

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 8, Issue 10, October 2019

Characterization of Hot Pressed-Fixed Oil Extracted from *Ricinus communis* L. Seeds

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ABSTRACT: Castor oil has a number of medicinal, industrial and pharmaceutical uses. The oil was extracted from seeds of *Ricinus communis* L. by hot mechanical pressing and characterized physically and chemically. The physical and chemical properties of the oil were found to be similar to those literated. The crude oil was chemically analyzed using GC/MS after methylation. Accordingly, the major constituents of the oil were detected as methyl or methyl esters derivatives. The primary constituent is the ricinoleic acid, making up to 74.99%, followed by palmitic acid derivatives (10.95%), stearic acid derivatives (8.43%), linoleic acid (4.32%), and oleic acid (3.31%). The oil yield obtained (36.12 %) and its quality were very encouraging for candidating such species as a pivot of small-scale industrial projects.

KEYWORDS: Fixed oil; Fatty acids; Ricinolic acid; Saponification; Methylation; GC/MS

I. INTRODUCTION

Ricinus communis L., known as castor oil plant, is a perennial flowering plant and the unique species in the genus, *Ricinus*. The plant is widespread throughout tropical and subtropical regions [1,2] and is planted occasionally in agricultural spots as windbreaks in Saudi Arabia.

Stems are thick generally greyish-green in colour, moderately branched, hollow, and hairless bearing leaves with very large blades [3].

The plant is tolerant to drought and can grow in different soils and climatic conditions produce castor oils with different composition and physical-chemical properties [5,6,7]. For example, castor oil extracted from Malaysian castor reaches up to 43.3 % per dry weight and a saponification value of 182.96 mg KOH/g [5], while the Nigerian castor seeds yield castor oil up to 48 % per dry weight with a saponification value of 178.00 mg KOH/g [6]. Furthermore, the castor oil has relatively high viscosity and specific gravity, soluble in alcohols with very low solubility in petroleum solvents [4,5,8].

The crop can yield up to 350 – 900 kg oil per hectare [7] and the seeds contain between 30 % and 60 % w/w oil by weight and this average differs according to varieties, geographical location and extraction method [1,9,10].

The castor oil has advantages over petroleum-based oils, especially at high and low temperatures because of its high boiling and low melting points [4,11,12].

Beside the ricinoleic acid (about 90 % wt/wt), castor oil also contains about 4% linoleic, 3% oleic, 1% stearic, and less than 1% linolenic fatty acids [9,13]. Ricinoleic acid is the major constituent of castor oil that governing the chemistry of this oil due to the presence of the three functional groups in the acid, which are the main factors for the production of variety of castor oil based products such as natural and synthetic resins, waxes, polymers and elastomers plasticizers. For instance, the carboxylic group can give wide range of esterification products and the single point of unsaturation can be altered by hydrogenation, epoxidation or vulcanization [1,14].

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It worth mentioning that castor oil is composed of esters (triglyceride molecules) composing of 3-carbon alcohol (glycerol) and three 18-carbons fatty acids, but castor oil is characterized among vegetable oils because it is the only commercial source of a hydroxylated fatty acid (ricinoleic acid), [9].

Castor oil is like all other vegetable oil exists as a mixture of saturated and unsaturated fatty acids attached to a glycerol [6,9,15]. Beside fatty acids, castor oil contains many beneficial constituents for health including flavonoids, phenolic compounds, amino acids, terpenoids and phytosterols [16].

In addition, this oil gets its importance from presence of hydroxyl groups and double bonds in the ricinoleic acid constituent, which forms 90% of the oil, thus making it an important industrial raw material [7]. Furthermore, the hydroxyl groups prevent peroxide formation thus providing the oil an oxidative stability, and the presence of the hydroxyl group in RA and RA derivatives provides a functional group location making it easy for a number of chemical reactions including halogenation, dehydration, alkoxylation, esterification, and sulfation [13,17]. Trevino and Trumbo [17] replaced the hydroxyl group in castor oil by β -ketoesters using t-butyl acetoacetate and obtained good glosses of films and film flexibilities. In addition, Thakur and Karak [18] prepared surface coating materials from castor oil-based hyperbranched polyurethanes.

People have used a multi-purpose vegetable oil for thousands of years. In the last couple of years, demand for castor oil has kept increasing in the international market, assured by more than 700 uses. Castor oil is an important oil with great utilization in pharmaceutical, medicine, food, chemicals industry, agricultural sectors, textile, paper, plastic, rubber, cosmetics, perfumeries, electronics, paints, inks, additives, lubricants and biofuels because of its unique ability to withstand thermal fluctuations [9,17,19,20,21,22]. The oil can easily be applied in many industrial applications [7], and it is characterized among other industrial vegetable oils due to its fatty acid composition. The carboxylic group and double bonds in the ricinoleate allow castor oil to enter into several chemical reactions and several applications such as esterification and amidation by the carboxylic groups [15,23], hydrogenation reactions are accessed due to presence of the double bond [15] as well as carbonylation [11] and epoxidation [24]. On the other hand, it is easy to either acetylate the hydroxyl groups in the oil [24] or alkoxylation [12,25]. In addition, hydroxyl groups can be removed from the oil by dehydration process to increase of the unsaturation degree of the oil [26,27]. The mid-chain hydroxyl group gives castor oil its physical and chemical characteristics that enabling it entering in many industrial applications, and among its uses are lithium grease, surfactants, cosmetics, polymers and engineering plastics [28].

In ancient Egypt, castor oil was burned as fuel in lamps, used as a natural remedy to treat ailments like eye irritation and even given to pregnant women to stimulate labour [29]. Today, castor oil remains a popular natural treatment for common conditions like constipation and skin ailments and is commonly used in natural beauty products [30]. Many of castor oil's benefits come from its chemical composition particularly because it is a type of triglyceride fatty acid and due to presence of ricinoleic acid [31]. When consumed by mouth, castor oil is broken down in the small intestine, releasing ricinoleic acid, thus stimulating a strong laxative effect [32].

In some applications, castor oil is used for production of soaps [31], waxes [33], or greases [34]. It can also be used in production of lubricants through the synthesis of acyloxy castor polyol esters [35]. Different lubricating oil from castor oil consisted of tolyl monoesters and performance additives, and discovered that it reduced smoke by 50%–70% at a 1% oil–fuel ratio, thus it can be used as a car engine lubricant as a smoke pollution reducer [36].

