

Chemical and Physical Characteristics and Fatty Acid Profile of Some Oil Seeds of Apiaceae Family in Iraq

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Abstract

Fixed oils (lipids) from the seeds of Anise (*Pimpinella anisum* L.), Cumin (*Cuminum cyminum* L.), Fennel (*Foeniculum Vulgare* L.) and Caraway (*Carum carvi* L.) were extracted by the cold press. The oil content, chemical and physical properties, as well as, minerals content were determined. Results approved that the oil content of the examined samples was at the range of 12.5-17.16%; the most dominant fatty acids were petroselinic acid (18:1- δ -6), which is a characteristic fatty acid of the Apiaceae family (anise, cumin, fennel, and caraway) at the range of 55.43 to 79.3%, followed by linoleic acid (13.16 to 331.71%). The obtained results from free fatty acid (FFA) and acid value (AV) found to be the lowest in anise seed oil (1.6%, 0.82 mg KOH/g oil, respectively); while, caraway seed oil had the highest values of PV and viscosity at 25 °C (3.7 meq. O₂/kg oil, 85.24 Cp, respectively). Chlorophyll and density measured from 0.09-0.43 mg/kg and 0.93-0.96 g/cm³. In this study, the mineral content of the Apiaceae plant s oils is detected by Emission Scanning Electron Microscopy (FE-SEM). Cumin seed oil had the lowest value of sulfur and carbon (0.04, 68.65, respectively). Aluminum and Bromine ranged from 0.79-20.5 and 1.47-14, respectively. The percentage of inhibition of caraway, cumin, Anise, and Fennel fixed oil in the linoleic acid system were 78.87, 75.31, 60.26, and 59.11%, respectively, compared with Standard synthetic antioxidant BHT which was 92.07%.

Keywords: Antioxidants, Apiaceae, Fatty acids, GC-MS, FE-SEM, petroselinic acid,

1. INTRODUCTION

Apiaceae family (also known as Umbelliferae) is one of the major families for culinary herbs and root crops comprising up to 400 genera of plants distributed throughout a wide variety of habitats in the temperate climate regions of the world (Dempewolf *et al.*, 2014). They are frequently used as vegetables, spices or drugs owing to the presence of useful secondary metabolites (Kubeczka *et al.*, 1982). Recently; a tremendous attention has been given to the cultivation of this family in Iraq; with a significant variety of Umbelliferae members planting in the south, middle and north of Iraq (Almehemdi *et al.*, 2011). Most therapeutic and aromatic plants are frequently utilized as flavors, vegetables or medications inferable from the nearness of helpful optional metabolites (Weber *et al.*, 1995). Oils and fats are important components in the human diets and more than 90% of the world production is used as food or a constituent in food production (Elaine, 1990). Some of them are known for their abnormal state of polyunsaturated fat in seed oil, for example, the seeds of the Apiaceae family (Matthäus and Özcan, 2015).

Fatty oils of the Apiaceae family were obtained as by-products and a potential use of these resulting seed oils depending on the fatty acid composition and the content of minor components in the oil (Kooti *et al.*, 2015). Fatty acid analysis can be used to evaluate the composition, stability and nutritional quality of fats and oils, but not always their functional properties (Aitzetmuller. 1993). Raw materials such as seeds are interesting and valuable sources for the production of vegetable oils used as suppliers of fatty acids in human nutrition or technical applications. Fatty acids obtained saturated fatty acids including Myristic, Palmitic, Stearic and Arachidic acid; as well as, unsaturated fatty acids such as Petroselinic, Oleic, Linoleic and Linolenic acid.

Petroselinic acid (C18:1 (6c) is one of the major fatty acids in Apiaceae seeds, which include in species such as fennel, cilantro, celery, parsley, etc., with a percentage of dominance up to 80% (Charvet *et al.*, 1991). This fatty acid and its cleavage products (lauric and adipic acid) are important oleo chemical raw materials (Reiter *et al.*, 1998). Many studies were employed GC-MS in a determination of the fatty acids composition of seed oils for Apiaceae family. GC-MS is the most powerful technique using to identify the presence components in the oils.

Different possibilities for the gas chromatographic determination of petroselinic acid have already been suggested. In general, fatty acid patterns of vegetable oils are detected, either qualitatively or quantitatively as fatty acid methyl esters by capillary gas chromatography alongside petroselinic acid, two other positional isomers of octadecenoic acid occur in Apiaceae seeds: oleic (C18:1 9c) and cis-vaccenic acid (C18:1 11c) (Reiter *et al.*, 1998).

Additionally, during the past few decades, extensive research on nutrient elements from seed oils have been carried out to define their role in the human diet. Their maximal levels have therefore become worldwide quality standards. Essential and non-essential elements are also recognized and their required or recommended contents in the human diet have been established. In spite of this reality, elevated levels of both essential and non-

essential elements can also cause morphological abnormalities, reduced growth, increased mortality and mutagenic effects in humans. This lead to the results to maintain desirable body weight is necessary (Takeuchi *et al.*, 1998 ; Malik *et al.*, 2008).

