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Comparative Studies of the Constituents of Fennel Essential Oils extracted from Leaves and Seeds with Those Extracted from Waste Plants after Harvest

H. E.Wahba, M. E. Ibrahim, M. A. Mohamed

[1]*Research of Medicinal and Aromatic Plants Department, National Research Center, Dokki, 12622, Cairo, Egypt*

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Hend wahba
hend_wahba@yahoo.com
+201006224477

Abstract

To preserve the environment and maximize the utilization of agricultural waste, this work focused on the recycling of residues of fennel plants after harvest The plant materials of the fennel (*Foeniculum vulgare* var. *vulgare*) were collected during seasons 2015 / 2016 from Asuit region (distance from Cairo 320 km) Egypt. The essential oil of the fennel plant was extracted from three stages, the first one was from the green herb in green seed formation stage, the second from the mature fennel seed and the third from the plant waste after harvest. The chemical constituents of fennel (*F. vulgare*) oils were analyzed by means of GC/MS. The results of the analysis of fennel essential oil showed that thirteen compounds, represent 96.71% of the Egyptian fennel herb essential oil were identified, against fourteen (84.33 %) and thirteen (90.81%) for seed and waste oil, respectively. The major constituents was *trans* anethole in green herb, dry seeds and waste oil of fennel plant respectively followed by limonene compound in the herb and seeds oil only, while linalool was the second compound in the waste oil. The high percentage of *trans* anethole was found in the green herb oil (71.5%) followed by the waste (61.5%) and dry seeds oil (45.84%) respectively. Obvious variation in the oil compositions of the three oils due to kind of plant materials of fennel as well as the growth stages was noted. In all cases the essential oils of fennel extracted from green herb, dry seeds or waste characterized by high amount of oxygenated monoterpenes (OMG), which means that the oil extracted from the waste is similar to the oil fennel extracted from green herb and seeds to a large extent.

1. Introduction

To overcome the environmental pollution caused by the phenomenon of burning agricultural residues in the fields after the harvest in Egypt, we worked on recycling the residues of medicinal and aromatic plants after harvest especially those belonging to the umbelliferae family to reduce pollution as well as maximizing the economic benefit by increasing the essential oil yield. The essential oil of the fennel plant was extracted in three stages. The first stage contains the essential oil extracted from the green herb in green seed formation stage, the second from the mature fennel seed and the third from the plant waste after harvest ,Fennel (*Foeniculum vulgare*) - umbelliferae family is perennial herb with yellow flowers. It is considered a very powerful aromatic herb with its many uses in food and medicine. It is widely cultivated, for its edible, strongly flavored leaves and fruits to study the most important compounds responsible for flavoring in fennel, it requires not only analysis of the components of oil seeds but also requires the analysis of essential oil extracted from other parts of the plant So, some investigators have reported comparison between seeds oil and herb oil from sweet fennel [1-4].

The essential oil isolated from air-dried fruits of *F. vulgare* of Turkish origin contained estragole (47.1%), limonene (29.1%), and fenchone (13.40%), as the main components [5]. The major constituents from these were found reported estragole (61.1%), fenchone (23.5%), limonene+ β-phellandrene + 1, 8-cineole (8.7%) and α-pinene (1.2%) [6-10] .Stefanini*et al* 2006 [11] found that, in all cases *trans*-anethole (78.25%) was found as the main constituents of fennel (*F. vulgare* var. *vulgare*) oil. High amount of limonene compound was observed (42.30%)in springinsteams/leaves. Also fenchone recorded (16.98%)in fennel greenseedsinautumn. Essential oils analysis of the seeds and leaves of *F. vulgare* Mill.cultivated in Bangladesh recorded that anethole was the main component (58.5% in seed oil and 51.1% in leaf oil), followed by limonene (19.6% in fennel seed oil and 22.9% in leaf oil). Other components present in leaf essential oil included anisaldehyde, fenchyl acetate and fenchone, while seed oil contained fenchone compound, [12]. On the other hand, Ouariachi*etal.*2014 [13]. Analysis of the

