

Effect of Distillation Period and Storage Conditions on Quality Attributes of Egyptian and Syrian Cumin Essential Oils

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Abstract

The aim of current study was to evaluate the effect of distillation time and storage conditions up to 12 months on quality and stability of Egyptian and Syrian cumin essential oil. The distillation time were run as 3 fractions (F₁: first 6 h; F₂: between 7 and 8 h; and F₃: between 9 and 12 h). The stability, physicochemical, and composition of cumin oil at room temperature and refrigerator up to 12 months were evaluated. The results demonstrated that the yield percentage of Egyptian cumin essential oil (ECEO) was (5.59%) and Syrian cumin essential oil (SCEO) was (3.36%). The oil produced at first 6 h of distillation (F₁) with best quality (~90%), followed by F₂ (~7.50%) and F₃ (2.50%). The 18 compounds were identified in CEO and the main compounds were cuminaldehydes, β -pinene, β -myrcene, *p*-cymene, d-limonene, and γ -terpinene. In addition, the results demonstrated that storage at different temperature influences on the quality and composition of cumin oil especially at room temperature. During the storage the components i.e. α -pinene, β -pinene, β -myrcene, d-limonene and γ -terpinene were decreased, while *p*-cymene was increased however, cuminaldehyde increased during 12 months at room temperature compared with refrigerator. The sensory attributes of CEO stored at refrigerator was significantly higher than room temperature. These results confirmed that ECEO is better than SCEO during processing and more stable during storage.

Keywords: essential oils, cumin seed, steam distillation, storage stability, quality.

Introduction

Cumin seed (*Cuminum cyminum* L.) one of the most commonly ancient spices native to Egypt and Syria, which regularly used as a flavoring agent in food industry (Al-Snafi, 2016). Egypt has a rich history in the production and trade of cumin seeds over the world. Generally, the cumin was utilized in food processing in different forms i.e. whole seeds, crushed, grind, and recently as essential oil (Sowbhagya, et al.; 2008).

Cumin essential oil (CEOs) has well known as generally recognized as safe (GRAS) in food application and medicine. It has widely used in food products such as meat, fish, canned food, pickles, and good products (Teneva, et al., 2016). While, in medicinal sector has utilized as carminative, astringent, stimulant, antispasmodic, sedative, stomachache, anti-inflammatory, diuretic, calmative, diarrhea, flatulence, and indigestion.

In addition, CEOs have many benefits i.e. antibacterial, antifungal, and antioxidant activities in food applications (Moghaddam et al., 2015; Aćimović, et al., 2016; and Mehdizadeh, et al., 2017). One study by Ochoa et al., (2014) found that the CEOs have antibacterial activity against *E. coli* O157:H7, *L. monocytogenes*, *S. enterica*, *Campylobacter jejuni*, and *S. aureus*. Moreover, Viuda-Martos et al. (2008) reported that cumin essential oil was active against *Lactobacillus sakei* and *Enterobacter gergoviae*. While, Lacobellis et al., (2005) demonstrated that CEOs more active against *E. coli* (MIC; 1 μ l/ml), while *S. aureus*,

and *L. monocytogenes* had MIC values of 1 and 2 μ l/ml, respectively. On the other side, Allahghadri et al., (2010) stated the CEOs have higher antioxidant activity compared with that of BHT and BHA.

The CEOs are highly complex mixtures of volatile compounds (Al-Zubairi, et al., 2017). The major components in CEOs are β -pinene, *p*-cymene, γ -terpinene, cuminaldehyde, *p*-mentha-dien-7-al, *p*-mentha-1,3-dien-7-al, and *p*-mentha-1,4-dien-7-al which representative more than 90% of total oil components (Teneva, et al., 2016; and Ingok and Guler, 2017). In addition, Mehdizadeh et al., (2017) demonstrated that the main effective components group of CEOs are oxygenated monoterpenes compounds, especially aldehydes.

The quality of CEOs is depending on extraction methods, extraction conditions, extraction time, and storage conditions. There are several methods for extraction of CEOs such as steam distillation, hydro-distillation, supercritical fluid extraction (SFF), and organic solvents. Al-Hashemi, (2014) found that steam distillation is the best method for CEOs extraction with high yield. However, Mehdizadeh et al., (2017) demonstrated that storage of CEOs at different temperature affected on oil quality and chemical composition i.e. increased such as cuminaldehyde (oxygenated component) while others decreased like β -pinene, and γ -terpinene (monoterpenes).

The aim of this study was to evaluate the effect of distillation time and storage conditions i.e. room temperature (25 \pm 1 $^{\circ}$ C) and refrigerator (4 \pm 1 $^{\circ}$ C) up to 12

months on quality and stability of Egyptian and Syrian cummin essential oil.

Materials and methods:

2.1. Materials

The Egyptian cummin seeds were purchased in season 2016 from Assiute farm, Egypt, while Syrian cummin seeds were purchased from a local market in Cairo, Egypt at the same season. The seeds were transported in a big package 50 kg for each and stored at ambient temperature $25\pm 1^\circ\text{C}$ until distillation.

2.2. Chemicals and Reagents

Methanol, acetonitrile, ethanol, sodium sulfate anhydrous, phenolphthalein, and sodium hydroxide were purchased from Sigma Aldrich Company, Cairo, Egypt. All chemicals and reagents HPLC grade.

2.3. Extraction of cummin essential oil (CEOs)

The cummin oil was extracted by steam distillation according to the method described by **Guenther (1961)** with slight modifications. Briefly, the seeds were soaked in water at ($25\pm 1^\circ\text{C}/8\text{ h}$), then put into distillation still. The essential oil was extracted by the steam distillation at commercial scale (Boiler, Babcock & Wilcox, Egypt) at pressure 1bar for 12 h at 3 fractions as follows; (F₁: first 6 h of the distillation, F₂: between 7th to 8th h of distillation, and F₃: between 9th to 12th h. The CEOs were condensed and received in the flask, then filtrated using sodium sulfate anhydrous and stored in a refrigerator until analysis.

2.4. Essential oils storage

The CEOs were placed into clean and dark glass bottles (30 mL) and kept at both room temperature ($25\pm 1^\circ\text{C}$) and at refrigerator ($4\pm 1^\circ\text{C}$). The oil samples were analyzed after 0, 3, 6, and 12 months of storage.

2.5. Physicochemical properties

The specific gravity was measured by density meter (DMA 35, Graz, Austria) at $20/20^\circ\text{C}$ according to **Baser and Buchbauer (2010)**. Refractive index was measured using Abbe Refractometer (BAushi & Lomb, USA) at 20°C according to **AOAC (2016)**. Optical rotation was measured by polarimeter (WXG-4 specifications) at wavelength 589.44 nm according to **Baser and Buchbauer (2010)**. The solubility in alcohol and acid number of CEOs were determined according to the method described by **AOAC (2016)**.