Many aromatic plants are medicinally important due to the presence of the rich diversity of secondary metabolite content and thus their usage in regular diet, not merely serve as a source of aroma and flavoring agent, but also provides dietary antioxidants (Schwab *et al.*, 2008) The seed oil of Apiaceae family is known as an excellent beginning of natural antioxidants, these antioxidant activities were compared to standard antioxidant such as butylated hydroxyl anisole (BHA), and butylated hydroxyl toluene (BHT), and α -tocopherol (Shan *et al.*, 2005).

To the best of our knowledge, there is no detailed study on the physical properties, chemical composition, fixed oil composition and mineral contents of some Apiaceae seeds in Iraq. The aims of the present work are to evaluate of unsaturated fatty acid in fixed oil extraction from Caraway, Cumin, Anise, and Fennel seeds oil and compare the oil contents as well as the chemical and physical properties and fatty acids of oils extracted from examined seeds and use the seed oil as an antioxidant.

2. MATERIAL AND METHODS

2.1. Plant material

The seeds of Caraway (*Carumcarvi* L.), Anise (*Pimpinellaanisum* L.), Fennel (*Foeniculum Vulgare* L.), And Cumin (*Cuminumcyminum* L.) were collected from Medicinal and Aromatic Plant unit in College of Agriculture, Basra University, Iraq. All chemicals and solvents were of analytical grade and used without further purification.

2.2. Preparation of Fatty Acid Methyl Esters (FAMES)

Fatty acid content and composition were determined simultaneously in the oil samples. Fatty acid analysis was completed in triplicate consisted of two consecutive steps, preparation of fatty acid methyl ester (FAME) and chromatographic analysis. The AOAC (1997) method was followed to esterified the oil extract. FAME was prepared from the oil extracted from 1 ml sample by heating with 5 ml methanolic NaOH first for esterification. 5 ml n-hexane was added to recover the methyl esters in the organic phase. Saturated NaCl solution was added to the mixture, then the aqueous and organic layers were separated using a profile-separating funnel. The upper n-hexane phase was pipetted out and kept in 5 ml glass vials and store under sub-zero temperature until the GC-MS analysis is done.

2.3. Total oil extraction

Total oils from seeds were extracted according to Bligh and Dyer (1959) with some modification, as mentioned by Marzouk and Cherif (1981). Thus, 0.5 g air-dried seed were fixed in boiling water for 5 min and then ground manually with chloroform/methanol/hexane mixture (1:2:1, v/v/v). After washing with water of fixation and decantation during 24 h at 4 °C, the organic phase containing total lipids were dried under a stream of nitrogen, dissolved in toluene-ethanol (4:1, v/v) and stored at -20 °C for further analysis. A triplicate of the total extracted lipid used.

2.4. Gas Chromatography Mass Spectrometer (GC MS) to Analysis Fatty Acid Methyl Ester (FAME)

GC-MS analysis was performed at the University of Basra, College of Agriculture, The analysis of methylated fatty acids was done by a Shimadzu QP2010 quadruple Gas Chromatography Mass Spectrometer (GC-MS) instrument a GC-MS equipped with (5% diphenyl/95% dimethyl polysiloxane) fused to capillary column 30 $\times$ 0.25 μ m ID (inner diameter of the column) $\times$ 0.25 μ mDF (film thickness). Injection one micro liter of the sample into the capillary column (intercut DB5MS, Japan). Helium gas (99.999%) was used as a carrier gas at a constant flow rate of 1 ml/min and an injection 1 μ l was employed. Injector and detector temperatures were set at 280 °C. The injection mode performed was split (1:30). The temperature program was followed at 50°C for one minute and then increase to a rate of 5°C per min with a final temperature of 280°C. For GC-MS detection, an ionization electrons system was operated in electron impact mode with ionization energy of 70 eV. Fatty acid methyl esters were separated at a stable pressure (100 kPa) and the spectrum of the unknown components was compared with a spectrum of the known components stored in the NIST 08 (National Institute of Standards and Technology, U.S.A.) database.

2.5. Chemical and physical properties of fixed oils

Free fatty acid% (as oleic acid %), Peroxide value (as meq.O₂/Kg oil) and Acid value (mg KOH/g oil), were carried out according to AOAC (1997). Refractive Index, Density (g/cm³) and Viscosity (CP) at 25 °C of oil seeds were determined at 25°C with an Abbe refractometer (Alamu *et al.*, 2008). Chlorophyll and Carotenoids content were measured depending on the procedure of (Minguez *et al.*, 1991).

2.6. Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-Ray (EDX) Spectroscopy FE-SEM-EDX analysis

Operation a lumpy mass was after a removal of the moisture. Recorded the dual observations by applying scanning electron microscopy (SEM) in a combination of energy-dispersive X-ray (EDX) spectrometer. For this task, the samples were first loaded on the sample holder using double side tape, then without Coating, the samples were loaded on FE-SEM from Zeiss Germany model supra 55VP. The EDX analyses were performed using EDX detector from Bruker Germany model QUANTAX Flash 6/100.

2.7. Inhibition of lipid peroxidation by ferric thiocyanate

The activity of antioxidant for the extracts was determined according to the ferric thiocyanate method as reported by Kikuzaki and Nakatani (Kikuzaki and Nakatani, 1993).

2.8. Statistical analysis

All the analyses of this study were carried out in triplicate and the results were reported as mean values $\pm$ standard deviation. It was analyzed by Microsoft Excel statistical software (Microsoft Office Excel 2010, Microsoft Corp., and Redmond, WA, USA).