essential oil of *F.vulgare*, the main components were limonene (20.8%) and β-pinene (17.8%), followed by myrcene (15.0%) and fenchone (12.5%). The essential oil content of *F. vulgate* fruits was 0.8% (v/w) and nineteen compounds were detected in the oil. Monoterpenes comprises the main constituents (98.06%), among which (80.67%) were oxygenated, whereas sesquiterpenes represent only about (0.66%) of the oil. [14]*F. vulgare* essential oil composition varies according to origin. The main compounds detected in *F. vulgare* oil from Portugal were fenchone (16.9–34.7%), estragole (2.5–66.0%) and trans-anethole (7.9–77.7%) [15].In essential oil of *F. vulgare* from Serbia, *trans*-anethole was dominant (83.43%) followed limonene (9.34%) [16]. The aim of this work was to conduct comparative studies on the components of fennel oil in the stages of seed formation and the final harvesting stage of mature seeds as well as increase the economic yield of the essential oil yield by recycling the plant residues after harvest, in addition to minimizing the environmental pollution caused by burning of agricultural wastes in the fields.

2. Material and Methods

2.1.Plant materials

The experiment was conducted at asuit region (distance from Cairo 320 km) Egypt during two successive seasons 2015-2016 to study the yield and chemical constituents of the essential oils produced from the green plants, the dry seeds and the waste of fennel plant.The seeds were obtained from the Department of Ornamental Horticulture, faculty of Agriculture Cairo University Giza, Egypt. The seeds were sown in the 15th of November in the two seasons. All agricultural practices of cultivation were done. Samples of green herb were collected during the formation of the green coriander seeds in March of each season. The dry seeds samples of fennel (*(F. vulgare*) plant were taken in May (mature seeds stage) and the dry waste was taken after harvest.

2.2. Plant extraction

The essential oils of the dry plant materials were extracted by hydro-distillation method for 3 hr. (Clevenger, 1928 [17]. The essential oils were dehydrated over anhydrous sodium sulfate and subjected to GC/MS analysis.

2.3. Gas chromatography

GC analysis was performed using a Shimadzu GC- 9A gas chromatograph equipped with a DB-5 fused silica column (30 m x 0.25 mm i.d., film thickness 0.25 μ m). Oven temperature was held at 40°C for 5 min and then programmed until 250°C at a rate of 4°C/min. Injector and detector (FID) temperature were 260°C; helium was used as a carrier gas with a linear velocity of 32 cm/s.

2.4. Gas chromatography- mass spectrometry

GC-MS analyses were carried out on a Varian 3400 system equipped with a DB-5 fused silica column (30 m x 0.25 mm i.d.); Oven temperature was 40 to 240°C at a rate of 4°C/min, transfer line temperature 260°C, injector temperature 250°C, carrier gas helium with a linear velocity of 31.5 cm/s, split ratio 1/60, flow rate 1.1 ml/ min, Ionization energy 70 eV; scan time 1 s ; mass range 40-350 amu.

2.5. *Qualitative and quantitative analysis of essential oil*

Identifications were made by library searches (Adams, 1995)[18] combining MS and retention data of authentic compounds by comparison of their GC retention indices (RI) with those of the literature or with those of standards available in our laboratories. The retention indices were determined in relation to a homologous series of n-alkanes (C8–C22) under the same operating conditions. Further identification was made by comparison of their mass spectra with those stored in NIST 98 and Wiley5 Libraries or with mass spectra from literature. Component relative concentrations were calculated based on GC peak areas without using correction factors.

3. Results and Discussion

3.1. Oil percentage

Table (1) showed that the dry seeds contained the highest percentage of oil (1.13%) followed by the green herb (0.49%) and waste oil (0.18%) respectively.