2.6. GC and GC/MS fingerprint of CEOs

The composition of the cummin essential oil was determined by GC and GC/MS. The GC equipment was an Agilent Chromatograph (Hewlett packard) HP-5890 series II instrument, with flame ionization detector

(FID) and a capillary column DBF restek, RXI@- 1 ms (100%- dimethylpolysiloxan, $30\text{ m} \times 0.25\text{ mm}$ i.d., and $0.25\text{ }\mu\text{m}$ thickness). The carrier gas was nitrogen at a volumetric flow rate of $1.1\text{ ml}\cdot\text{min}^{-1}$. Analysis was done with a sample quantity of $0.2\text{ }\mu\text{L}$, which was prepared by using acetonitrile HPLC grade, with split ratio 50:1, under the following temperature programmed: initial column temperature 60°C , hold 5 min, increased to 250°C at the rate of $3^\circ\text{C}/\text{min}$. the detector (FID) temperature was 280°C and the injector temperature was 250°C according to **Moghaddam et al. (2015)**. Area percentage of peaks were calculated with software DDS1032.

GC-MS analyses of cummin essential oil samples were performed on an Agilent Technologies 7890B gas chromatograph coupled to an Agilent 5977A, mass selective detector (MSD) and a quadrupole Electron Ionization (EI) mass analyzer. An HP-5MS 5% column (coated with methyl silicone) ($30\text{ m} \times 0.25\text{ mm}$, $0.25\text{ }\mu\text{m}$ film thicknesses) was used as the stationary phase. Helium was used as the carrier gas at $0.95\text{ mL}/\text{min}$ flow rate. The temperature programmed was initial temperature 60°C ; hold 2 min, increased to 250°C at a $4^\circ\text{C}/\text{min}$ ramp rate. The injector and the GC-MS interface temperatures were maintained at 250°C and 280°C , respectively. Mass spectra were recorded at 70 eV. The ion source and the detector temperatures were maintained at 230 and 150°C , respectively. The samples ($0.5\text{ }\mu\text{L}$) were injected neat with a 1:100 split ratio according to **Mehdizadeh et al., (2017)**, with some modification. Compound identification was made from the mass spectra of compounds using Agilent library (wily9 and nist11 lib.).

2.8. Sensory evaluation

The sensory evaluation of essential oil was done according to **Atawia et al. (1988)**. Panelists were chosen from the professional personnel in the Phatrade essential oil company. The panelists given orientation sessions to become familiar with the test procedures and compounds. All testing took place between 9.00 and 11.00 Am at room temperature between $25\pm 1^\circ\text{C}$.

The oil samples were placed into 10 mL glass bottle, then plugged coded with 3-digit random numbers and allowed to stand at room temperature few minutes prior to evaluation. The panelists were asked to characterize odor and color using nine-point hedonic scale with score being as follows; 1 = extremely poor or dark brown, 2 = very poor or brownish yellow, 3 = poor or slightly brownish yellow, 4 = below fair or reddish yellow, 5 = fair or slightly reddish yellow, 6 = below good or dark yellow, 7 = good or slightly pale yellow, 8 = very good or yellow, and 9 = excellent or pale yellow.

2.9. Data analysis

The obtained results were analyzed statistically using one-way ANOVA with a significance level of $P \leq 0.05$ using SPSS software, var. 19 (IBM; Armonk, N.Y., U.S.A.). The physical and chemical properties variance was analyzed as a completely randomized design according to **Steel and others (1997)**. All experiments tests were performed in triplicate, using three samples per treatment. Multiple comparisons were carried out applying least significant difference.

Results and discussion

3.1. Cumin essential oil extraction and yield

The extraction of cumin oil using steam distillation was selected due to inexpensive and keeps the fragrance constituents with high yield (**Beis et al., 2000**). **Li, et al., (2009)** found that cumin oil extraction by hydro-distillation keeps the quality but give low yield, while extracts by solvents caused chemical pollute of the fragrances, as well, the extraction using supercritical fluid extraction (SFE) was very expensive.

The yield of Egyptian and Syrian cumin essential oil extracted using steam distillation was shown in **Table (1)**. The results demonstrated that the oil yield of Egyptian cumin was higher than Syrian cumin. The

yield of Egyptian and Syrian cumin oil were 5.59 and 3.36%, respectively. The increasing in Egyptian cumin oil yield may be due to variety, soil, and climatic conditions. These results were agreement with those reported by **Teneva et al. (2016)** and **Al-Hashemi (2014)**. While, **El-Moshtohory (2007)** found that Egyptian cumin seeds contain 3.13% essential oil. Generally, the Egyptian cumin is the best variety compared with Iranian cumin (1.4- 2.2%), Indian cumin (3%), and Tunisian cumin (1.21-1.62%) (**Hashemian et al. 2013; Rana, 2014; Bettaieb et al., 2011**).

Furthermore, the yield of Egyptian and Syrian cumin oil at different fractions times were evaluated. A significant difference ($p \leq 0.05$) was observed between distillation time and oil yield. In general, the yield of CEOs was decreased during distillation period, thus at the first 6 h (F_1), the yield of the Egyptian and Syrian cumin was (90.38 and 94.05%), F_2 (7.15 and 4.46%), and F_3 (2.45 and 1.49%), respectively of total oil yield. The results are partially agreement with those reported by **Sowbhagya et al. (2008)**. These separations in fractions can helps consumers and essential oil producers to use these oils and its compounds in different industries application such as food, medicinal, and cosmetic.

Table 1. Yield percentage of cumin essential oil at different times of distillation.

Cumin origin	Yield (%)			Total Yield (%)
	(F_1)	(F_2)	(F_3)	
Egyptian	5.05±0.15	0.40±0.21	0.14±0.11	5.59±0.05 ^a
Syrian	3.16±0.12	0.15±0.18	0.05±0.14	3.36±0.03 ^b

F_1 : first 6 hours of distillation

F_2 : 7th - 8th hours of distillation

F_3 : Last 9th - 12th of distillation

^{abc} Values in the same column for each attribute followed by different letters are significantly different ($P < 0.05$).