3. RESULTS AND DISCUSSION

3.1. Oil content and fatty acid composition

The fatty acid composition of anise, cumin, caraway and fennel oils, which are critical for their potential health benefits in food applications, have not been widely investigated in Iraq. As shown in Table 1, the oil content of samples was found in the range of 12.5 – 17.16%. The highest average was found in anise seed oil (17.16%) (Fig 1, A), while the lowest average was observed in caraway seed oil which was 12.5% (Fig 1, D). These findings are in accordance with the results of Coşge *et al.* (2013) when they reported that the oil content for sweet and bitter fennel were 12.22, 14.41, respectively. As shown in Fig. 1 and Table 1, the range of total saturated fatty acid (SFA) of examined samples was between 5.61% to 9.41%. The lowest SFA was seen in cumin seed oil (5.61%).

The caraway seed oil had the highest SFA level with the value of 9.14%, and the majority of them was palmitic acid (16:1), as predominant fatty acid (7.08%), followed by stearic acid (18:0) (1.74%) and myristic acid (14:0) (0.07%). The palmitic acid levels of the seed oils ranged from 4.74% in cumin seed oil to 7.08% in caraway seed oil. The stearic acid considered as the second acid in SFA ranged between 0.86% in cumin seed oil to 1.74% in caraway seed oil. Our results are in a good agreement with the findings of Nguyen *et al.* (2015) when they reported that palmitic acid was the predominant fatty acid in anise seed oil, followed by stearic and myristic acid; as well as, the results of Yetim *et al.* (2008) in their determination of saturated fatty acids (SFA) in Apiaceae plants, they found the range was between 6.01 % in fennel seed oil to 13.99% in anise seed oil. Additionally, the results of Laribi *et al.* (2011) showed that SFA in caraway seed oil ranged from 10.36% to 16.32%; the total unsaturated fatty acid (UFA) contents of the samples ranged from 90.85% to 94.38%, and the highest (UFA) was found in cumin seed oil (94.38%). In contrast, the UFA level of the caraway oil was the lowest (90.85%). Yetim *et al.* (2008) determined total unsaturated fatty acid in anise seed oil (UFA) (85.64%) which close to our findings.

Monounsaturated fatty acid (MUFA) had a dietary benefit and could be vital for the clinical investigation of fat absorption via its ingestion monitoring in blood lipids. Their percentages in the examined samples were found to be within the range from 56.29% in caraway seed oil to 79.65% in fennel seed oil. The highest value (MUFA) was determined in fennel seed oil. Monounsaturated fatty acid presented by petroselinic acid (18:1- δ -6), which is a characteristic fatty acid of the Apiaceae family, and interesting because of its antimicrobial activity (Shahat *et al.*, 2011), and its oxidation gives lauric acid (12:0), as important fatty acid used in the soap, cosmetic, medical and perfume industries (Kleiman and Spencer, 1982). The highest value of petroselinic acid was found in fennel (79.3%), with an accordance to their content in other fennel seed oil (Reiter *et al.*, 1998; Rebey *et al.*, 2016; Mathäus & Özcan, 2015), followed by anise (65.18%), cumin (61.13%), and finally caraway seed oil (55.43%). More interestingly, Reiter *et al.* (1998) study on different varieties of caraway was analyzed the fatty acid profiles by automated gas chromatograph, and their results showed that the values of petroselinic acid content (33.5-42.7%), and linoleic acids (34.8-36.5%). Compared with a study of Moura *et al.* (2005) when they reported that palmitoleic acid in ripped and dried fennel seed oil was (2.5, 3.7%, respectively), which higher than those seen in this study (0.35%).