3.2. Fennel ((F. vulgare)green herb oil

Data in Table 2 showed that, thirteen compounds, represent 96.71% of the Egyptian fennel herb volatile oil were identified. The main constituents of the essential oil are trans- anethole (71.5%), limonene (10.88%) and α-fenchone (9.97%). Fennel herb oil classified into three groups which are monoterpene hydrocarbons group (MHG) , oxygenated monoterpenes group (OMG) and sesquterpenes hydrocarbons group (SHG).

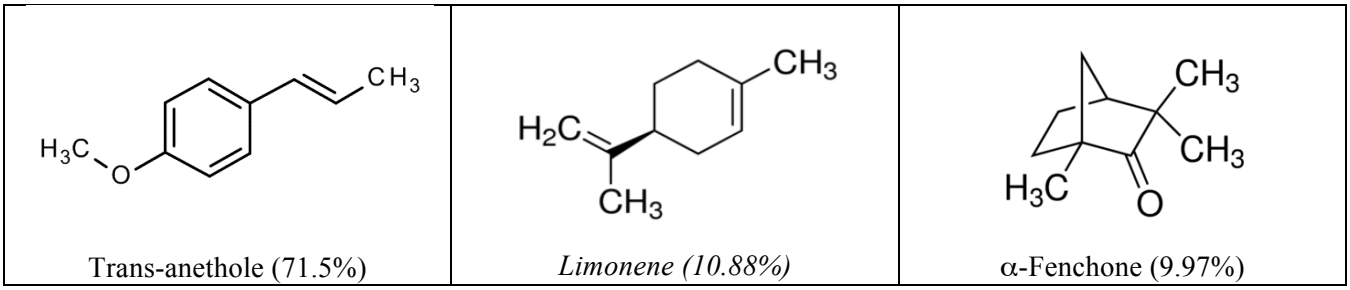
Table 1. Oil percentage of fennel ((*F.vulgare*) in herb, seed and waste

Stage	%
Herb	0.49
Seeds	1.13
Waste	0.18
LSD at 5% 0.050	

Fennel green herb oil is characterized by its higher values of OMG compoundswhich registered 82.48 % followed by(MHG) (13.54%) and SHG (0.15%) .Limonene (10.88%) was found as the major constituents of MHG. Minor amounts of α-pinene (0.94%), sabinene 0.21%), camphene (0.04%), β-pinene (0.80 %), myrecene (0.63 % and terpinene gamma (0.04%) were recorded in the same group. (OM) group included, trans-anethole (71.5%), α-fenchone (9.97%) and estragole (0.81%).The compound of β-Curcumene (0.12 %) and β-Caryophyllene (0.03) were found in a low concentration in (SHG) group. These results were in agreement with those obtained byJasim*et a*l 2009,[12].

Table 2. Essential oil constituents of fennel ((*F. vulgare*) green herb essential oils

Peak No	Compound	KI	%
(MH)monoterpene hydrocarbons			
1	α–pinene;	939	0.94
2	Sabinene	976	0.21
3	Camphene	953	0.04
4	β–Pinene	980	0.80
5	Myrecene	991	0.63
6	Limonene	1031	10.88
7	y-Terpinene	1061	0.04
Total			13.54
(OM)oxygenated monoterpenes			
1	α-Fenchone	951	9.97
2	Camphor	1143	0.20
3	Estragole	1195	0.81
4	Trans-anethole	1283	71.5
Total			82.48
(SH)*sesquterpenes hydrocarbons*			
1	α-Curcumene	1483	0.12
2	β-*caryophyllene*	1418	0.03
Total			0.15
Total identified			96.71



Trans-anethole (71.5%) | *Limonene (10.88%)* | α-Fenchone (9.97%)

3.3. Fennelseed essential oil

Fourteen compounds were detected in Fennel dry seed essential oil represented 84.18 %. The main constituents of Fennel seed oil were Trans-anethole (45.48%), Limonene (23.0%) and α-Fenchone (8.5%)

(OMG) was found as the major group in the dry fennel seed oil, which amounted to (54.33%) against 28.57 and 1.28% for (MHG), (OMG) and (SHG), respectively. Limonene was found as the main constituents of MHG. Also α-pinene was found at a reasonable concentrationin the same group which recorded 4.60 %, while camphene, sabinene, terpinene and terpinolene were found in minor concentrations in the MHG.

