 1981). Hydrolysis of the ester bonds could also be responsible for this action. Triglycerides are hydrolysed to their free fatty acids when heated.

**Peroxide Value:** The peroxide value (PV) of the fresh Avocado seed oil was determined as 45meq/kg as shown in table 2. Rachimoella, et al (2009), reported a value of 3.3meq/kg. The PV of the oil after 20 hours was 62meq/kg. This shows great stability of the oil to oxidation (drying). On the other hand, the peroxide value of the fresh African seed oil was 30meq/kg. Ajayi and Adesanwo (2009), reported the peroxide value of African Pear seed oil as 20meq/kg. The differences could be due to varying laboratory practices. After exposure to heat, light and oxygen for 20 hours, the peroxide value of the African Pear seed oil rose to 60meq/kg. The increase in peroxide value of both seeds is as a result of oxidation. However, peroxide values less than 100meq/kg for both oils after 20 hours show that the rate of oxidation is quite slow, thus implying slow rate of drying/film formation.

**Active Oxygen Method (AOM):** The active oxygen method is the number of hours taken by an oil sample to reach a peroxide value (a measure of the present state of rancidity or oxidation of an oil) of 100meq/kg- an assumed rancid value. The active oxygen method hours tend to increase with the degree of unsaturation since an unsaturated oil especially a polyunsaturated one is readily oxidised (table 2). As expected, Avocado seed oil with a greater amount of unsaturated fatty acids gave slightly higher peroxide values than African Pear seed oil, implying that it is more prone to being oxidised than the latter. However, the time taken by both oil samples to reach the assumed rancid value of 100meq/kg, reported as AOM number of hours (32 and 33 hours respectively) is far too long. This means that both oils will need over 24 hours to begin drying and for indoor/outdoor painting purpose, this is unsuitable.

**Results: Paint Formulation:**

**Table 3:** Major Constituents of Oil Paint

Component	Weight(kg)
TiO <sub>2</sub>	12.939
Talc Powder	21.94
White Spirit	15.03
Alkyd Resin	49.60

**Table 4:** Drying Time of Paints

Time	Avocado seed oil paint	African Pear seed oil paint
Set-To-Touch-Time,STT(hrs)	48	-----
Dry-To-Touch-Time,DTT(hrs)	528	-----
Dry-Hard-Time,DHT(hrs)	-----	-----

**Table 5:** Chemical Resistance of Paint Films

Medium(Avocado)	Immersion Time(days)	Appearance of film	Medium(African Pear)	Immersion Time(days)	Appearance of film
Water	3	5	Water	3	5
5%HCL	3	3	5%HCL	3	4
5%H <sub>2</sub> SO <sub>4</sub>	3	3	5%H <sub>2</sub> SO <sub>4</sub>	3	0
5%NaOH	3	1	5%NaOH	3	0
Methanol	3	5	Methanol	3	5
Toluene	3	5	Toluene	3	3

**Key:** 5 – Film unaffected

4 – Slight loss in gloss

3 - Slight blushing and loss in gloss

2 –Loss in gloss and partially removed fill

1 – Partially removed film

0 – Completely removed film

**Discussion: Colour:** The colour of the paints varied from light brown for the Avocado seed oil synthesized paint to off white for the African Pear seed oil paint. The colours of the prepared alkyds were transmitted to the paint samples. Since majority of the constituents of the paint mixtures were white (table 3), the dark colours of the alkyds were tinted by them so that lighter colours were obtained.

**Drying Time:** This is a very important consideration in a coating formulation as some coated surfaces may need to dry so that they can be put into service immediately after the coating has been applied. Avocado seed oil paint achieved the set-to-touch and dry-to-touch times of 48 and 528 hours respectively. The paint formulation with African pear seed oil did not dry at room temperature as the paint layer remained liquid on the substrate after four weeks of air drying. The drying time of both paints could not be determined as shown in table 3. They had difficulty in drying

in the absence of a drying agent. It is thus evident that the curing of paint films does not depend on the volume of air but on the type/nature of film forming material that is used. The greater the level of unsaturation, the faster the drying time, (Wicks, *et al*, 1999). Alkyds and paints formulated with the non-drying oils do not readily form films without the aid of a catalyst which in this case is a drying agent. Driers fasten crosslinking in the resin. The resin becomes denser, viscous and more compact conferring a curing tendency on itself. A paint produced with a drying oil is expected to dry hard within four days of application with the exclusion of a drier.

**Adhesion:** This is the single most important property of paints as it determines the durability of the painted film. It is the ability of a paint film to remain on the surface without blistering, flaking or cracking. A coating must adhere well in order to protect the surface of the substrate and to be used for a long time. In order to carry out this test, the painted panels were heated in a temperature controlled oven at 150<sup>0</sup>C for two days; a process referred to as baking. The classification of the adhesion test method is in accordance with ASTM-D-3359-78 standard. The adhesion of the paint films on the surface was found to be fairly

strong. Detachment of small particles of the films was observed at the intersections and edges of the cuts applying the adhesive tape. According to Shailesh, *et al*, (2008), the good adhesion of the films to the substrate is attributed to the inherent chemical structure and flexibility of the alkyd resin. The firm adhesion exhibited by both paint films is attributed to the presence of the polar carboxylic and hydroxyl groups in the resin. These are very active promoters of adhesion, due to their attraction to the substrate, or their influence in improving the wetting properties of the paints.