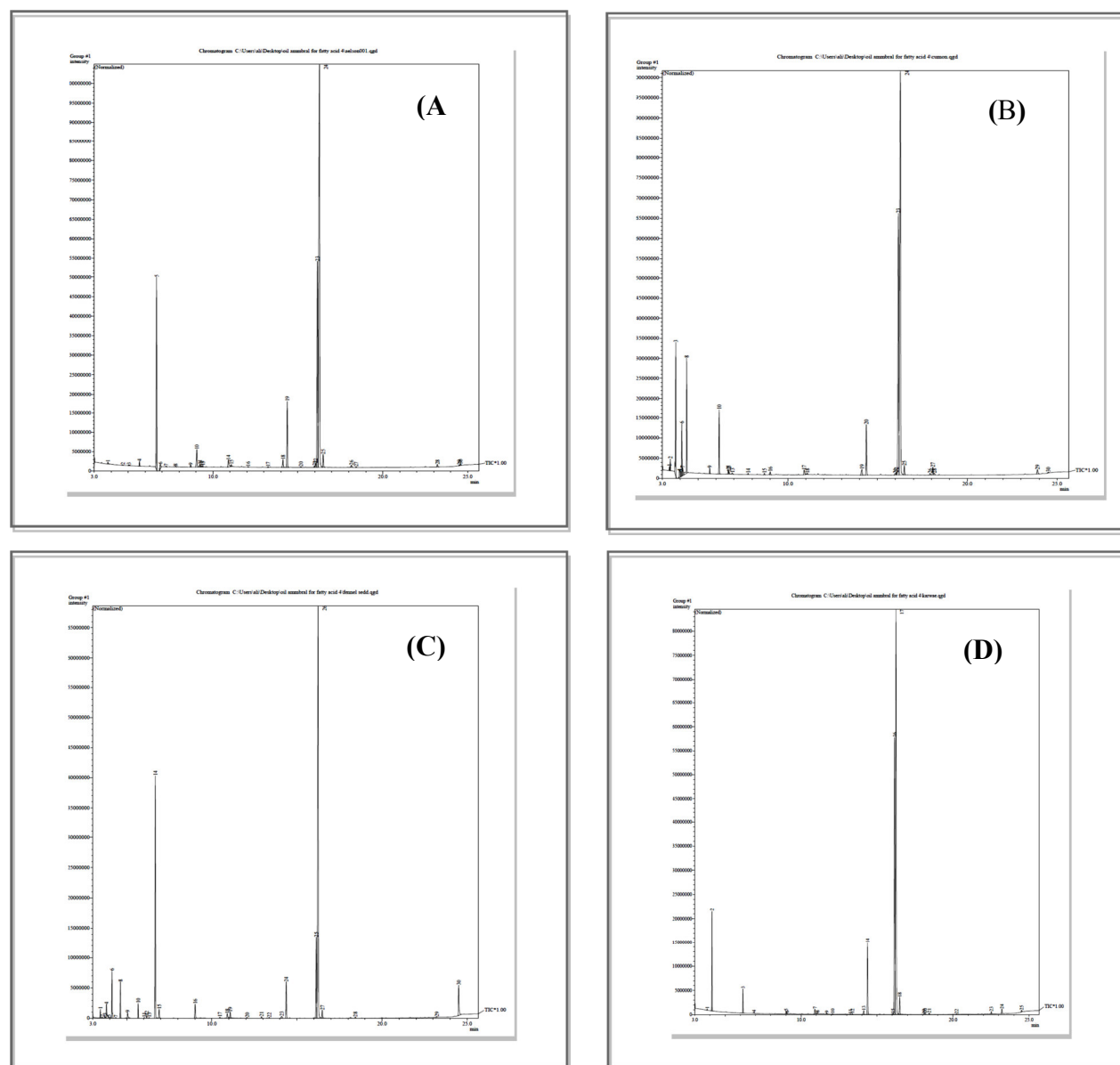


Fig. 1. Chromatograms of (A) Anise, (B) Cumin, (C) Fennel and (D) Caraway seed oil, analyzed as fatty acid methyl esters (ME)

Table 1. Oil content and Fatty acid composition of (Anise, Cumin, Fennel, Caraway) seeds

R.Tim	Fatty Acids	No. of carbo	Fatty Acids (%) Sample of seed oils			
			Anise	Cumin	Fennel	Caraway
12.07	Meristic acid	C 14	0.07±0.01	ND**	0.16 ±0.01	0.08 ±0.01
13.24	Pentadecanoic acid	C15	0.07±0.02	ND	ND	0.08 ±0.005
14.12	Palmitoleic acid	C 16:1	0.79±0.02	0.77±0.02	0.35 ±0.20	0.52 ±0.10
14.37	Palmitic acid	C 16	6.15±0.05	4.74±0.01	5.60 ±0.12	7.08 ±0.19
15.17	9-Octadecynoic acid	18:1	0.09±0.02	ND	ND	ND
15.98	6,11-octadecadienoate	18:2 6,11-	0.24±0.02	0.22±0.01	ND	ND
16.04	6,9-Octadecadienoic acid	C18:2 n-6	0.45±0.00	0.28±0.01	ND	0.07±0.15
16.15	Linoleic acid	18:2-6-9,12	25.12±0.02	31.71±0.01	13.16 ±0.14	34.41±0.09
16.25	petroselinic acid	18:1-6-6	65.18±0.05	61.13±0.05	79.3 ±0.6	55.43±0.02
16.48	Stearic acid	C18	1.34±0.01	0.86±0.05	1.22 ±0.05	1.74±0.05
18.15	cis-13-Eicosenoic acid	C20:1	0.31±0.02	0.26±0.01		0.28±0.02
18.43	Nonadecylic acid	C19	0.16±0.19	ND	0.18 ±0.07	0.26±0.05
Oil content (%)			17.16±0.02	15.64±0.02	13.4±0.02	12.5±0.02
	SFA		8.51±0.01	5.61±0.01	7.18±0.02	9.14±0.02
	UFA		91.48±0.02	94.38±	92.82±0.02	90.85±0.04
	MUFA		65.66±0.02	62.16±0.03	79.65±0.04	56.29±0.03
	PUFA		25.82±0.02	32.22±0.05	13.16±0.04	34.56±0.04
	SFA/PUFA		0.33	0.17	0.55	0.26

* values as average of three replicates ± standard deviation

**ND No Detected

SFA: sum of saturated fatty acids; UFA: sum of unsaturated fatty acids; MUFA: sum of monounsaturated fatty acids; PUFA: sum of polyunsaturated fatty acids

Regarding polyunsaturated fatty acid (PUFA), the results revealed that Linoleic acid was the predominant fatty acid in PUFA at the range between 13.16% to 34.56%.. The lowest value was found in fennel seed oil (13.16%), while caraway seed oil had the highest value (34.41%). This study showed higher polyunsaturated fatty acid (PUFA) in caraway seed oil (34.56%) compared with other study on Egyptian caraway seed oil (PUFA, 30.23%) (Laribi *et al.*, 2013) and Tunisian caraway seed oil (PUFA, 27.41%) (Laribi *et al.*, 2011). The results of total fatty acids distribution in fennel seed oil is not agreed with the findings of sweet fennel seed oil in Tunisia, PUFA represented 0.11% (Rebey *et al.*, 2016), but in a good agreement with Nassar *et al.* (2010) on fennel fruit oil in Egypt, UFA (20.32%). Furthermore; Kozłowska *et al.* (2016) study revealed that fatty acids of oils extracted from anise seeds by using n-hexane, polyunsaturated fatty acids (PUFA) (32.05%), which differed than our results; thus, could be explained by the extraction coefficients.