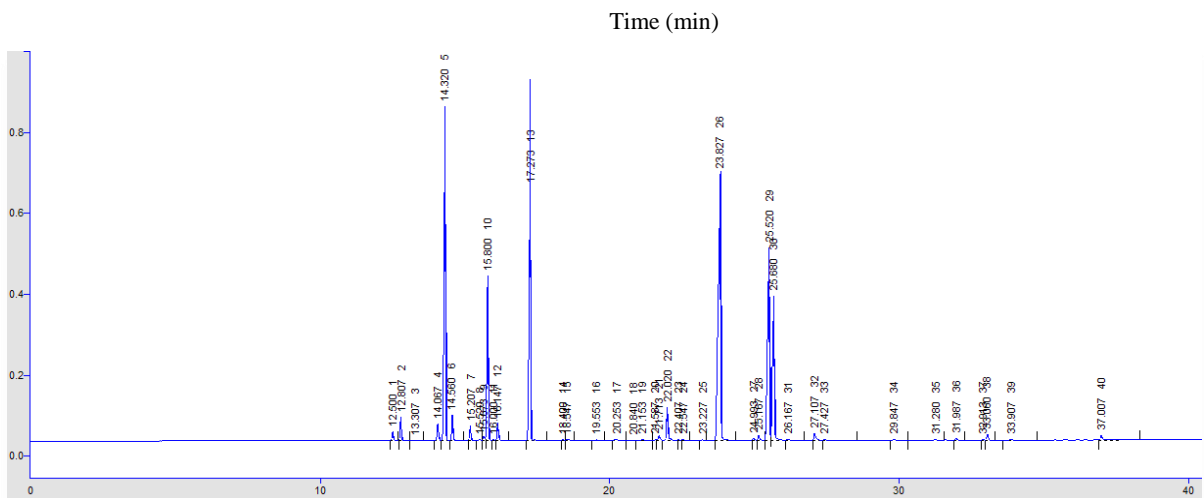
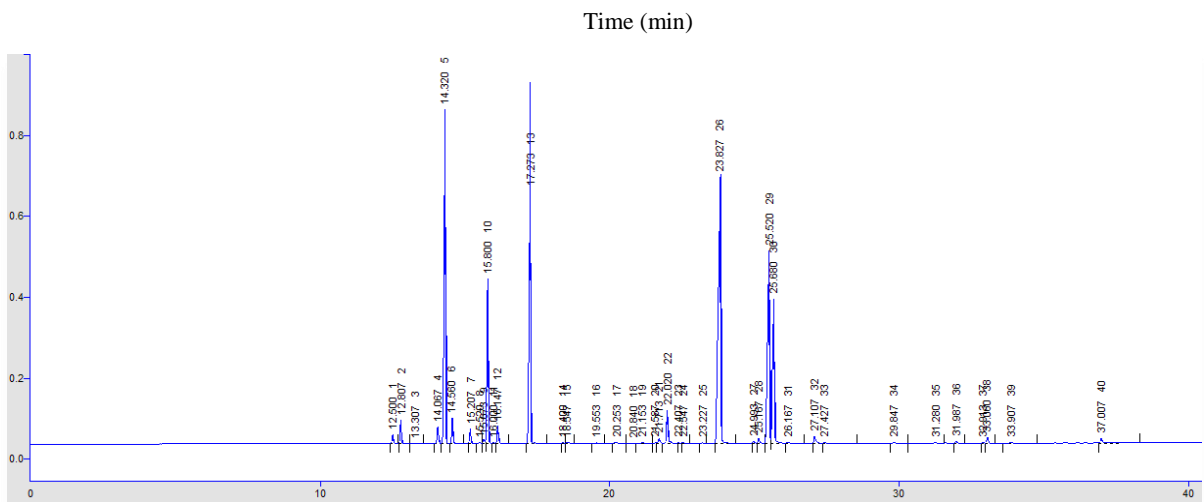
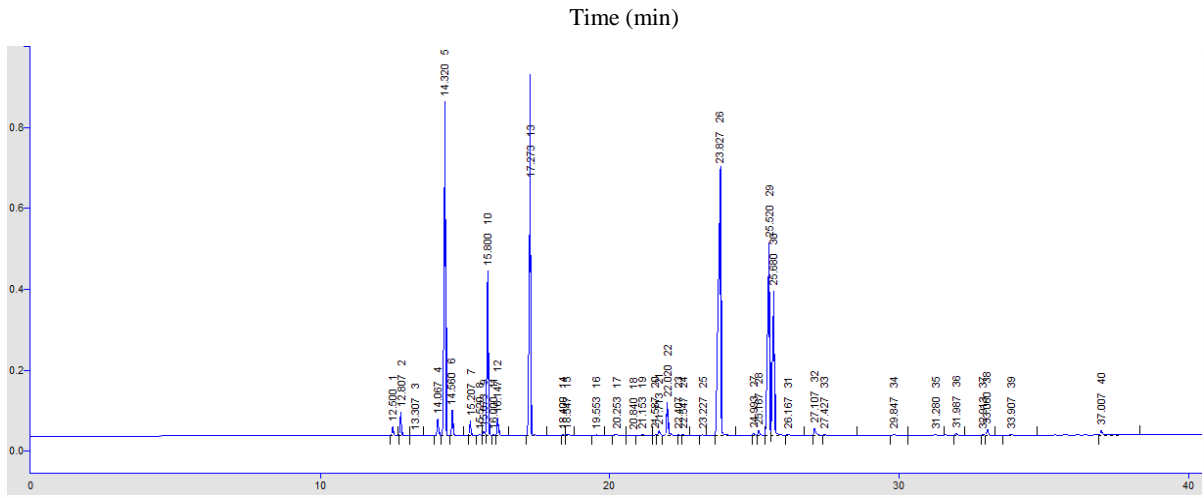
Mean ± SD, n= 3.

3.2. GC/MS fingerprint of cumin essential oil

Table (2) and **Fig. (1 and 2)** showed the chemical composition of the Egyptian and Syrian essential oils analyzed by GC/MS. A total 18 compounds were identified (~ 95- 99% of the total components). The main compounds in CEOs are β -pinene, *p*-cymene, γ -terpinene, cuminaldehyde, 3-para menthanal- 7-al, 1,3 para mentha diene -7-al, and 1,4 para mentha diene -7-al. Furthermore, the cuminaldehyde is the major component in CEOs. These results were agreement with those reported by **Moghaddam et al. (2015)** and **Mehdizadeh et al. (2017)**.

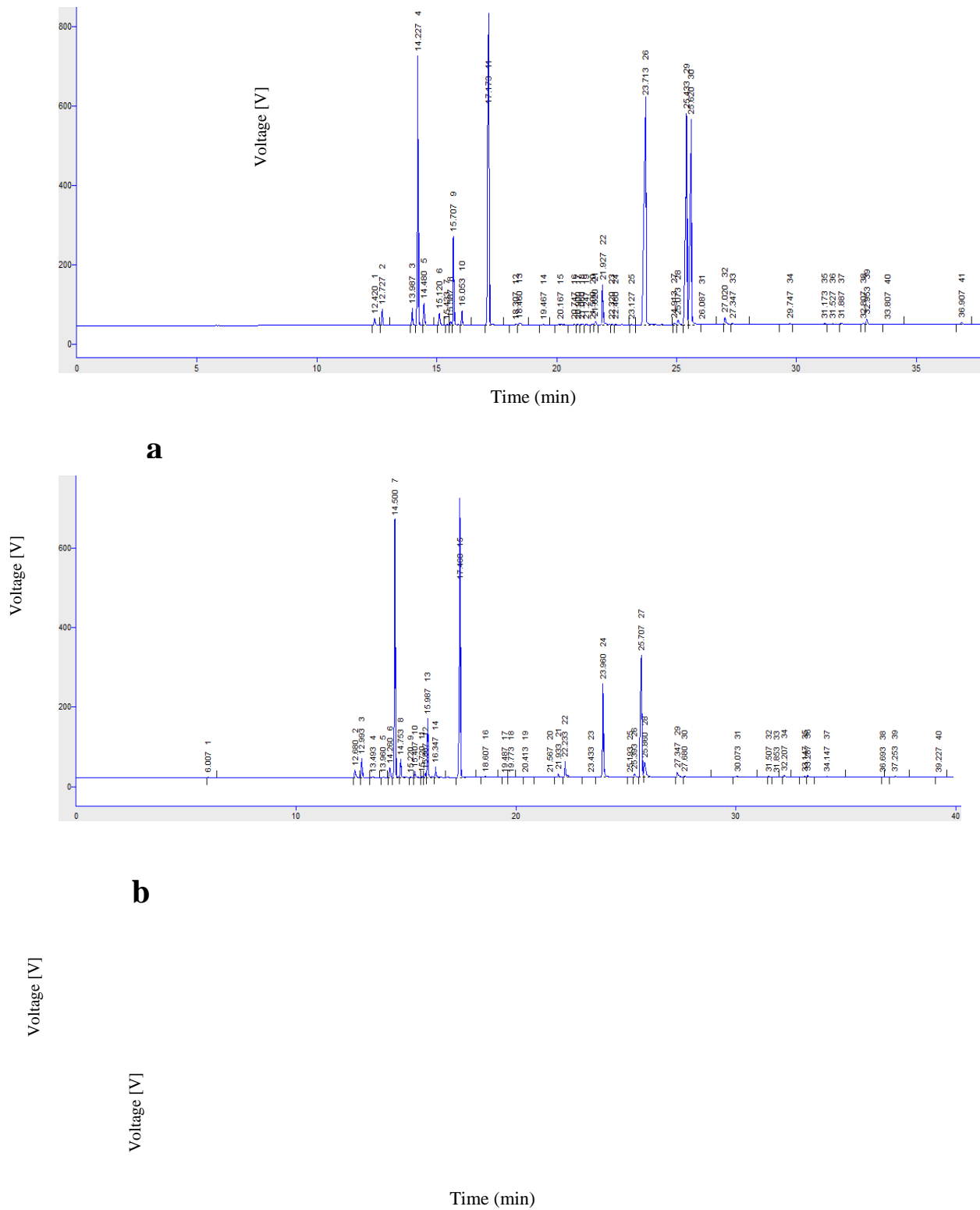
Furthermore, the area percentage of CEOs components influences during distillation time (fractions), some of components increased during distillation time such as monoterpene hydrocarbons