In addition to the presence of *trans*-anethole and α-Fenchoneat high concentrations of (OMG), also this group contains camphor and estragole in low concentrations.
α–Curcumene, β–Caryophyllene,γ–Muurolene and γ–Cadinene were detected in (SHG) But in small quantities
Similar results have been reported by many investigators [7, 8], which showed that the main compound in fennel seed essential oil was *trans*-anethole, limonene and α-Fenchone.

Table 3. Essential Oil constituents of fennel ((*F. vulgare*) seeds essential oils

Peak No	Compounds	KI	%
MH (monoterpene hydrocarbons)			
1	α-pinene	939	4.60
2	Camphene	953	0.20
3	Sabinene	976	0.31
4	Limonene	1031	23.0
5	γ-terpinene	1061	0.40
6	α-Terpinolene	1088	0.06
Total			28.57
(OM) Oxygenated monoterpene			
1	α-Fenchone	951	8.5
2	Trans-anethole	1283	45.48
3	Camphor	1151	0.20
4	Estragole	1195	0.15
Total			54.33
(SH)*sesquterpenes hydrocarbons*			
1	α-Curcumene	1483	0.76
2	β-Caryophyllene	1418	0.11
3	γ–Muurolene	1477	0.28
4	γ–Cadinene	1538	0.13
Total			1.28
Total identified			84.18

3.4. Fennelwaste essential oil
Twelveconstituents representing 90.81% of the Egyptian waste essential oil of fennel were identified. Anethole<*trans*-> was found as the main compound of fennel waste oil which recorded 61.50% followed by, linalool (7.91%), estragole (7.39%) -pinene2.50%), and limonene (1.97%)
Essential oil of fennel waste consists of four chemical groups. These groups were (MHG), (OMG), (SHG)) and (VC). Data in Table 4 recorded that the fennel waste oil is rich in group compounds (OMG) which recorded 82.86 %, against 4.51, 1.64 and 1.7% for (MHG), (SHG) and (VCG), respectively.
Comparison of oil components of fennel oil extracted from green herb, dry seeds and dry waste after harvest, it was found that, in all cases the main constituent was Anethole<*trans*->, while limonene came in second place in both fennel oil extracted from green herb and dry seeds respectivelyand it was found in small amounts in fennel oil extracted from plant residues after harvest.
The high percentage of anethole<*trans*>was found in the dry green herb oil (71.5 %), followed by the waste oil (61.5%) and dry seeds oil (45.84%), respectively. At the same time, there is a clear variation in the oil components of the three oils due to the type of plant material as well as the growth stage. Therefore, some compounds were found in all samples of the three oils extracted from green grass, dry seeds and fennel plant wastes with only differences in their concentrations. These compounds were α–pinene. Camphene, limonene., Anethole<*trans*-> and estragole It was also noted that some compounds were found in some oils and absent in others and some compounds have emerged only in one type of oil and did not appear in the other oil (Table 2,3,4,).
In all cases the essential oils of fennel extracted from dry green herb, dry seeds or waste characterized by high amount of OM group. It ranged from 54.33 % in fennel seed oil to 82.86 % in the waste oil. The composition of waste oil was close to green herb and dry seed oil. This was also evident in the percentage of the main group (OMG) which means that the oil extracted from the waste is similar to the fennel extracted from green herb and seeds to a large extent.