Castor oil can be extracted from the seeds through two manners, either mechanical pressing (cold or hot) or by solvent extraction, or by combination of both [37]. One drawback related to mechanical pressing method is the lower oil yield extracted from seeds, (about 45 % of the oil). Accordingly, the remainder aliquot of the oil in the seed cake must be re-extracted using a solvent. It was found that about 80% of the oil could be obtained by using high-temperature hydraulic pressing in the extraction process [38]. In addition, cold-pressed castor oils have low acid and iodine value, and has slightly higher saponification value than solvent-extracted oil [9]. Maximum yield of 50.16% of castor oil was obtained by Muzenda *et al.* [38] by using 60 minutes pressing time, temperature of 108°C, and a solvent system of isopropanol/hexane (50:50 v/v) for castor oil extraction. Solvents used for extraction include heptane, hexane and petroleum ethers. Optimization of castor oil recovery and moisture content were 48.75% and 5.8% respectively [39,40].

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After pressing, the obtained oil is filtered to free the oil from contaminants using filter press [10]. After filtration the oil is refined according to the steps, degumming by addition of hot water then removal of this the aqueous layer, neutralization by addition of sodium hydroxide, then bleaching to remove colour, remaining phospholipids, and any leftover oxidation products [38].

II. MATERIALS AND METHODS

2.1. Raw Material

Five shrubs of *Ricinus communis* L. (Family: Euphorbiaceae) were collected randomly from Agricultural Research Center belonging to King Abdulaziz University at Hada Al-Sham village that is apart from Jeddah, Saudi Arabia by about 120 km (Figure 1a). The shrubs were cultivated in a sandy soil located at a latitude of 21° 46'.839N and a longitude of 39° 39'.911E above the sea level by 206 m during 2018-2019. The seeds (Figure 1a-d) were collected from each of the selected shrubs, air dried, and separated from their hulls by a bean dehuller machine. The seeds were cleaned to remove any foreign materials such as sticks, stems, leaves, sand, or dirt [10]. Figure 1 presents the extraction process of the castor oil from the seeds.

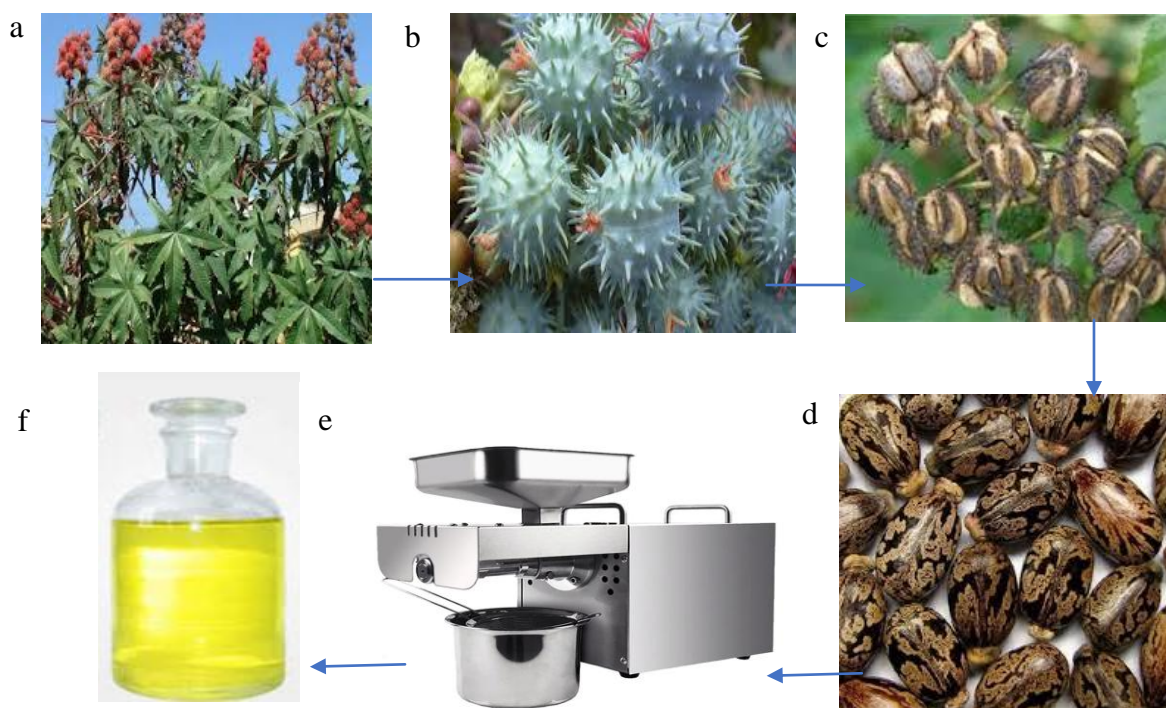


Figure 1. *Ricinus communis* L.: a) a shrub, b) Green capsules, c) Air-dried capsules, d) Air-dried seeds, e) The hot-pressing machine, and f) The castor oil.

2.2. Extraction of the Castor Oil

About one kg of the clean air-dried beans were heated in an electric oven to reduce moisture of the seeds [31] as well as reducing the oil viscosity within bean's tissues that can maximize the oil yield. Then, the beans were hot-pressed mechanically using the pressing machine with the aid of heating by assembling heat element in front of the extruder's pressing machine (Figure 1e).

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The obtained oil was settled for an hour; the oily supernatant was collected individually apart from the settled cake and filtered to free the oil from contaminants using vacuum filtration. The remaining oil saturating the settled cake was pressed hydraulically to be released [10]. The crude oil was weighed and stored (Figure 1f) without refining until subjected to the different characterization.

2.3. Characterization of the Castor Fixed Oil

The oil specifications were determined according to the techniques reported in the standard methods or applied by researchers investigating in the same or related field.

2.3.1. Physical Characterization

The physical properties of oils depend on their chemical composition as well as operation parameters such as pressure and temperature. For an unknown physical parameter of an oil, it can be determined and compared to the cited standard[41].

2.3.1.1. Yield

The yield was calculated using the following equation[41]:

$$Y = (W_1/W_2) \times 100, \text{ where}$$

W_1 is the extracted oil weight (kg), and

W_2 is the initial seeds weight (kg).

2.3.1.2. Specific Gravity (δ)

The δ of the castor oil was determined pycnometrically at 25 °C using an oven-dried clean stoppered bottle of 25 mL. After the empty weight of the bottle was recorded (W_0), it was re-weighed (W_1) after filling with the oil and stoppered. After washing and oven drying the bottle, the oil was substituted with distilled water and weighed (W_2). The δ is calculated based on the following equation: $\delta = [(W_1 - W_2) / (W_2 - W_0)]$ according to [41, 42, 43].

2.3.1.3. Refractive Index (RI)

The RI is a useful rapid measure of purity and quality of an oil [44]. A refractometer model No. 922313 (Bellingham and Stanley Ltd., London) was used for the determination of refractive index of the castor oil at 30 °C. About one drop of the sample was spread over the glass slide of the refractometer. Through the refractometer's eyepiece, the dark portion view was adjusted to be in line with the intersection of the cross. Five repetitions were done and recorded for the castor oil [40, 41, 45].