group, while oxygenated monoterpenes group were decreased during distillation. As well, the main component cuminaldehyde was decreased during distillation time; the F_1 was highest value compared with F_2 and F_3 . In addition, the total aldehydes (3-para menthanal- 7-al, cuminic aldehyde, 1, 3 para mentha diene -7-al and 1, 4 para mentha diene -7-al) of CEOs were decreased because the most of aldehydes extracted at first 6 h of distillation. In F_1 the total aldehydes were 46.49% in Egyptian cumin essential oil (ECEO) and 60.51% in Syrian cumin essential oil (SCEO), however in F_2 the total aldehyde were 20.88% in ECEO and 29.47% in SCEO, while in F_3 was the least value in ECEO to 13.16% and 17.79% in SCEO and caused unacceptable smell of cumin oil. These results were matched with those reported by **Sowbhagya et al. (2008)**.



As shown in **Fig. (1 and 2) and Table (2)**, the result demonstrated that, the hydrocarbon terpenes compounds such as α -pinene, β -pinene, β -myrcene, *p*-cymene, d-limonene and

Figure 1. GC-Volatile compounds of Egyptian cumin essential oil at different extraction time (a) first 6 h, (b) at 7 and 8 h, and (c) from 9 to 12 h.



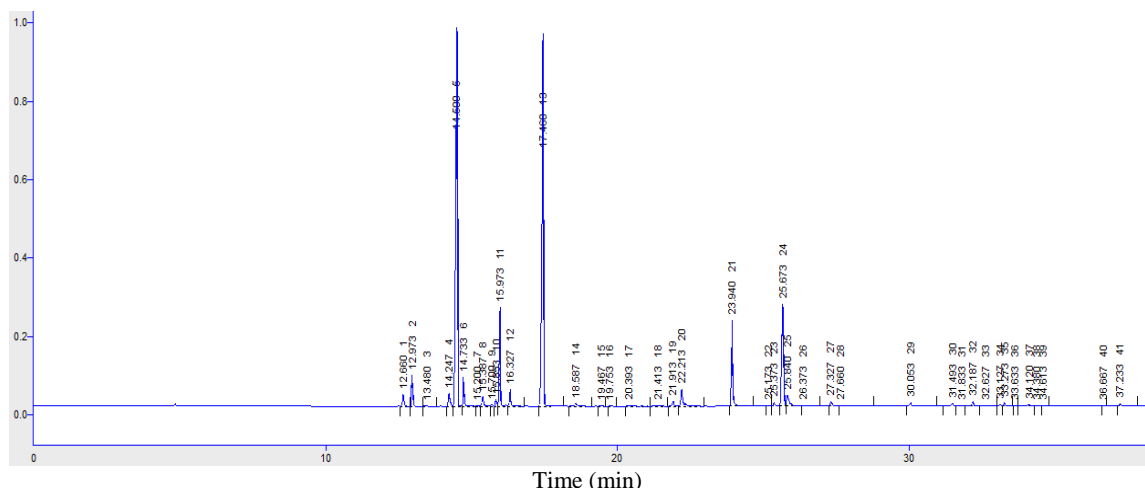


Figure 2. GC-Volatile compounds of Syrian cumin essential oil at different extraction time (a) first 6 h, (b) at 7 and 8 h. and (c) from 9 to 12 h.

Table 2. Volatile compounds of Egyptian and Syrian cumin essential oils at different time of distillation.

No	Compounds	RT	Area %					
			Distillation time					
			Egyptian			Syrian		
			F ₁	F ₂	F ₃	F ₁	F ₂	F ₃
1	Alpha thujene	12.50	0.36	0.62	0.64	0.30	0.10	0.71
2	α -Pinene	12.80	0.91	1.94	2.12	0.57	1.48	1.81
3	Sabinene	14.06	0.80	0.69	0.800	0.77	0.91	0.94
4	β - pinene	14.32	16.47	28.37	32.84	13.41	24.64	29.97
5	β - myrcene	14.56	1.07	1.62	1.69	1.03	1.63	1.84
6	α - phellendrene	15.33	0.57	0.89	1.11	0.42	0.69	1.25
7	<i>P</i> -cymene	15.80	5.56	7.22	7.54	3.52	6.19	6.50
8	d-Limonene	16.14	0.80	1.02	1.32	0.76	1.010	1.17
9	γ -terpinene	17.27	21.65	33.05	33.36	17.64	30.34	34.25
10	Linalool	18.40	0.06	0.20	0.300	0.07	0.20	0.26
11	Beta-ocimene	18.54	0.07	0.00	0.00	0.16	0.00	0.00
12	Terpinene - 4- ol	21.71	0.27	0.300	0.32	0.25	0.37	0.38
13	3-para menthinal- 7-al	22.02	1.74	1.36	1.14	2.40	1.91	1.52
14	Cuminaldehyde	23.82	22.74	8.47	5.59	18.96	10.61	6.76
15	1,3 para mentha diene -7-al	25.52	13.01	8.09	3.93	19.57	14.00	8.05
16	1,4 para Mentha diene -7-al	25.68	9.00	2.96	2.50	19.58	2.95	1.46
17	Cuminol	27.10	0.45	0.78	0.35	0.04	0.77	0.46
18	β -caryophellene	33.06	0.28	0.41	0.55	0.24	0.19	0.24
Grouped components (%)								
	Monoterpene hydrocarbons		48.19	75.42	81.42	38.42	66.99	78.44
	Oxygenated monoterpenes		47.28	21.96	13.83	60.96	30.61	18.63
	Others		0.28	0.41	0.55	0.24	0.19	0.24
Total aldehydes (%)								
	Total aldehyde		46.49	20.88	13.16	60.51	29.47	17.79
Total identified compounds (%)								
	Total		95.81	97.99	96.10	99.69	97.99	97.57

F₁: first 6 hours of distillation

F₂: 7th - 8th hours of distillation

F₃: Last 9th - 12th of distillation

RT: Retention time

γ -terpinene were increased during distillation time. The F_3 was the highest value compared F_2 and F_1 respectively. These variations caused undesirable odor in oil and low quality.