Finally, the ratio of saturated fatty acids to unsaturated fatty acids (SFA/PUFA) was significantly different and varied from 0.17 to 0.55 for the examined plants. Cumin seed oil had the lowest ratio (0.17); while the highest ratio was reported in fennel seed oil (0.55) (Table 1). This finding is in accordance with work of Cosge *et al.* (2013) in sweet and bitter fennel seed oil, with a ratio of (0.61 and 0.44, respectively); as well as, Laribi *et al.* (2013) determined the ratio of SFA/PUFA 0.33 in caraway seed oil.

3.2. Chemical and physical properties of seed oils

The Chemical and physical properties of four types seed oils of the Iraqi Apiaceous family (Caraway, Cumin, Fennel, and Anise) are presented in Table 2, caraway had the highest average of free fatty acid (3.73%), followed by fennel seed oil (2.3%); cumin and anise had the similar value (1.6%). Our results, herein, are in a good agreement with the findings of Shahnaz *et al.* (2004) when they determined free fatty acid of the oil of cumin seeds in Pakistan (1.4%). The free fatty acid value of examined seed oils falls within the maximum limit of 5% free fatty acids in the high-grade palm oil (Bligh and Dyer, 1959).

Regarding peroxide parameter as an index of rancidity, which is the proportion of the speed of light in the vacuum to the velocity of light in a medium, is an indication of the degree of intensity of the oil (Kaleem *et al.*, 2015). For this extent, the high peroxide value of oil indicates a poor resistance to the oil to peroxidation during storage. The highest average for peroxide was observed in caraway seed oil (3.70 meq.O₂/kg), the opposite was seen in anise seed oil which showed the lowest value (0.8 meq.O₂/kg). High averages of peroxide were reported in the study of Moser and Vaughn, (2012), in anise seeds with the values of 10.3 meq.O₂/kg; and cumin seed oil 15.3 meq.O₂/kg, thus, could be attributed to the differences in climate, cultural practices and post harvest factors. A similar trend of results was indicated in the study of Albulushi *et al.* (2014) and Salim *et al.* (2016) in their determination of acid value in anise seed oil (1.29 and 0.39, respectively).

Tab 2. Chemical and physical properties of seed oil.

Chemical and physical properties	value			
Free fatty acid% (as oleic acid)		C	F	Car
Peroxide value (as meq.O ₂ /kg)	1.6	1.6	2.3	3.73
Acid value (mg KOH/g)	0.82	1.5	1.2	3.70
Chlorophyll (mg/kg)	0.82	0.89	1.12	1.75
Carotene (mg/kg)	0.09	0.43	0.27	0.29
Refractive index	1.49	1.48	1.44	1.48
Density(g/cm ³)	0.93	0.93	0.94	0.96
Viscosity (cP) at 25°C	38.72	49.14	69.13	85.24

The chlorophyll and its derivatives have long history in traditional medicine, including wound healing, anti-inflammatory agent and internal deodorant (Mishra *et al.*, 2012). Many studies support that chlorophyll and its derivatives have anti properties, but some studies have shown that chlorophyll was responsible for a pro-oxidant effect on the oxidation of oils (İnanç, 2011). Chlorophyll In present study, chlorophyll values ranged from 0.82 mg/kg to 1.75 mg/kg. The highest value determined in caraway seed oil (1.75 mg/kg), but anise seed oil had the lowest value (0.82 mg/kg). Carotenoids form one of the most important classes of plant pigments and play a crucial role in defining the quality parameters of fruit and vegetables., (Jaswir *et al.*, 2011).

Carotene showed the highest value in cumin (0.43 mg/kg), followed by caraway (0.29mg/kg), fennel (0.27 mg/kg) and finally anise seed oil (0.09 mg/kg). Compared with studies, Al-Snafi (2016) showed the pharmacological activities of Cuminum cyminum in and pointed to the content of α -carotenoid (RE) (2.54 μ g) and β -carotene (15.24 μ g) in 2 g of seeds. On the other hand, Zzaman *et al.* (2014) studied the physicochemical and quality characteristics of cold and hot press of Nigella sativa L seed oil (Black Cumin), carotenoid ranged from 1.95 mg/kg to 2.46 mg/kg pressed at different temperatures (50°C to 100°C).

In terms of refractive index in the present analysis; results showed similar trends to those reported by Agrawal (2001) in fennel (1.48); Shahnaz *et al.* (2004) in cumin (1.47) and Salim *et al.* (2016) in anise seeds (1.56). The high refractive index of this oil seems to sustain the high number of carbon molecules in their fatty acids, Refractive index also increases as the double bond increases (Falade *et al.*, 2008; Eromosele and Pascal, 2003).