2.3.2. Chemical Characterization

2.3.2.1. Determination of Iodine Number (IN)

The IN is weight of iodine reacted with 100 grams of the oil that indicates the amount of unsaturation (presence of double bonds) in the castor oil. The higher the IN, the more double bonds are found in the oil [46]. We suggest that the IN value is counted by so-called iodine unit that is equivalent to g I_2 / 100g oil.

The IN was examined according to the method applied by Omari et al., [41] and AL-Hamdany and Jihad, [47]. About 0.25 g of the castor oil was dissolved in 10 mL of chloroform followed by 30 mL of Hanus iodine solution. The flask was tightly closed and vigorously swirled for 30 minutes in the dark. Subsequently, about 10 mL of potassium iodide (15%)

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was added under shaken, as well as addition of 100 mL of distilled water. The solution was titrated with the iodine solution against sodium thiosulfate (0.1 N) until the yellowish appearance. After that, about 2 - 3 drops of starch solution was added converting the solution color into the blue. The titration was continued until fading the blue color and the volume of $\text{Na}_2\text{S}_2\text{O}_3$ at this end point was recorded. The same procedure was used for blank test (without oil). The iodine number (IN) was calculated by the following expression[41]:

$$\text{IN} = 12.69 \times C(V_1 - V_2)/m, \text{ where}$$

C = Concentration of sodium thiosulphate used,

V1 = Volume of sodium thiosulphate used for blank

V2 = Volume of sodium thiosulphate used for the oil, and

m = Mass of the castor oil.

2.3.2.2. Determination of Saponification Value (SV)

The SV is the amount of potassium hydroxide in milligrams needed to saponify one gram of an oil under certain conditions. It is an indicator to molecular weight or chain length of the fatty acids found in the oil.

The SV was determined according to the standard procedure applied by Akpan *et al.* [40]. About 0.5 g of the castor oil dissolved in 10 ml of absolute ethanol was mixed with 10 ml of potassium hydroxide (2.5N) under two hours-refluxing duration and finally was cooled. The blank solution is simply about 10 ml of oil free-KOH. For either oil sample or blank-solution, the unreacted portion of the KOH was titrated with oxalic acid (2.5N) using phenolphthalein indicator. Then, the saponification SV value was determined using the following equation.

$$\text{SV} = [56 \times (V_1 - V_2) \times 1000] / [2 \times 1000 \times W], \text{ where } W \text{ is the castor oil weight (g), } V_1 \text{ is the volume of 0.5N oxalic acid for blank solution (mL), and } V_2 \text{ is the volume of 0.5N oxalic acid for the castor oil (mL).}$$

2.3.2.3. Determination of Acid Value (AV)

The AV of an oil is the milligrams amount of potassium hydroxide needed for neutralization of one gram of the oil. It is a measure of amount of carboxylic acid groups (-COOH) in a fatty acid constituting an oil. The AV of the castor oil was determined by dissolving about 0.5 g of the oil in 25 ml of absolute ethanol phenolphthalein indicator. The mixture was heated in a shaking water bath for 5 minutes. Subsequently, while hot, the free acid was drop-wisely titrated with KOH (0.1N) at a rate of 30 alkali drops per minute. The solution was continuously agitated until the first appearance of the true pink colour that did not fade within 10 seconds. Vigorous shaking was done when approaching the endpoint to ensure thorough mixing. The volume of KOH (0.1N) reacted with the oil was recorded. The AV was determined using the following equation [41,48]:

$$\text{AV} = 5.61(V \times N)/W, \text{ where } V \text{ is the volume of the KOH (ml), } N = \text{KOH normality, and } W \text{ is the weight of the castor oil (g).}$$

2.3.2.4. Determination of pH Value

About 2g of the castor oil was mixed with 13ml of hot distilled water in a beaker with a slow stirring. Then, the emulsion was cooled in a cold-water bath up to 25°C. After standardizing the electrode using suitable buffer solutions, the electrode was immersed into the oil and its pH value was recorded [41,42]

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2.3.2.4. Obtaining the Methyl Esters

The extracted castor oil was passed through a silica gel column and eluted with hexane. The hexane was evaporated under reduced pressure giving the so-called hexane fraction.

2.3.2.5.1. Saponification

It is a process in which an oil is converted into soap and alcohol by heating the oil in the presence of aqueous alkali such as KOH or NaOH.

This process was done before the methylation of the fatty acids present in the castor oil according to Silva *et al.* [49]. For the hexane fraction, about 10 g was dissolved in about 80 mL of methanol, mixed with about 10 g of KOH and refluxed for 1 h. After cooling, distilled water (240 mL) was added and the alkaline hydroalcohol solution was extracted with hexane (3 times x 50 mL) in a decantation funnel. The organic phases were combined, dried over Na₂SO₄ and concentrated under reduced pressure, the unsaponifiables giving the pale yellow solid (1.87 g). The hydroalcoholic phase was acidified with 20% HCl to pH 3-4 and then subjected to extraction with acetone (3 times x 50 mL). The organic phases were combined, dried over Na₂SO₄ and concentrated under reduced pressure to give the saponifiables as a bleached solid (7.15 g).

2.3.2.5.2. Methylation of the Fixed Oil

Chet *et al.* [50] stated that methylation enhanced the determination of both the fatty acids and the other components in the volatile oil extracted from *Houttuyniacordata* Thunb. Accordingly, this process was done for the saponifiable fatty acids present in the castor oil according to Silva *et al.* [49].

2.3.2.6. Analysis and Identification by GC-MS

Using the saponification/ methylation route is helpful for identification of fatty acids [49]. The castor fixed oil was analyzed using a Thermo GC-Trace ultra-system (Thermo Co. USA). Its chemical constituents were fractionated and separated on a fused-silica capillary column (Elite- 5MS column, Thermo Scientific GC Column) with chemically bonded phases DB1 (J&W Scientific). The operational parameters of the GC-MS analysis used are summarized at Table 1. The peaks were tentatively identified based on library search using National Institute of Standard and Technology (NIST), USA and Wiley Registry 8 Edition as well as by comparison of their retention indices with literature data. In addition, the yields of the chemical constituents of the oil were determined using the peak area normalization method [49].

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Table 1. The operational parameters of the GC-MS used for analyzing the castor oil.

Parameter		Value	
GC	Column dimension	Length	30 m
		Internal diameters	0.25 mm
		Solvent's thickness film	0.25 μ m
	Column temperature	Initial temperature (IT)	40 $^{\circ}$ C
		Residence time (RT) of the IT	4 min
		Maximum final temperature (MFT)	220 $^{\circ}$ C
		RT of the MFT	15 min
		Heating rate	4 $^{\circ}$ C/min
	Injector temperature	250 $^{\circ}$ C	
	Injection volume	1 μ l	
	Flow rate of the carrier gas (helium)	20 ml/min	
Transfer temperature	280 $^{\circ}$ C		
MS	Electron ionization (EI) mode	Negative chemical ionization	
	Ionization voltage	70 eV	
	Ion source temperature	180 $^{\circ}$ C	
	Scanning range	50-600 Da	

III. RESULTS AND DISCUSSION

3.1. Physical Characterization of the Castor Fixed Oil

The values of the investigated physical properties of the castor oil, namely yield, specific gravity, refractive index, iodine number, saponification value, acid value and pH value are shown in Table 2.