Table 4. Essential Oil constituents of fennel ((*F. vulgare*) waste essential oils

Peak No	Compound waste	KI	%
(MH)monoterpene hydrocarbons			
1	α–pinene;	939	2.50
2	Camphene	953	0.04
3	Limonene	1031	1.97
Total			4.51
(OM)oxygenated monoterpenes			
1	Linalool	1098	7.91
2	α-Terpinolene	1088	0.04
3	Estragole	1195	7.39
4	Anethole<*trans*>	1283	61.5
5	Carvacrol	1298	6.02
Total			82.86
(SH)*sesquterpenes hydrocarbons*			
1	Longifolene	1402	1.07
2	α-Curcumene	1483	0.67
Total			1.74
(VC)*various compounds*			
1	Decanal	1204	0.66
2	Geranyl acetate	1383	1.04
Total			1.7
Total identified			90.81

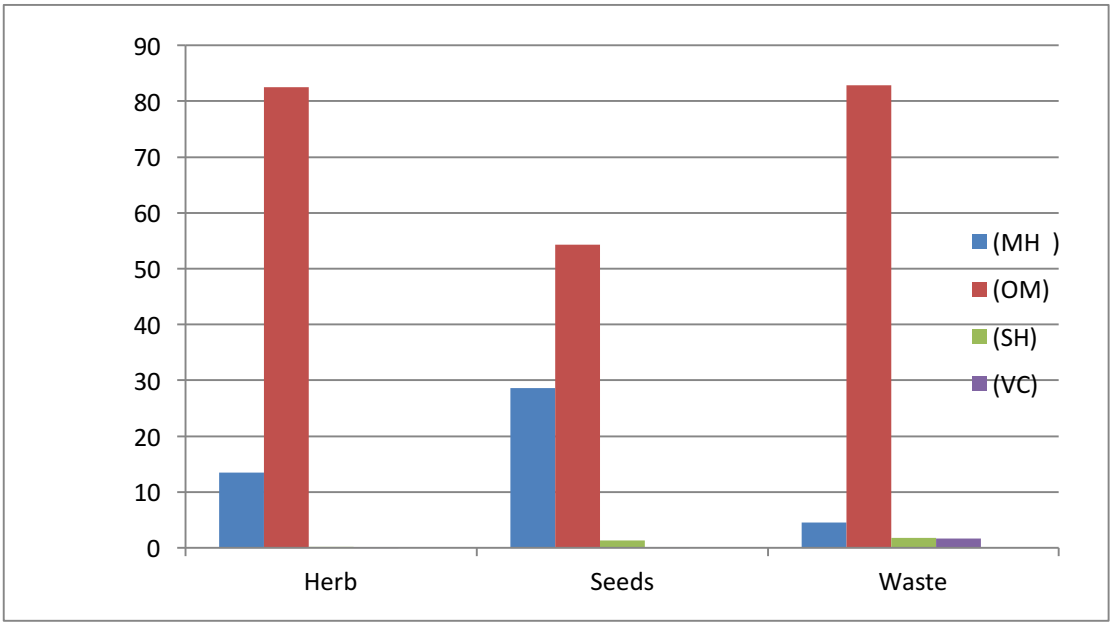


Figure1: Percentage the main chemical classes of essential oil extracted from herb, seeds and fennel waste

Conclusion

In the framework of efforts to preserve the environment and maximize the utilization of agricultural waste, this work focused on the recycling of dry plant residues of fennel after harvest for the purpose of obtaining more volatile oil and then working on the evaluation of this oil in terms of chemical content and the similarity or difference with the chemical composition of fennel oil extracted from its natural sources (green herb and dry seeds). Comparing the volatile oils isolated from green herb and dry seeds with the oil extracted from the fennel waste, Encouraging results to benefit from waste as a new source of oil. In most cases there was a great similarity between fennel oil constituents isolated from the dry waste after harvest with oil extracted either from green herb or dry seeds. *Trans*-anetholewas found as the major constituents in most samples of fennel.

It is clear that the extraction of volatile oil from waste is of great economic benefit, especially since the content of dry seeds and dry waste oils is very close to each other.
So, we highly recommend recycling of aromatic fennel leaves by re-extracting essential oil from plant residues after harvest in order to reduce pollution and increase crop economics.

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