From abovementioned results, the fraction technique is the best way for CEOs extraction, because it gives options to manage and control of the proportions of CEOs (addition and/or deletion).

3.3. Physical and chemical properties of cumin essential oil fractions

The effect of distillation in fractions on physical and chemical properties of the CEOs was evaluated. As shown in **Table (3)** the physical and chemical properties of CEOs influence by distillation time. Results demonstrated that specific gravity and refractive index for Egyptian and Syrian cumin oils were decreased in F_2 and F_3 than F_1 , this due to high concentration of terpenes (low in molecular weight) and low concentration of aldehydes (high molecular weight). Whereas, the optical rotation in ECEO was decreased while SCEO increased during distillation time, may be due to environmental conditions. On the other hand, the acid number was increased during distillation time because of high concentration of oil terpenes that causes oil oxidation and gives indicator of oil degradation (**Saha et al., 2016**).

3.4. Storage stability of cumin essential oil

There are few researches on the storage conditions of essential oils (**Mehdizadeh et al., 2017**). The storage of CEOs at room temperature and refrigerator up to 12 months was shown in **Table (4 and 5)** and **Fig. (3 and 4)**. The decreasing in α -pinene, β -pinene, β -myrcene, γ -terpinene and d-limonene, as well, the increasing in *p*-cymene, given an indicator for cumin essential oil degradation and low quality with an unacceptable odor. Moreover, the best odor of CEOs were found when area

percentage of cuminaldehyde ranged between 18-26% and total aldehyde between 45-55%.

The result showed in **Table (4 and 5)** and **Fig. (3 and 4)**, indicate that the concentration of components with a low molecular weight such as α -pinene, β -pinene, β -myrcene, γ -terpinene and d-limonene decreased gradually with storage time especially at room temperature, due to evaporation or degradation of these components with time. These results agreement with **Mehdizadeh et al., (2017)**. While, *p*-cymene was increased at room temperature than refrigerator condition, due to oil oxidation and/or deterioration. This result contrary with those found by **Mehdizadeh et al., (2017)**.

Moreover, the CEOs after 12 months of storage at room temperature and refrigerator, the concentration of β -pinene decreased in ECEO from 16.47% to 12.57% and 15.99%, with decreased ratio 23.68% and 2.91%, respectively. While SCEO decreased from 13.41% to 9.26% and 12.29%, with decreased ratio 30.94% and 8.35%, respectively. As well, γ -terpinene decreased in ECEO from 21.65% to 17.41 and 20.23%, with decreased ratio 19.58% and 6.56% whereas, SCEO decreased from 17.64% to 6.00% and 13.01% with decreased ratio 65.99% and 26.25%, respectively. On the other hand, *p*-cymene increased in ECEO from 5.56% to 11.12% and 7.65% with increased ratio 50.00% and 27.32% while SCEO increased from 3.52% to 17.83% and 12.98% with increased ratio 80.26% and 72.88%, respectively.

However, the cuminaldehyde (4 - isopropyl benzaldehyde) was increased gradually at room temperature and refrigerator during storage. The cuminaldehyde increased in ECEO from 22.74% to 29.02% and 24.10% with rate of growth 21.64%

Table 3. Physicochemical properties of Egyptian and Syrian cumin essential oils after distillation at different periods.

Specifications	Egyptian				Syrian			
	F ₁	F ₂	F ₃	Total fractions	F ₁	F ₂	F ₃	Total fractions
Specific gravity	0.9154±0.11 ^a	0.8879±0.09 ^b	0.8828±0.15 ^b	0.9126±0.12	0.9228±0.12 ^a	0.8930±0.16 ^b	0.8792±0.11 ^b	0.9208±0.13
Refractive index	1.5007±0.05 ^a	1.4905±0.03 ^b	1.4881±0.01 ^b	1.4997±0.04	1.5480±0.02 ^a	1.4939±0.05 ^b	1.4872±0.11 ^b	1.5447±0.04
Optical rotation	+4° 20'±0.01 ^a	+3° 50'±0.00 ^b	+2° 80'±0.03 ^c	+4° 10'±0.01	+4° 10'±0.00 ^a	+6° 30'±0.03 ^c	+8° 10'±0.03 ^b	+4° 28'±0.02
Acid number	0.87±0.12 ^c	2.99±0.13 ^b	4.40±0.21 ^a	1.11±0.14	1.10±0.17 ^c	2.83±0.12 ^b	3.53±0.28 ^a	1.21±0.18

All analysis done at 20°C

^{abc} Values in the same row for each attribute followed by different letters are significantly different (P < 0.05).

Mean ± SD, n= 3.