Table 2. Physical characterization of the castor oil as compared to the ASTM specifications

Properties	Mean values ¹	
	Present investigation	ASTM ² specifications
Oil yield	36.12 \pm 1.03	Not defined
Specific gravity	0.973 \pm 0.001	0.957 - 0.968
Refractive index	1.48 \pm 0.092	1.476 - 1.479
Iodine number (g I ₂ /100 g oil)	84.8 \pm 0.247	82 - 88
Saponification value (mg KOH/g oil)	181.55 \pm 3.79	175 - 187
Acid value [mg KOH/g oil]	0.869 \pm 0.004	0.4 - 4.0
pH value	6.48 \pm 0.359	Not defined

¹Each value is an average of 5 samples \pm standard deviation.

²American Society for Testing and Materials

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3.1.1. Castor Oil Yield

It can be seen from Table 2 that high oil yield was obtained from castor seeds (36.12 %) by pressing and can be maximize by re-extracting the seed cakes by solvents. The percentage yields of the castor fixed oil are approach to those found in the literature. The yield value was lower than those produced by Omari *et al.* [41] who have extracted their castor oil by hexane solvent obtaining higher yields of the oils.

3.1.2. Specific Gravity (SG)

The SG of an oil is an indicator of its purity and can be used to differentiate various oily solutions [41]. In addition, they added that the SG of oil the floating degree over an aqueous solution as a spill where a compound can be found in water in case of a spill [41]. Examining Table 2, the mean value of the SG of the castor oil was found to be 0.973. This value is slightly higher the ASTM specification range (0.957 - 0.968) stated for the castor oil. The minor differences in the SG values between literatures can be attributed to the presence of some impurities present in the castor oil in the present investigation due to using the hot-pressing extraction technique [41].

3.1.3. Refractive Index (RI)

Examining Table 3 indicates that RI of the castor oil (1.48) lies within the cited values [40,41]. The minor differences between cited data may be attributed to differences in conditions of planting and harvesting conditions of the mother shrubs as well as the researches conditions as reported by Omari *et al.* [41]. In addition, presence of impurities such as gums, phosphates...etc in the oil might alter the RI values. Generally, the higher the RI of castor oil, the higher the unsaturation degree or conjugation and vice versa [41]. However, the moderate value of the RI property for the castor oil is matched with its moderate iodine number (84.8 iodine unite) since two direct relationships between the unsaturation and each of iodine number and refractive index can be understood.

3.1.4. Iodine Number (IN)

The result obtained for the IN for the castor oil is shown in Table 2. The mean value of the IN under investigation was found to be 84.8 (g I₂/100 g oil) within the normal range for the castor oil literature. In addition, this IN value is higher than those for fixed oils extracted from coconut and palm kernel (7-10 and 16-19 g I₂/100 g oil, respectively) as shown in Table 3. Furthermore, the IN of the castor oil was lower than those for sunflower, soybean, linseed and tung oil that ranged from 118-178 g I₂/100 g oil (Table 3). The lower IN than the later species can be attributed to the presence of more saturated fatty acids in the castor oil comparing to them, which did not react with the Hanus iodine solution [41]. On the other hand, higher IN values indicate excess unsaturation level of the oil, which increase the amount of iodine absorbed by unsaturated acids. Based on these findings, since the IN of the castor oil was lower than 100 iodine unit, the oil could be classified as a non-drying oil and is not suitable for paint industry but can be oriented the soap industry [51]. For more illustration, It can be seen from the Table 3 that coconut and palm kernel oils are very saturated (7-19 iodine unit) which means that they are suitable for soap industry. On the other hand, tung and linseed oils are highly

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unsaturated, which makes the ideal as drying oils in paint cosmetic, vanishand coating industries as well as nutritional purposes.

Table 3. Comparisons between the castor oil and othercommercial fixed oils in their iodine number.

Seed Oil Source ¹	Value in Iodine unit ⁴		Meaning	Application
Coconut	7-10	Lower than 100	Highly saturated	Soap industry
Palm kernel	16-19		High saturated	
Jojoba ²	80 ~82		Medium unsaturated	
Castor ³	84.8		Medium unsaturated	
Sunflower	118 – 144	Higher than 100	High unsaturated	Drying oil in paint industry
Soybean	120-136		High unsaturated	
Linseed	136-178		Highly unsaturated	
Tung oil	163-173		Highly unsaturated	

¹From Thomas[46].

²From Sandha and Swami [52].

³ From the present investigation.

⁴ g I₂ /100g oil

3.1.5. Saponification Value (SV)

The SV property of the castor oil under the present investigation was recorded as a mean value to be 181.55 SV-unit (mg KOH/g oil).It is worth for mentioning that higherSVrefers to lower molecular weight (MW) of the triglycerides and vice versa [41]. Accordingly, the castor oil was expected to have lower MW of the triglyceride than other fixed oils with lower SV. From Table 2, it was shown that castor oil had ahigh SV that lies within the ASTM specification range (175-187 SV-unit) and comparable to those cited in literatures [41,53]. The values are characteristic of castor oil and the variations noticed between cited data canbe attributed to little disparities in the fatty acid composition.

3.1.6. Acid Value(AV)

The AV of the castor oil had low value (0.869 mg KOH/g oil) as compared to literature [38,41] although it lies within the ASTM-specification range (0.4 - 4.0 mg KOH/g oil) as presented at Table 2.Since the AV is a measure of amount of carboxylic acid groups in a fatty acid constituting an oil, it is also a measure for quantifying the fatty acids. Accordingly, the castor oil had low content of free fatty acids. The obtained AV of the castor oil was lower than one obtained by Omari *et al.*[41] duethe researcher had collected the seeds from the ground through a period after curing. Accordingly, the seeds had spent an adequate time to hydrolyse their content of triglycerides by lipase enzyme into freefatty acid and hence enhancing the acid value.

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3.1.7. pH Value

Because of the presence of free fatty acids in the castor oil, it is worth to mention that it is essential to estimate the pH to know its dissociation state. As shown in Table 2, the pH value was found to be high (6.48) and higher than those found by Omari *et al.*, [41]. This higher pH value can be attributed to the expected higher free fatty acids content in the castor oil, which is related to its acid value [41].

3.2. Chemical Characterization of the Castor Oil Using GC-MS

Analysis of the oil by GC coupled with MS using the saponification/ methylation route helped the identification of the fatty acids.