Our results indicate that viscosity (cP) ranged from 38.72 to 69.13, the highest value was seen in fennel seed oil (69.13), while the lowest average was reported in anise seed oil (38.72) (Table 2). Different results were reported in the study of Moser and Vaughn (2012), the viscosity (cP) of anise and cumin at 60°C were 204 and 216, respectively; which differs than our results; which could be explained by the incubation temperature which was 25 °C in their study.

3.3. FE-SEM-EDX analysis of seeds oil.

The technology of metal detection in vegetable oils is new, especially using an electron microscope. In the current study, this is the first time to detect and measure the mineral content of the Apiceae plant's oils by Emission Scanning Electron Microscopy (FE-SEM).

Microelement, also called "trace elements", include a wide number of compounds with physiological activity and some of them accomplish decisive functions to maintain human health (Palmer *et al.*, 2008).

The biological activities of Cu and Mn are strongly associated with the presence of unpaired electrons that allow their participation in redox reactions. It is assumed that these trace metals play a key role in the protection mechanisms by scavenging free radicals (Rahman , 2007).

The micro nutrient analysis revealed that the copper results was ranged from 0.18 to 3.63%, the highest average was reported in anise seed oil, while the lowest average was observed in fennel seed oil (Table 3) (Fig 2). Copper is widely known to play an important role in the human metabolism largely because it allows many critical enzymes to function properly (Prashanth *et al.*, 2015).

The metal content average in the plant usually ranged from 4 to 20 mg of Cu per kg of dry weight. The average of adult human of 70 kg weight is 2-5 mg of which 50% is absorbed from the gastrointestinal tract. A deficiency of Cu in the diet for prolonged period especially during stages of active growth leads to anemia, growth retardation, and pigmentation of hair, as well as, changes in the skeletal system (Prashanth *et al.*, 2015). Aluminum results showed that Anise seed had the highest average which reached the percentage of 21.1%; followed by cumin seed (10.61%); while the lowest percentage of Aluminum was detected in Fennel seed and reached 0.79%. Most recent researches showed that Al involvement in some important human disease pathologies, such as Alzheimer's disease, Parkinsons disease and dialysis encephalopathy (Malik *et al.*, 2008). Our results showed that the level of Al was in the range of 0.79-20.5. The lowest value belonged to fennel seed

oil, and anise seed oil had the highest value (Fig. 2). Al-Snafi, (2016) showed the pharmacological activities of *Cuminum cyminum* in and pointed to the content of elements in 2g of seeds, copper (0.02 mg), iron (1.32mg), magnesium (7.32mg) and potassium (35.76mg) Bukhari *et al.*(2014) determined compositional profiling of fennel seed, potassium (852.45 mg/100g) and iron (9.72 mg/100g).

Regarding Lanthanum and Palladium; this is the first study focused on seed oil content for these elements; the results showed that Lanthanum was detected only in Anise seed with the percentage of 5.85%; Palladium was detected at different levels according to the type of examined seeds; the highest percentage was reported in Anise seed with a percent of 0.35%; while the lowest percentage was 0.28% which detected in cumin seed. No detection of Pd was reported in both Fennel and Caraway seeds.

It is noteworthy that biogenically palladium (in nanoparticles form) can be used as a medicine in cancer treatment; as well as a drug carrier. A new protocol may be developed for cancer therapy using palladium nanoparticles which may be more effective and less toxic than the existing in the traditional drugs (Siddiqi and Husen, 2016).

Table 3. Mineral contents from (Anise, Cumin, Fennel, and Caraway) seeds oil.