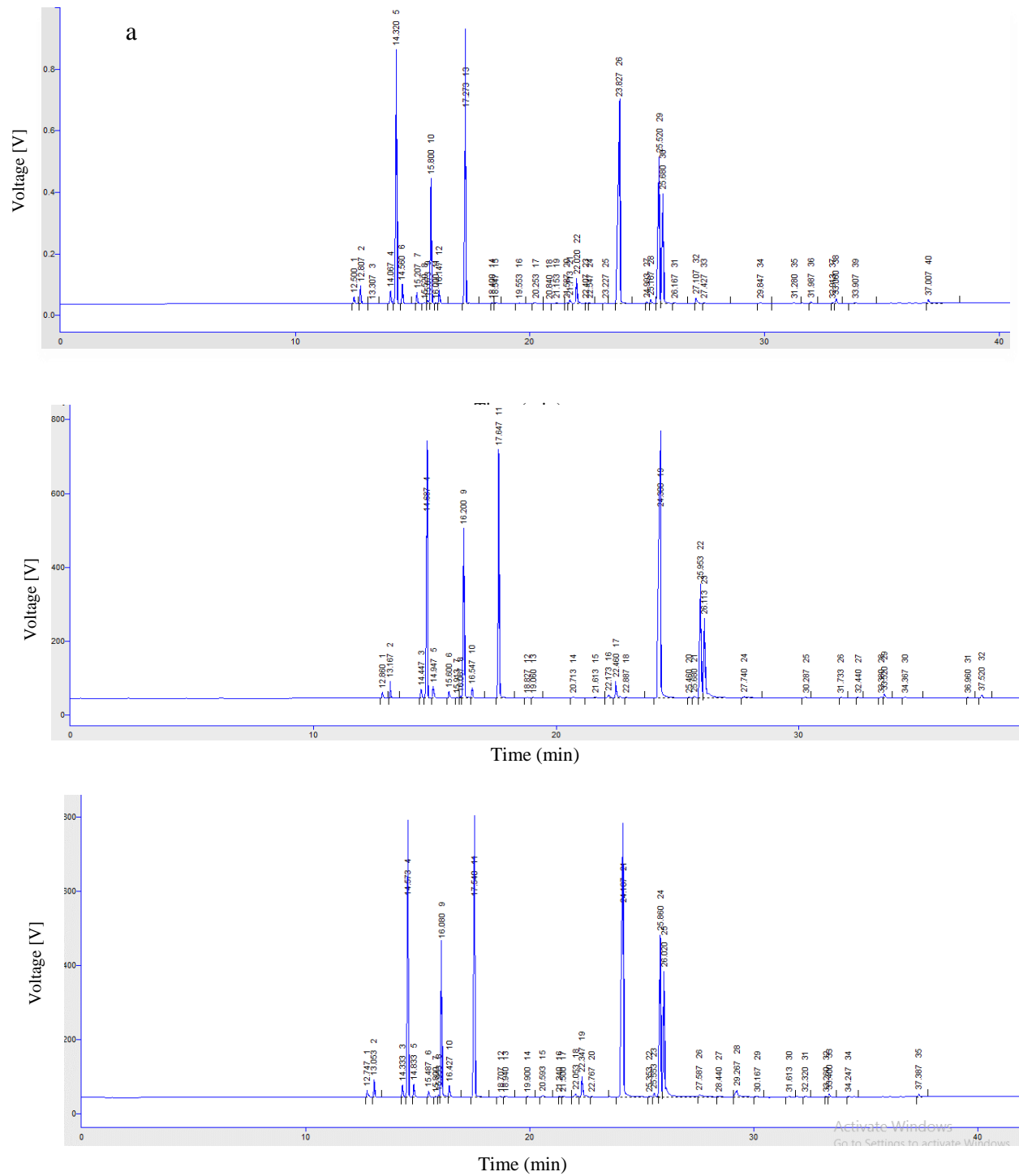


Figure 3. GC-volatile compounds of Egyptian cumin essential oil (control; a) and stored 12 months at room temperature (25±1°C) (b) and at refrigerator (4±1°C) (c).

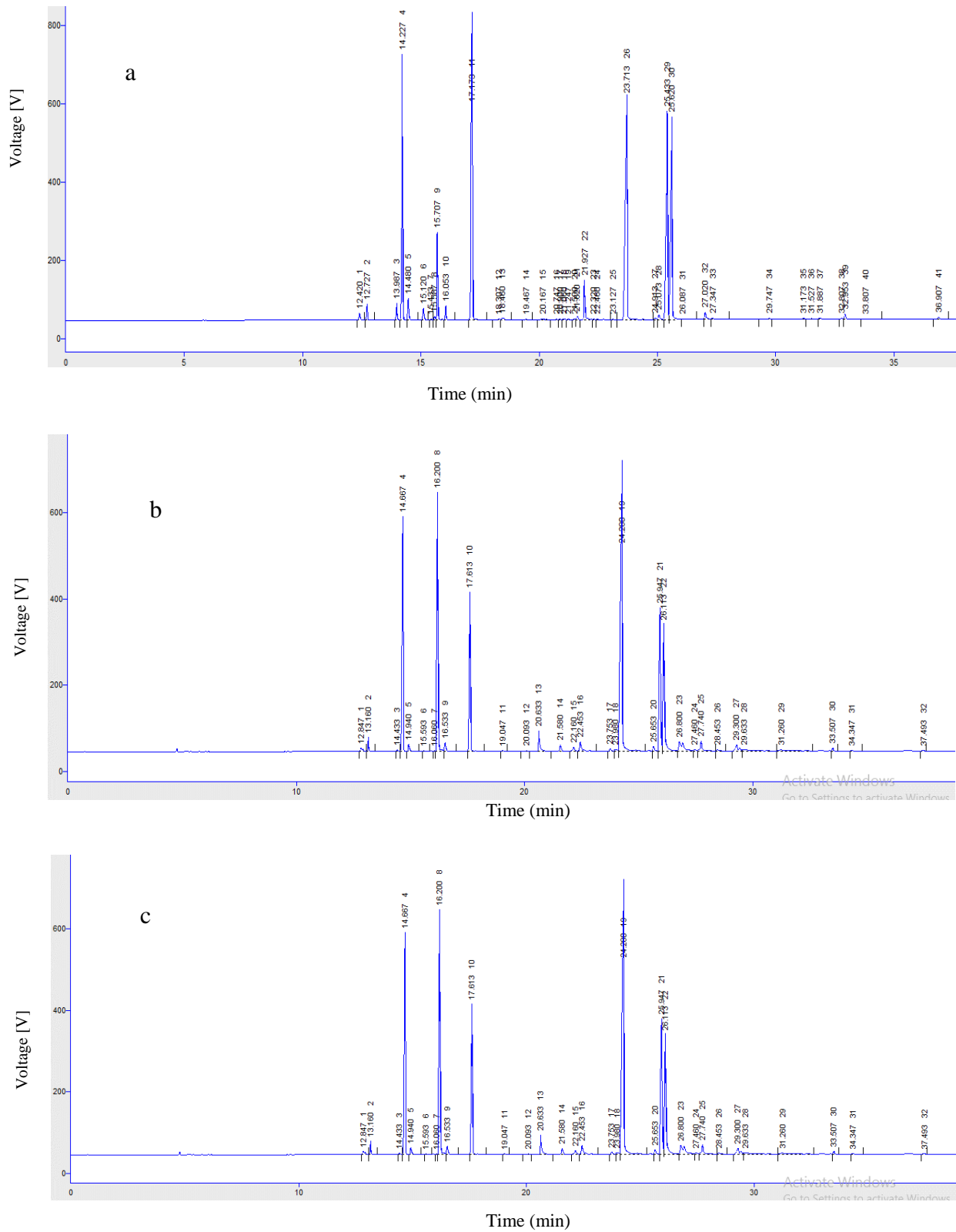


Figure 4. GC-volatile compounds of Syrian cumin essential oil (control; a) and stored 12 months at room temperature ($25\pm 1^\circ\text{C}$) (b) and at refrigerator ($4\pm 1^\circ\text{C}$) (c).

Table 4. Volatile compounds of Egyptian cumin essential oils during storage up to 12 months at room temperature and refrigerator.

NO	Components	RT	Control (%)	Storage conditions (%)					
				Room temperature (25±1°C)			Refrigerator (4±1°C)		
				3	6	12	3	6	12
1	Alpha thujene	12.74	0.36	0.36	0.34	0.29	0.36	0.36	0.36
2	α- pinene	13.04	0.91	0.91	0.90	0.86	0.91	0.91	0.90
3	Sabinene	14.32	0.80	0.79	0.78	0.71	0.80	0.79	0.78
4	β- pinene	14.50	16.47	15.58	14.50	12.57	16.14	16.00	15.99
5	β- myrcene	14.82	1.07	1.07	1.00	0.98	1.07	1.07	1.05
6	α- phellendrene	15.46	0.57	0.57	0.44	0.34	0.57	0.55	0.51
7	P-cymene	16.06	5.56	7.35	9.89	11.12	6.01	6.87	7.65
8	d-Limonene	16.42	0.80	0.79	0.74	0.710	0.80	0.79	0.79
9	γ-terpinene	17.52	21.65	19.99	19.33	17.41	21.38	20.63	20.23
10	Linalool	18.70	0.06	0.06	0.06	0.10	0.06	0.06	0.06
11	Beta-ocimene	18.94	0.07	0.08	0.09	0.10	0.07	0.08	0.08
12	Terpinene - 4- ol	22.04	0.27	0.26	0.24	0.07	0.26	0.26	0.25
13	3-para menthanal- 7-al	22.33	1.74	1.34	0.65	0.32	1.65	1.56	1.32
14	Cuminaldehyde	24.14	22.74	25.94	26.89	29.02	23.05	23.41	24.10
15	1,3 para mentha diene -7-al	25.83	13.01	13.86	14.00	14.75	13.11	13.19	13.45
16	1,4 para Mentha diene -7-al	25.99	9.00	9.11	9.29	9.57	9.00	9.06	9.10
17	Cuminol	27.56	0.45	0.45	0.46	0.46	0.45	0.45	0.46
18	β-caryophellene	33.38	0.28	0.28	0.28	0.29	0.28	0.28	0.29
			Grouped components (%)						
	Monoterpene hydrocarbons		48.19	47.41	47.92	44.99	48.04	47.97	48.26
	Oxygenated monoterpenes		47.28	51.04	51.62	54.29	47.59	48.01	48.76
	Others		0.28	0.28	0.28	0.29	0.28	0.28	0.29
			Total aldehydes (%)						
	Total aldehyde		46.49	50.25	50.83	53.66	46.81	47.22	47.97
			Total identified compounds (%)						
	Total		95.81	98.79	99.88	99.67	95.97	96.32	97.37