The GC-MS chromatogram of the crude castor seed oil is presented at Figure 2. The chromatogram shows the peaks concerning the chemical constituents of the crude oils represented as methyl or methyl esters. It is clear from Figure 2. that the identified peaks are varied according to their concentration in the oil.

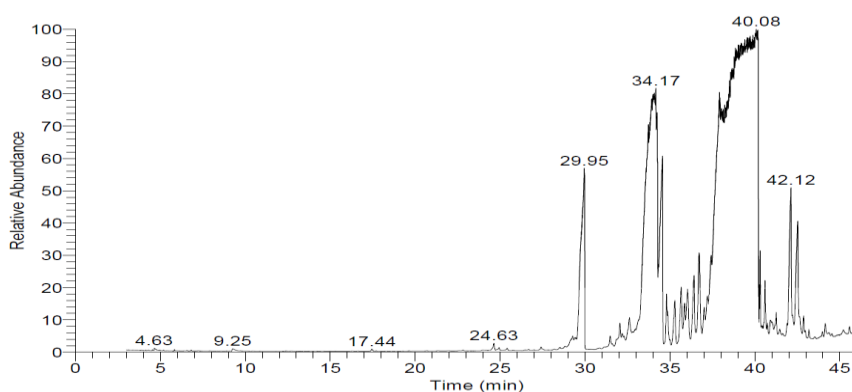


Figure 2. Typical GC-MS total ionic chromatogram of the castor oil.

The major chemical constituents of the castor fixed oil are shown in Figure 2 and Table 4. Important specification details, namely trivial name, formula, molecular weight (MW), and yield were included in the Table 4. Seven major compounds were detected in the castor oil. These constituents can be classified in three divisions according to the length of the carbon chain: 1) Lower chain (17 carbon atoms), namely hexadecanoic acid, methyl ester (6.48%) and methyl hexadec-9-enoate (4.47%), 2) Medium chain (18 carbon atoms), namely 9-octadecenoic acid, 12-hydroxy-, [R-(Z)]-, methyl ester (74.99%), (9Z,12Z)-octadeca-9,12-dienoic acid (4.32%), (9Z)-octadec-9-enoic acid (3.31), and 3) Longer chain (19 carbon atoms), namely, heptadecanoic acid 16-methyl, methyl ester (4.75%), and octadecanoic acid, 9,10-dihydroxy, methyl ester (3.68%) as clear in Table 4.

It can be noticed that all the chemical constituents of the castor oil presented at Table 4 are in the form of methyl ester derivative because of methylation of the oil prior to the GC-MS analysis except for methyl hexadec-9-enoate and (9Z)-octadec-9-enoic acid whereby they are methylated derivative. The methylation increased the volatility of the oil to be adapting the Programme Temperature Volume of the injector of the GC-MS device [54,55]. It is worth mentioning that methyl esters derivatives of free fatty acids have the same fragmentation patterns as their parent free fatty acids, except for

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the molecular weight of the methyl esters are higher than their parent free fatty acids by 14 g/moles [55]. In addition, all the analyses of the castor oil were performed for the crude castor oil since there are no differences between the crude and the dehydrated castor oil in this concern except for acid value and iodine number [55].

Based on the trivial names, the seven chemical constituents detected in the castor oil can be classified into five groups as follow:

1) Palmitic acid derivatives (10.95 %), 2) Ricinoleic acid (74.99 %), 3) Linoleic acid (4.32%), 4) Oleic acid (3.31%), 5) Stearic acid derivatives (8.43 %) as shown in Table 4.

For the ricinoleic acid, about thirty five trivial synonyms are included in the literature. It is one of the most important industrial vegetable oils. It is unsaturated omega-9 fatty acid [54] and a hydroxy acid. The higher yield value of the ricinoleic acid (74.99%) falls within the cited range (70-90%) reported by numerous researchers [9,13,56]. Castor oil is the unique vegetable oil as a source of the hydroxylated fatty acid known as ricinoleic acid [57]. Examining the chemical structure of the ricinoleic acid (Figure 5), the hydroxyl groups in its chain can be removed to create double bonds converting the oil from non-drying to drying oil. This is useful in the production of alkyd resin coating [55] and add additional importance to its industrial benefits.

In the present investigation, three prominent saturated fatty acids and or their derivatives were identified, namely palmitic, linoleic, and stearic acids (Table 4). Palmitic acid accounted about 6.48% of the total fatty acids in the castor oil. A derivative of this fatty acid was also detected, namely methyl hexadec-9-enoate that constituted about 4.47% of the total fatty acids. Palmitic acid has a potential economic value whereby its sodium salt is used for soap and cosmetic industries [45,54]. Linoleic acid accounted about 4.32% of the fatty acids in the castor oil. It has anti-inflammatory and moisture retention effects in cosmetics [58]. Octadecanoic acid termed as stearic acid was appeared in the form of two derivatives, namely heptadecanoic acid, 16-methyl, methyl ester (known as methyl isostearate) that yielded 4.75% of the total fatty acids, and octadecanoic acid, 9,10-dihydroxy (known as methyl 9,10-dihydroxy stearate) with a yield of 3.68% of the total fatty acids as shown in Table 4.

Table 4. Trivial names, formula, molecular weight (MW), retention time (RT), and yield of the prominent chemical constituents of the castor oil.

Chemical compound ¹	Trivial names		Formula	MW g/mole	Yield, %	
Hexadecanoic acid, methyl ester	Palmitic acid	Palmitic acid derivatives	C ₁₇ H ₃₄ O	270.45	6.48 ² ± 0.082	10.95 ± 1.12
Methyl hexadec-9-enoate	Methyl palmitelaidate		C ₁₇ H ₃₂ O ₂	268.44	4.47 ² ± 0.86	
9-Octadecenoic acid, 12-hydroxy-, [R-(Z)]-, methyl ester	Ricinoleic acid		C ₁₈ H ₃₄ O ₃	298.46	74.99 ³ ± 2.74	
(9Z,12Z)-Octadeca-9,12-dienoic acid	Linoleic acid		C ₁₈ H ₃₂ O ₂	280.45	4.32 ± 0.63	7.63 ± 0.86
(9Z)-Octadec-9-enoic acid	Oleic acid		C ₁₈ H ₃₄ O ₂	282.47	3.31 ± 0.42	
Heptadecanoic acid, 16-methyl, methyl ester	Methyl isostearate	Stearic acid derivatives	C ₁₉ H ₃₈ O ₂	298.50	4.75 ² ± 0.042	8.43 ⁴ ± 1.09
Octadecanoic acid, 9,10-dihydroxy, methyl ester	Methyl 9,10-dihydroxy stearate		C ₁₉ H ₃₈ O ₄	330.50	3.68 ² ± 0.027	

¹According to the International Union of Pure and Applied Chemistry (IUPAC).