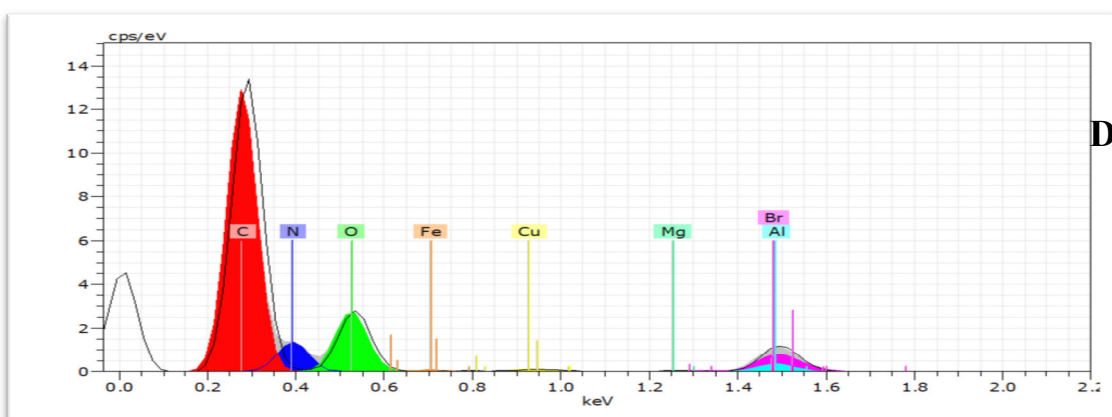
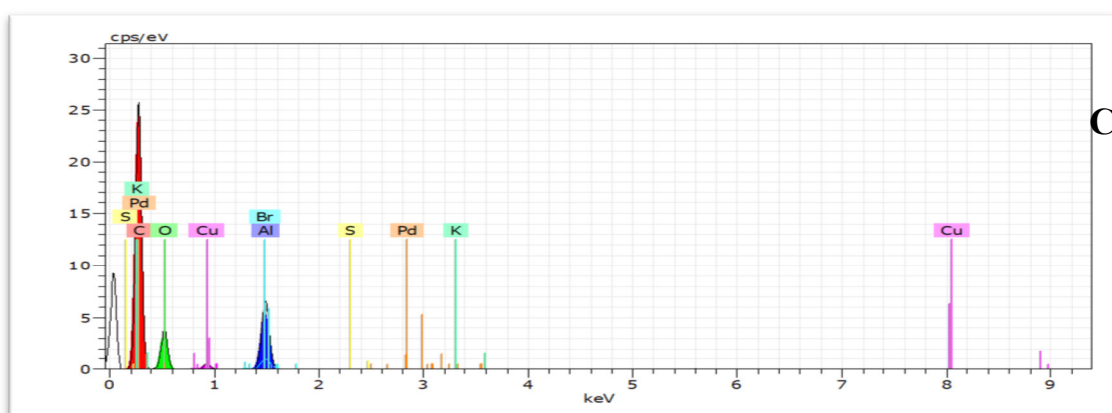
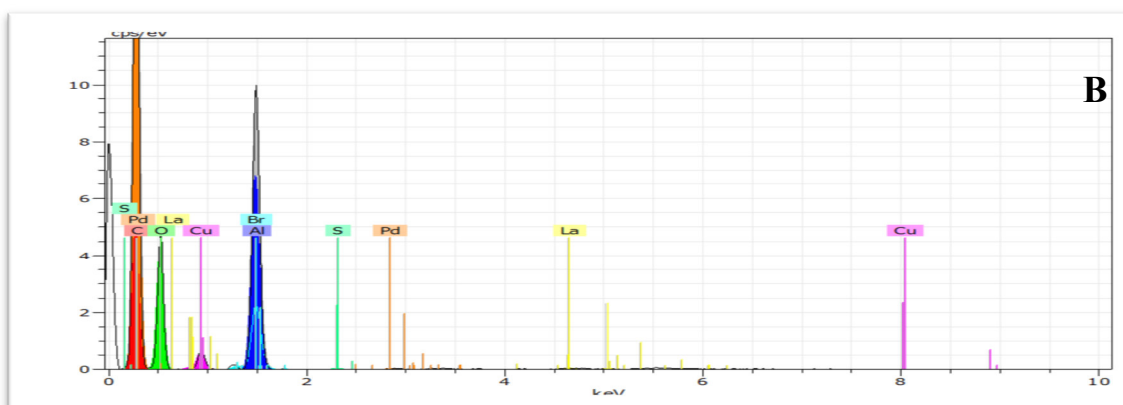
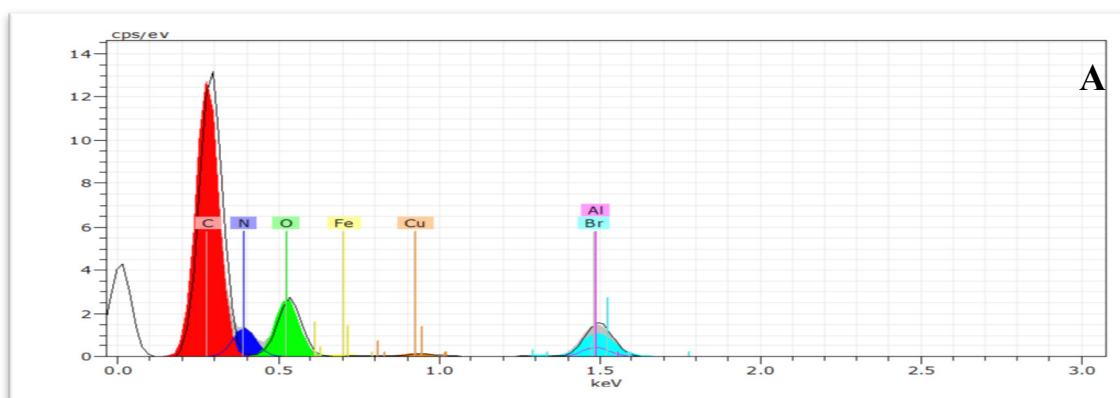
Element		Mineral contents %			
		Anise	Cumin	Fennel	Caraway
Carbon	C	34.5	68.65	65.01	54.99
Oxygen	O	21.1	14.52	15.5	18.71
Nitrogen	N	ND	ND	16.85	17.41
Aluminum	Al	20.5	10.61	0.79	1.3
Bromine	Br	14	3.88	1.47	6.22
Iron	Fe	ND	ND	0.2	0.71
Copper	Cu	3.63	1.9	0.18	0.64
Lanthanum	La	5.85	ND	ND	ND
Palladium	Pd	0.35	0.28	ND	ND
Sulfur	S	0.15	0.04	ND	ND
Potassium	K	ND	0.12	ND	ND
Magnesium	Mn	ND	ND	ND	0.02
		100	100	100	100

The results of Bromine showed that fennel seed oil had the average of 1.47%, while the average of 3.88% was reported in cumin seeds oil, 6.22% in caraway and 14% in anise seed oil (Table 3) (Fig 2). Bromine (Br) belongs to physically promotive trace elements; even though the Br is not an essential element, but it can be pharmacologically beneficial (McCall *et al.*, 2014).