RT: Retention time

and 5.64% while SCEO the cuminaldehyde increased from 18.96% to 47.19% and 24.77% with rate of growth 59.82% and 23.46%, respectively. This increase is due to high molecular weight of cuminaldehyde and to the breakdown of some terpenes during storage period. These results agreement with those reported by *Mehdizadeh et al., (2017)*.

Results, confirmed that the stability of Egyptian cumin oil during storage is better than Syrian. In addition, the storage of CEO in refrigerator is relatively better than room temperature.

From the results presented in **Table (6)**, the physical and chemical characteristics were slightly affected by storage conditions. The specific gravity, refractive index, and optical rotation were increased gradually during storage time. This change was a significant in Syrian cumin oil than Egyptian, especially at room

temperature, due to degradation of low molecular weight components. While, the acid numbe was increasing during storage time especially in Syrian cumin oil at room temperature because of intensified the oxidative reactions and increase in free fatty acids (*Almeida et al., 2018*).

In general, there are many factors affecting on the yield and chemical composition of cumin in different regions. This difference in chemical composition of the oils depends on various factors, including plant part, harvest time, type of cultivar, storage conditions, climatic effects on the plants, seasonal changes even sunlight duration, geographic origin and processing of plant materials such as extraction methods and the conditions of analysis (*Zhang et al., 2011; and Roustakhiz and Raissi, 2017*).

Table 5. Volatile compounds of Syrian cumin essential oils during storage up to 12 months at room temperature and refrigerator.

NO	Components	RT	Control (%)	Storage conditions (%)					
				Room temperature (25±1°C)			Refrigerator (4±1°C)		
				3	6	12	3	6	12
1	Alpha thujene	12.81	0.30	0.20	0.18	0.13	0.29	0.28	0.25
2	α- pinene	13.12	0.57	0.46	0.39	0.15	0.57	0.55	0.53
3	Sabinene	14.39	0.77	0.76	0.75	0.51	0.77	0.76	0.68
4	β- pinene	14.64	13.41	12.77	11.10	9.26	13.34	12.68	12.29
5	β- myrcene	14.89	1.03	0.37	0.31	0.17	0.99	0.80	0.66
6	α- phellendrene	15.51	0.42	0.34	0.28	0.11	0.39	0.38	0.33
6	P-cymene	16.15	3.52	13.40	15.05	17.83	10.57	11.50	12.98
7	d-Limonene	16.49	0.76	0.76	0.61	0.27	0.75	0.68	0.64
8	γ-terpinene	17.59	17.64	11.11	8.95	6.00	15.01	13.94	13.01
9	Linalool	18.78	0.07	0.04	0.03	0.00	0.06	0.05	0.05
10	Cis- sabinene hydrate	19.01	0.16	0.16	0.15	0.14	0.16	0.16	0.15
11	Terpinene - 4- ol	22.12	0.25	0.22	0.20	0.16	0.25	0.24	0.23
12	3-para menthanal- 7-al	22.41	2.40	1.02	0.74	0.57	2.31	2.09	1.89
13	Cuminaldehyde	24.25	18.96	31.69	35.54	47.19	21.80	22.89	24.77
14	1,3 para mentha diene -7-al	25.90	19.57	14.67	12.77	9.22	17.85	17.22	16.46
15	1,4 para Mentha diene -7-al	26.06	19.58	11.09	9.45	6.42	14.01	13.80	13.00
16	Cuminol	27.68	0.04	0.04	0.05	0.06	0.04	0.04	0.04
17	β-caryophellene	33.46	0.24	0.24	0.25	0.26	0.24	0.24	0.25
Grouped components (%)									
	Monoterpene hydrocarbons		38.42	40.16	37.62	34.41	42.68	41.59	41.35
	Oxygenated monoterpenes		60.97	58.89	58.90	63.76	56.41	56.44	56.54
	Others		0.24	0.24	0.25	0.26	0.24	0.24	0.25
Total aldehydes (%)									
	Total aldehyde		60.51	58.47	58.50	63.40	55.96	56.01	56.12
Total identified compounds (%)									
	Total		99.70	99.33	96.79	98.43	99.38	98.32	98.19

RT: Retention time

Table 6. Physicochemical properties of Egyptian and Syrian cumin essential oils during storage up to 12 months at room temperature and refrigerator.

Cumin Origen	Storage conditions	Storage time (months)	Specific gravity	Refractive index	Optical rotation	Acid number
Egyptian	Control	0	0.915±0.15 ^d	1.5007±0.03 ^d	+ 4° 25'±0.07 ^a	0.87±0.29 ^h
		3	0.916±0.13 ^d	1.5030±0.04 ^c	+ 4° 25'±0.03 ^a	9.69±0.15 ^e
		6	0.921±0.11 ^c	1.5040±0.10 ^c	+ 4° 30'±0.05 ^a	10.62±0.21 ^e
	Refrigerator (4±1°C)	12	0.929±0.17 ^c	1.5056±0.09 ^c	+ 4° 35'±0.01 ^a	12.94±0.25 ^e
		3	0.915±0.11 ^d	1.5012±0.06 ^a	+ 4° 25'±0.03 ^a	3.10±0.05 ^g
		6	0.919±0.09 ^c	1.5018±0.09 ^a	+ 4° 40'±0.01 ^a	4.58±0.08 ^f
	12	0.922±0.09 ^c	1.5031±0.05 ^c	+ 4° 95'±0.04 ^a	4.84±0.18 ^f	
Syrian	Control	0	0.922±0.07 ^c	1.5080±0.03 ^b	+ 4° 10'±0.11 ^a	1.10±0.13 ^h
		3	0.959±0.11 ^b	1.5083±0.02 ^b	+ 3° 30'±0.04 ^b	43.26±0.30 ^c
		6	0.965±0.14 ^a	1.5099±0.12 ^b	+ 3° 10'±0.08 ^b	48.06±0.27 ^b
	Refrigerator (4±1°C)	12	0.978±0.17 ^a	1.5124±0.11 ^a	+ 2° 40'±0.03 ^b	57.40±0.28 ^a
		3	0.954±0.09 ^b	1.5081±0.08 ^a	+ 3° 80'±0.02 ^b	39.22±0.16 ^d
		6	0.957±0.04 ^b	1.5111±0.04 ^a	+ 3° 50'±0.01 ^b	41.78±0.22 ^c
	12	0.959±0.09 ^b	1.5189±0.02 ^a	+ 3° 10'±0.03 ^b	43.30±0.19 ^c	

All analysis done at 20°C

^{abc} Values in the same row for each attribute followed by different letters are significantly different (P < 0.05).