²Each value is an average of 3 observations.

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³Each value is an average of 6 observations.

⁴Each value is an average of 12 observations \pm standard deviation.

The mass spectra and the fragmentation patterns of the major chemical constituents of the crude castor oil resulted from the GC/MS analysis were compared with the spectra in the database of mass spectra library of National Institute of Standards and Technology (NIST) for their identification [55].

For the confirmed compounds, the chemical structures, the molecular mass and fragmentation patterns of the major constituents of the castor oil are presented at Figures 3-9.

The qualitative and quantitative mass ion helped in determining the prominent chemical constituents detected in the crude castor oil (Figures 3-9). In addition, fragmentation patterns of the MS- chromatograms of the prominent chemical constituents of the castor oil are presented at Table 5.

For the hexadecanoic acid, methyl ester, its chemical structure and mass spectrum are shown in Figure 3 and Table 5. Its mass spectrum showed that the prominent peaks were arisen 41, 43, 56, 74, 87, and 143 m/z. Comparing its mass spectrum with the standard hexadecanoic acid, methyl ester profile (Fig. 3), the compound existence was confirmed since they have the same fragmentation patterns [55,60].

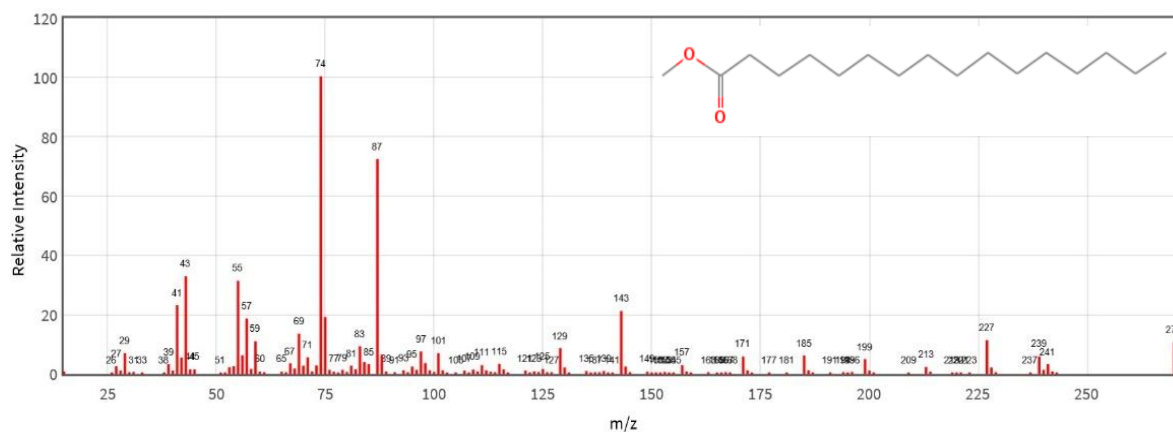


Figure 3. Chemical structure and the mass spectra-chromatogram of hexadecanoic acid, methyl ester detected in the castor oil.

Concerning the hexadecanoic acid, methyl ester detected in the castor oil, its chemical structure and mass spectrum are shown in Figure 3 and Table 5. Its mass spectrum showed that the prominent peaks were arisen 41, 43, 56, 74, 87, and 143 m/z. Comparing its mass spectrum with the standard hexadecanoic acid, methyl ester profile [62] as indicated by Figure 3, the compound existence was confirmed since they have the same fragmentation patterns [55,60,61].

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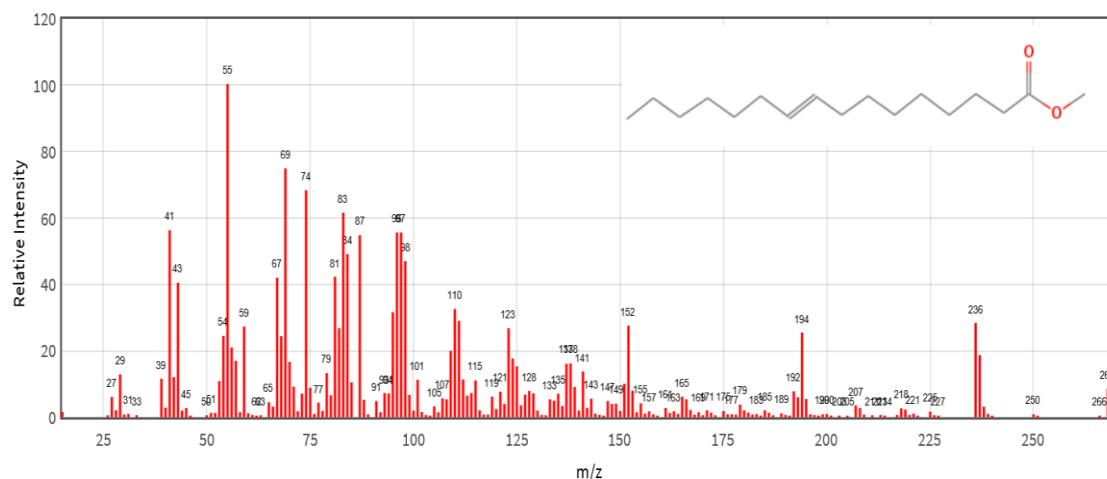


Figure 4. Chemical structure and the mass spectra-chromatogram of methyl hexadec-9-enoate detected in the castor oil.

Regarding the methyl hexadec-9-enoate detected in the castor oil, each of chemical structure and mass spectrum is shown in Figure 4 and Table 5. Its mass spectrum showed that the prominent peaks were arisen 41, 43, 56, 74, 87, and 143 m/z. Comparing its mass spectrum with the standard methyl hexadec-9-enoate profile (Fig. 4), the compound existence was confirmed since they have the same fragmentation patterns [55,60,61].