Both Sulfur (S) and potassium (K) are classified according to Frieden (1985) into quantity elements, sulfur is needed for a number of chemical reactions involved in the metabolism of drug, steroids and xenobiotics (Parcell, 2002). Our results showed that both Anise and cumin seed oil had sulfur in their oils (0.15 and 0.04% , respectively) and only cumin seed oil had potassium (0.12%) (Table 3). Iron element is identified only in fennel and caraway seed oil (0.2 and 0.71%, respectively).

The daily requirement from Fe is 1-2 mg which has to provide as 20 mg of iron in food. Deficiency of Fe cause anemia, lowered memory, tiredness, and heart failure. Recently, it has been found that iron may play a role in esophageal carcinogenesis (Prashanth *et al.*, 2015).

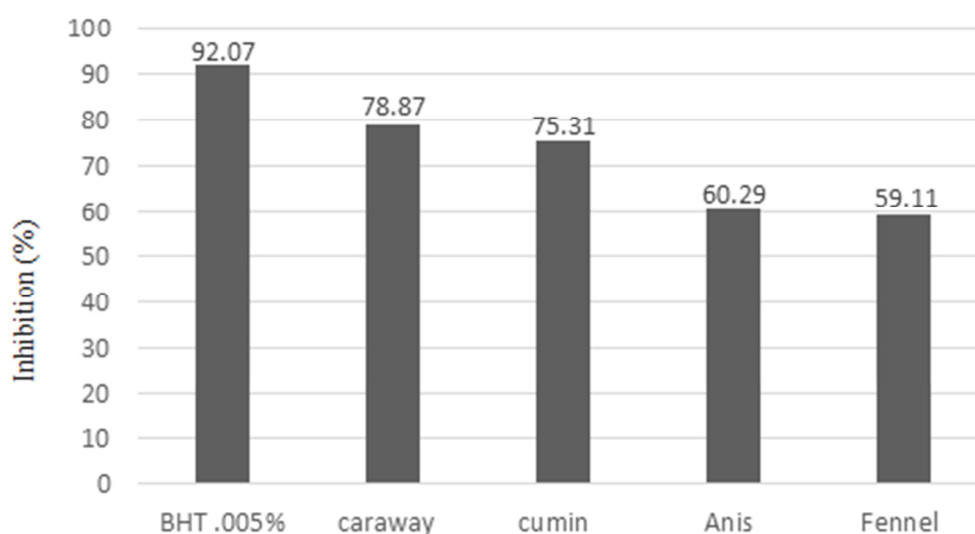
Regarding Carbon and Oxygen content, results showed that Carbon ranged from 34.5 to 68.65%. The highest value determined in cumin seed oil, while the lowest value was reported in anise seed oil. Anise seed oil had the highest value of oxygen (21.1%), followed by caraway (18.71%), fennel (15.5%) and finally cumin seed oil (14.52%) (Table 3).



2). Field emission scanning electron microscope (FESEM) analysis of. (A) Anise, (B) Cumin, (C) Fennel and (D) Caraway seed oil,.

3.4 Antioxidant activity of the four fixed oils

According to the results represented in Fig. 3, all the oils, as well as reference antioxidants (BHT) effectively inhibited the peroxide formation. The percentages of inhibition of caraway, cumin, Anise, and Fennel fixed oil in the linoleic acid system were 78.87, 75.31, 60.26, and 59.11%, respectively, compared with Standard synthetic antioxidant BHT which was 92.07%. From the obtained results, was found that the caraway oil showed the highest antioxidant activity; while cumin oil showed the lowest antioxidant activity. The Unsaturated fatty acids play an essential role as antioxidant agents in plants. The obtained results revealed that the increase in the antioxidants activity is a consequence of the increase in an amount of unsaturated fatty acids in the oil extracted from the examined seeds, this results are in a good agreement with Elagbar *et al.* (2016) when they reported that the antioxidant activity may be correlated to the presence of unsaturated fatty acids, α -tocopherol and phenolic compounds in Fixed Oil of *Annona muricata* L. Seeds



Figures 3, Antioxidant activities as measured by the FTC method for caraway, cumin, Anise, and Fennel fixed oil in linoleic acid. BHT: butylated hydroxyl toluene. Data present means $\pm$ SD(n=3). Results demonstrate the inhibition at 72 h.

4. CONCLUSION

The highest oil content was reported in Anise seed, petroselinic acid was the main fatty acid in all examined samples. The percentages of the fatty acids were found to be varied among samples, whereas the highest percentage of saturated fatty acids (SFA) was recorded in caraway seed oil (9.14). In regard to unsaturated fatty acids (UFA), the highest percentage was observed in cumin seed oil (94.38%). Cumin seed oil had the lowest value of sulfur and carbon (0.04, 68.65, respectively). Antioxidant activity of cumin was stronger (0.39%) and caraway was weaker (0.09%) than standard BHT (0.07%). The high-unsaturated fatty acid content in these seeds oil favors its use both for edible purposes, pharmaceutical, and oleo chemical industries.

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