**Chemical Resistance:** The films showed no change after immersion in distilled water for three days. Water in its pure form is unreactive. The paint films had very high resistances in the organic solvents employed as shown in table 5. This was so because the films dried by crosslinking and once this happened, they could no longer dissolve in the solvents. The films of both paints were slightly affected in acidic media. This may be due to the phenyl groups present in their alkyds. Phenylene groups in a polymer chain proffer stiffening action leading to hardness, strength and high resistance of the polymer. The complete removal of the film of the African Pear paint by sulphuric acid may be due to the poor adhesion of the liquid paint film to the substrate as a result of baking. It was observed that the liquid paint layer dripped to the sides of the substrate during baking, leaving the surface lightly coated, hence its easy removal by the sulphuric acid. The poor resistance of the paints in sodium hydroxide solution is attributed to hydrolysis of the ester bonds in the alkyds. Being essentially

polyesters, alkyds are susceptible to alkaline hydrolysis.

#### IV. CONCLUSION

Avocado and African pear seed oils were extracted and used in the preparation of white gloss paints. The gas chromatographic analysis revealed the chemical compositions of both seed oils with oleic acid as the predominantly fatty acid in both oils. The study established that the iodine and peroxide values of both oils are typical of non-drying oils. This was further confirmed by the relatively slow drying rate of the paints as they were unable to dry without the incorporation of driers. Thus, based on their iodine values and drying times of the formulated paints, it is concluded that the investigated species of the Avocado and African pear seed oils are unsuitable for interior/exterior paintings and for use as primers. If however, the oils are to be used in the preparation of air drying paints, driers must be included in the formulation. Since they do not readily form films, the oils can be used as plasticizers or lubricants. These are areas where oxidation is undesirable. The extremely dark colours possessed by these oils also make them unsuitable for the production of pale coloured paints as the likelihood of discoloration abounds. On the other hand, the slow drying rate of the paint formulated with these oils make them suitable for use in artists' paintings where they aid in gradual development of a painting.

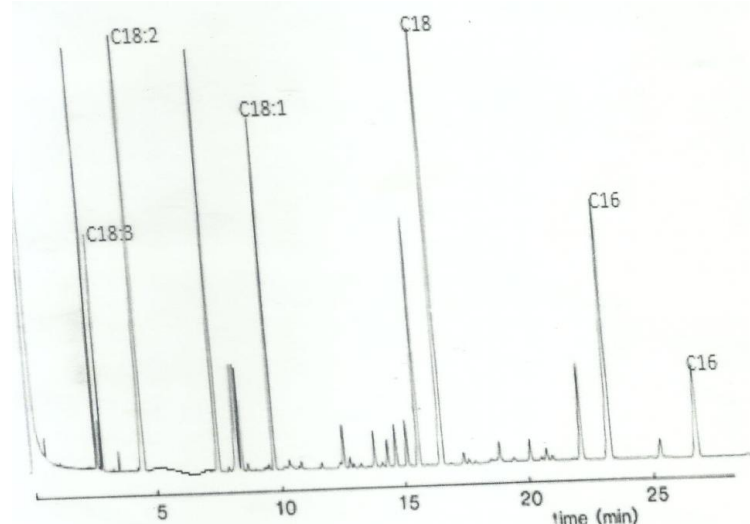


Fig.1:Fatty Acid Chromatogram of Avocado Seed Oil

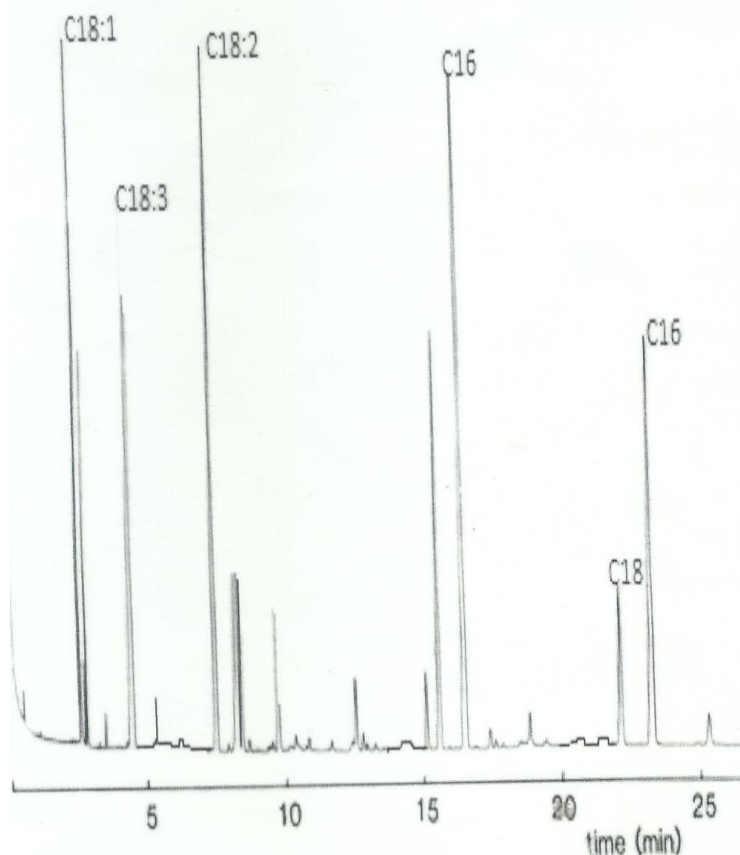


Fig.2:Fatty Acid Chromatogram of African Pear Seed Oil

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