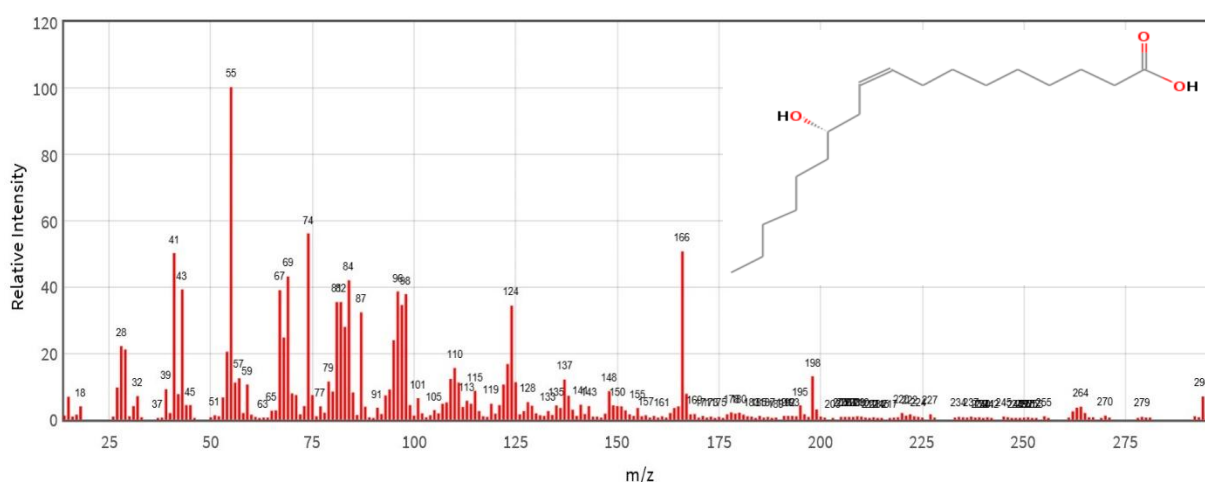


Figure 5. Chemical structure and the mass spectra-chromatogram of 9-octadecenoic acid, 12-hydroxy-, methyl ester, [R-(Z)]-known as ricinoleic acid methyl ester detected in the castor oil.

For the 9-octadecenoic acid, 12-hydroxy-, methyl ester, [R-(Z)]-detected in the castor oil, the chemical structure and mass spectrum of this compound are shown in Figure 5 and Table 5. Its mass spectrum showed that the prominent peaks

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were arisen 28, 29, 41, 43, 55, 67, 69, 74, 82, 83, 84, 87, 96, 97, 98, 124, 166, and 198 m/z. Comparing its mass spectrum with the standard 9-octadecenoic acid, 12-hydroxy-, methyl ester, [R-(Z)]- profile (Fig. 5), the compound existence was confirmed since they have the same fragmentation patterns [55,60,61].

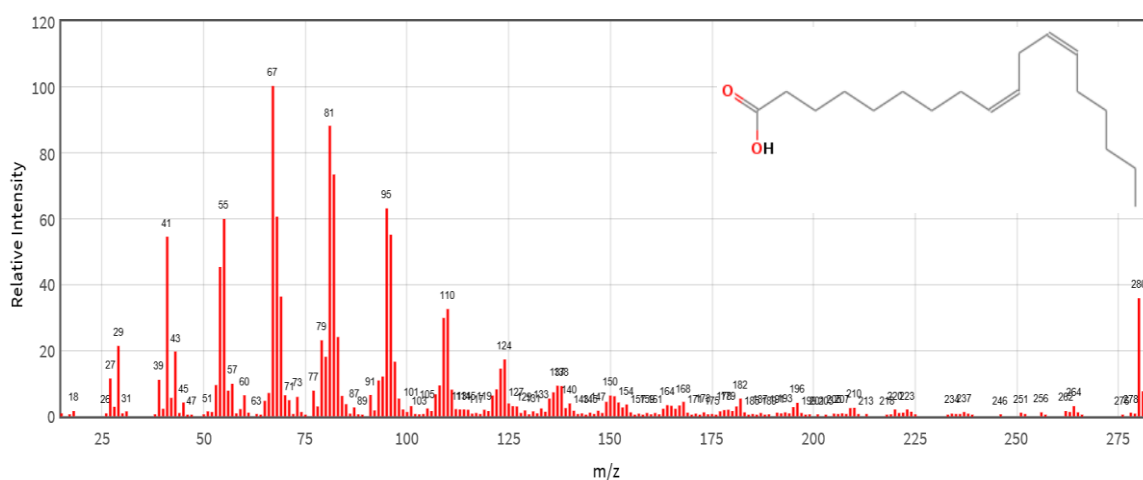


Figure 6. Chemical structure and the mass spectra-chromatogram of (9Z,12Z)-octadeca-9,12-dienoic acid detected in the castor oil.

Regarding the chemical structure and mass spectrum of (9Z,12Z)-octadeca-9,12-dienoic acid detected in the castor oil (Figure 6 and Table 5), the prominent peaks were clearly present at 29, 41, 55, 67, 68, 81, 96, 110, and 124 m/z. Comparing its mass spectrum with its standard profile (Fig. 6), the compound existence was confirmed where they have the same fragmentation patterns [55,60,61].

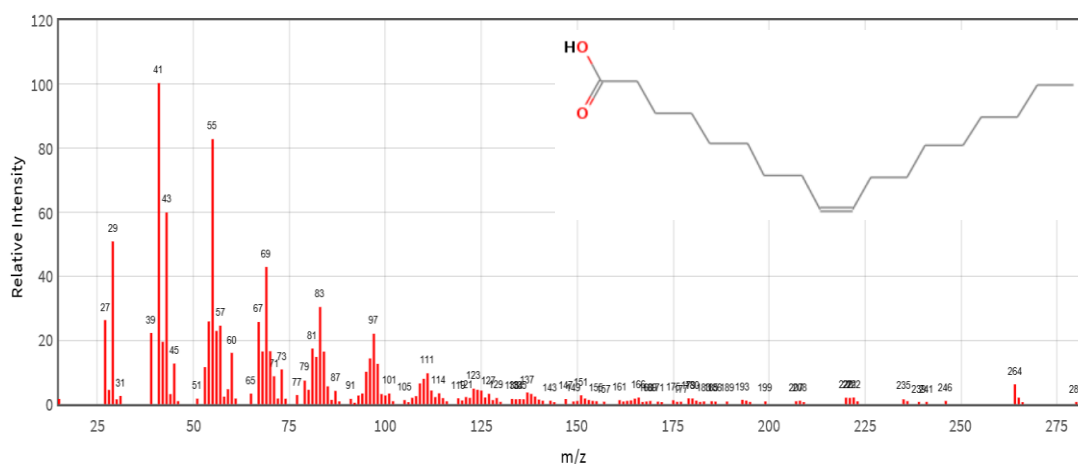


Figure 7. Chemical structure and the mass spectra-chromatogram of (9Z)-octadec-9-enoic acid detected in the castor oil.

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Concerning the (9Z)-octadec-9-enoic acid detected in the castor oil, its chemical structure and mass spectrum are shown in Figure 7 and Table 5. Its mass spectrum showed that the prominent peaks were appeared at 27, 29, 41, 43, 55, 83, and 97 m/z. Comparing its electron ionization chromatogram with the standard (9Z)-octadec-9-enoic profile (Fig. 7), the compound existence was confirmed since they have the same fragmentation patterns [55,60,61].