Mean ± SD, n= 3.

3.6. Sensory evaluation of cumin essential oil during storage

Temperature and refrigerator are presented in (Table 7). Results indicate that the odor and color were decreased and unacceptable that leads to consumer's rejection. In general, no difference was recorded at zero time of storage for both Egyptian and Syrian cumin oil ($p \geq 0.05$). The scores of odor and colors decreased with the time of storage increased, at the first 3 months of storage no significant differences were noticed in ECEO, while SCEO record slight significant differences. While, after storage oil for 6 months the ECEO stored in refrigerator revealed the lowest score of difference and significantly results at ($P \leq 0.05$) compared with room temperature. Whereas, SCEO after storage for 6 months at room and refrigerator temperature record high score of difference in color and odor. After storage oil for 12 months the odor and color

in ECEO became rancid and unacceptable while SCEO became off odor and mostly unacceptable especially oil storage at room temperature, which was indicative of oil degradation of some components and increase of free acids. The samples were quite stable in odor and color for 3 months of storage at room and refrigerator temperature for both ECEO and SCEO while some differences became apparent after 6 months of storage especially SCEO and room temperature. After 12 months of storage, the color of SCEO was dark brown at room temperature and refrigerator, and had rejected odor (off odor) while the color of ECEO was brownish yellow at room temperature and yellow in refrigerator, and had burned odor at room temperature and spicy odor in refrigerator. Thus, the acceptance degree of the oil decreased during storage especially at room temperature, addition the odor and color of ECEO was more stability than SCEO.

Table 7. Sensory responses for color and odor of Egyptian and Syrian cumin essential oil during storage for 12 months at room temperature and refrigerator.

Attributes	category	Temperature	Storage period (months)			
			0	3	6	12
Color	Egyptian	Room	9±0.09 ^a	8±0.07 ^b	7.6±0.11 ^b	5±0.03 ^b
		Refrigerator	9±0.13 ^a	9±0.12 ^a	8.5±0.18 ^a	8.1±0.01 ^a
	Syrian	Room	9±0.10 ^a	6±0.13 ^c	4.4±0.15	1.4±0.07 ^d
		Refrigerator	9±0.08 ^a	7±0.09	5.2±0.06 ^c	2.2±0.13 ^c
Odor	Egyptian	Room	9±0.14 ^a	9±0.11 ^a	8.3±0.10 ^a	4.6±0.09 ^b
		Refrigerator	9±0.11 ^a	9±0.04 ^a	8.8±0.06 ^a	8.3±0.05 ^a
	Syrian	Room	8±0.12 ^b	7±0.07 ^c	2.6±0.05 ^c	ND
		Refrigerator	8±0.16 ^b	8±0.13 ^b	3.7±0.04 ^b	ND

^{abc} Values in the same row for each attribute followed by different letters are significantly different ($P < 0.05$). Mean \pm SD, n= 3.

Conclusion

The present study has clearly demonstrated that the distillation time which run as 3 fractions (F_1 : first 6 h; F_2 : between 7 and 8 h; and F_3 : between 9 and 12 h) effected on the yield and quality of CEOs. The yield percentage of Egyptian cumin essential oil (ECEO) was (5.59%) and Syrian cumin essential oil (SCEO) was (3.36%). The most oil obtained at first 6 h (F_1) of distillation (~90%) with best sensory (color and odor) and quality, followed by F_2 (~7.50%) and F_3 (~2.50%). The main compounds in CEOs were cuminaldehydes, 1,3para-mentha diene-7-al, 1,4para-mentha diene-7-al, β -pinene, β -myrcene, *p*-cymene, d-limonene, and γ -terpinene. Moreover, the results demonstrated that storage at different temperature influences on the quality and compositions of cumin oil especially at room temperature. During the storage the components such as α -pinene, β -pinene, β -myrcene, d-limonene and γ -terpinene were decreased due to evaporating and degradation during the storage, while *p*-cymene was increased however, cuminaldehyde

increased during 12 months at room temperature compared with refrigerator, as well, the CEOs, which was stored in a refrigerator possess its primary quality better compared with stored at room temperature. The sensory attributes of CEOs stored at refrigerator was significantly higher than room temperature. These results also confirmed that ECEO is better than SCEO during processing and more stable during storage.

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تأثير زمن التقطير وظروف التخزين على خصائص جودة زيت الكمون المصري والسوري

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يعتبر زيت الكمون واحداً من أكثر الزيوت العطرية شيوعاً في مجال التصنيع الغذائي لتعزيز طعم ونكهة المنتجات الغذائية وإطالة فترة صلاحيتها والمحافظة على ثباتها خلال فترة التخزين. إستهدفت هذه الدراسة تقييم تأثير زمن التقطير وظروف التخزين لمدة 12 شهراً على جودة وثبات الزيت العطري للكمون المصري والسوري. كذلك التعرف على خصائص زيت الكمون خلال عملية التقطير على ثلاث مراحل (فصل تجزيئي) " علماً بأن التجربة تمت على نطاق تجارى المرحلة الاولى: أول 6 ساعات من التقطير (ف₁) ، المرحلة الثانية: الساعتين السابعة والثامنة (ف₂)، المرحلة الثالثة (ف₃): بداية من الساعه التاسعة حتى الساعة الثانية عشر من زمن التقطير". أيضاً دراسة الخصائص الفيزيائية والكيميائية والتركييب الكيميائي ودرجة الثبات لزيت الكمون المخزن على درجة حرارة الغرفة (25±1م) والثلاجة (4±1م) خلال 12 شهر من التخزين. أظهرت النتائج أن نسبة الزيت العطري في الكمون المصري 5,59% أما في الكمون السورى 3,36%. كما أوضحت النتائج أن أول 6 ساعات من زمن التقطير (ف₁) أعطت حوالي 90% من إجمالي الزيت الموجود بالبذرة مع أفضل جودة، يليها ف₂ 7,5% ثم ف₃ 2,5%. أمكن التعرف على حوالي 18 مركب كيميائي في زيت الكمون وكان من أهم هذه المركبات الكيومين ألدهيد، بيتا بينين، بيتا ميرسين، باراثيمين، ليمونين و جاماتربين. كما أوضحت النتائج أن تخزين الزيت على درجات حرارة مختلفة يؤثر على جودة الزيت وتركيبه الكيماوى وخصوصاً التخزين على درجة حرارة الغرفة. حيث لوحظ انخفاض نسبة بعض المركبات مثل ألفا بينين - بيتا بينين - بيتا ميرسين - ليمونين - جاماتربين، بينما زيادة نسبة مركب الباراثيمين. كما أشارت النتائج أن زيت الكمون المخزن على درجة حرارة الثلاجة احتفظ بخصائصه الحسية بدرجة كبيرة عن الزيت مقارنة بالمخزن على درجة حرارة الغرفة. بناءً عن النتائج المتحصل عليها يتضح أن تقطير زيت الكمون على ثلاثة مراحل أفضل تكنولوجياً، كما أن زيت الكمون المصري ذات جودة تركيبية عالية، أكثر ثباتاً أثناء التخزين مقارنة بزيت الكمون السورى.

الكلمات الدالة: الزيوت العطرية، بذور الكمون، التقطير بالبخار، الثبات التخزيني، الجودة.