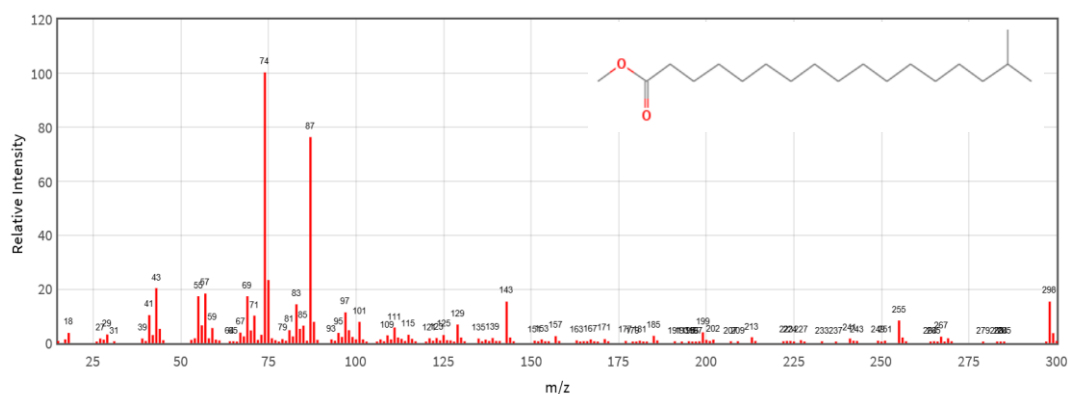


Figure 8. Chemical structure and the mass spectra-chromatogram of heptadecanoic acid, 16-methyl, methyl ester detected in the castor oil.

The chemical structure and mass spectrum of heptadecanoic acid, 16-methyl, methyl ester detected in the castor oil are presented at Figure 8 and Table 5. Its mass spectrum showed that the prominent peaks were found at 43, 55, 57, 69, 74, 87, 143, 256, and 290 m/z. Comparing its electron ionization chromatogram with the standard heptadecanoic acid, 16-methyl, methyl ester profile (Fig. 8), the compound existence was confirmed since they have the same fragmentation patterns [55,60,61].

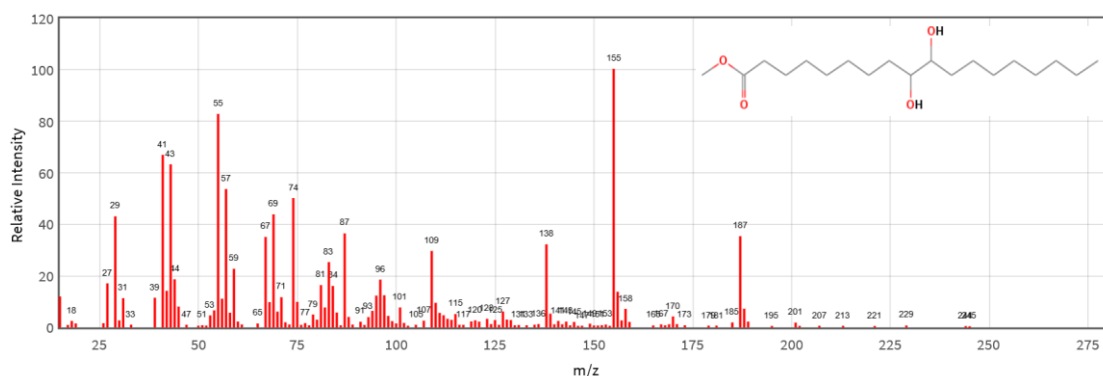


Figure 9. Chemical structure and the mass spectra-chromatogram of octadecanoic acid, 9,10-dihydroxy, methyl ester detected in the castor oil.

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The chemical structure and mass spectrum of octadecanoic acid, 9,10-dihydroxy, methyl ester detected in the castor oil are shown in Figure 9 and Table 5. The mass spectrum of this compound shows that the prominent peaks were arisen at 29, 41, 43, 55, 57, 67, 69, 74, 83, 87, 96, 109, 138, 155, and 187 m/z. Comparing its mass spectrum with that for its standard profile [60] as indicated in Fig. 9, the compound existence was confirmed since they have the same fragmentation patterns [55,60,61].

Table 5. Fragmentation patterns of the mass spectrometry (MS) chromatograms of the prominent chemical constituents of the castor oil.

Compound ¹	Major peaks of the fragmentation pattern m/z
Hexadecanoic acid, methyl ester	41, 43, 56, 74, 87, 143.
Methyl hexadec-9-enoate	41, 55, 69, 74, 83, 87, 96, 97, 98, 119, 121, 132, 133, 152, 194, 236.
9-Octadecenoic acid, 12-hydroxy-, [R-(Z)]-, methyl ester	28, 29, 41, 43, 55, 67, 69, 74, 82, 83, 84, 87, 96, 97, 98, 124, 166, 198.
(9Z,12Z)-Octadeca-9,12-dienoic acid	29, 41, 55, 67, 68, 81, 96, 110, 124.
(9Z)-Octadec-9-enoic acid	27, 29, 41, 43, 55, 83, 97.
Heptadecanoic acid, 16-methyl, methyl ester	43, 55, 57, 69, 74, 87, 143, 256, 290.
Octadecanoic acid, 9,10-dihydroxy, methyl ester	29, 41, 43, 55, 57, 67, 69, 74, 83, 87, 96, 109, 138, 155, 187.

¹ Based on International Union of Pure and Applied Chemistry (IUPAC).

Based on the results of the present investigation about the assessment of yield and quality of the castor oil extracted using hot-pressing machine from local *Ricinus Communis* L., The oil yield and its quality were very encouraging for candidating such species as a pivot of small-scale industrial projects.

IV. CONCLUSIONS

- High castor oil yield was obtained for seeds (36.12 %) by hot-pressing and can be maximize by re-extracting the seed cakes by solvents.
- The specific gravity, refractive index, and iodine number of the castor oil was found to be 0.973, 84.8, and 1.48 (g I₂ /100 g oil), respectively.
- The castor oil had a saponification value of 181.55 mg KOH/g oil and was expected to have lower molecular weight of the triglycerides than other fixed oils with lower saponification.
- The pH value was found to be high (6.48) and can be attributed to the expected higher free fatty acids content in the castor oil, which is related to its acid value (0.869 mg KOH/g oil).
- Analysis of the oil by gas chromatography coupled with mass spectrometry using the saponification/methylation route helped the identification of the fatty acids.

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- The primary constituent is the ricinoleic acid, making up to 74.99%, followed by palmitic acid derivatives (10.95%), stearic acid derivatives (8.43%), linoleic acid (4.32%), and oleic acid (3.31%).

Acknowledgments

The authors thanks the following sectors at KAU for their technical support: 1) The Central Laboratory for the Industrial Skills Development/the Intellectual Property Investment/Vice Presidency for Business and Knowledge Creativity, 2) The Wood Technology Laboratory -the Arid Land Agriculture Dept./Faculty of Meteorology, Environment and Arid Land Agriculture, and3) The Central Lab/ the Environment.

Conflicts of Interest

The authors declare no conflict of interest.

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