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Gas Chromatography/Mass Spectrometry Analysis of Essential Oil From Different Vegetative Organs and Fruits of *Foeniculum vulgare* Mill. var. *vulgare* Growing in Turkey

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The essential oils obtained by hydrodistillation of fruit, stem, leaf stalk and leaf of bitter fennel (*Foeniculum vulgare* Miller, Apiaceae) were analyzed by GC-MS. Essential oil content was obtained 7.25 % in fruit, 0.375 % in stem, 0.857 % in leaf stalk and 0.75 % in leaf. *trans*-Anethole was the major component in the fruit (75.05 %), stem (64.09 %) and leaf stalk (75.64%) and the leaf oil which contained α-phellandrene (38.23%) and α-pinene (31.79%) as the main components. The chemical composition of the essential oils investigated was found both quantitatively and qualitatively different.

Key Words: *Foeniculum vulgare*, α-Phellandrene, *trans*-Anethole.

INTRODUCTION

Fennel (*Foeniculum vulgare* Miller, Apiaceae) has been known as a medicinal and aromatic herb since classical times. The parts used of the plant are leaves, stems, roots, fruits and oil from fruits. Dried ripe fruit commonly called seeds is used as drug. These aromatic fruits are used in folk medicine as a stimulant, diuretic, carminative or sedative and to increase the milk of nursing mothers. In addition, it is recommended to remedy various diseases or sicknesses (indigestion, wind, bronchitis, coughs, sore throat and gum disease)[1-4]. Fennel oil is used as a flavouring in the food industry and in liqueurs, such as *Fenoullette* and *Sambuca* also in toothpastes, soaps, air fresheners and perfumes. The leaves, leaf bases and seeds of the plant have been commonly used to flavour liqueurs, breads, fishes, salads and cheeses[5].

All parts are aromatic, with an anise-like scent and flavour and the fruits of fennel contain 1-4 % of essential oil. The main constituents of essential oil are *trans*-anethole which has a sweet anise aroma and bitter-tasting fenchone and

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estragole[6,7]. A lot of works have recently been done on essential oil composition of fennel seed oil. However, little research has been conducted on the chemical composition of essential oil from some aerial parts such as stem, stalk and leaf.

The aim of this work was to examine the content and chemical composition of essential oil from the stems, stalks, leaves and fruits of bitter fennel.

EXPERIMENTAL

This study was carried out at laboratories of Field Crops Department, Faculty of Agriculture of Ankara University in 2007. The stems, stalks, leaves and fruits of bitter fennel (*Foeniculum vulgare* Mill. var. *vulgare*) were collected from population grown at the experimental field of the same department on 10 October 2007.

The aerial parts and fruit of the plant collected to study were separated and the aerial parts were dried in the shade at room temperature. Average 50 g of these parts were ground and subjected to hydrodistillation for 3 h in 500 mL water using a Clevenger-type apparatus.

The essential oil was analyzed by GC-MS. The analysis was performed using a Hewlett Packard 6890 N GC, equipped with HP-5 MS capillary column (30 m × 0.25 μm) and HP 5973 mass selective detector. For GC-MS detection an electron ionization system with ionization energy of 70 eV was used. Helium was carrier gas, at a flow rate of 1 mL/min. Injector and MS transfer line temperatures were set at 220 and 290 ºC, respectively. Column temperature was initially kept at 50 ºC for 3 min, then gradually increased to 150 ºC at a 3 ºC/min rate, held for 10 min and finally raised to 250 ºC/min. Diluted samples (1/100 in acetone, v/v) of 1.0 μL were injected automatically and in the splitless mode[8]. Individual components were identified by spectrometric analyses using computer library.

RESULTS AND DISCUSSION

Table-1 shows the essential oil colours and contents from the bitter fennel stem, leaf stalk, leaf and fruit. As can be seen, oil colours and contents varied investigated vegetative organs and fruit. The essential oil content in fruit (> 7 %) was found higher remarkably than in the others samples, which were obtained below 1 %.

TABLE-1
COLOUR AND PERCENTAGE ESSENTIAL OIL
OF BITTER FENNEL FRUIT AND VEGETATIVE PARTS

Plant material	Colour	Oil ratio (%)
Fruit	Dull white	7.250
Stem	Bright yellow	0.375
Leaf stalk	Bright yellow	0.857
Leaf	Dull yellow	0.750

The results obtained in the qualitative and quantitative analysis of the investigated essential oils are given in Tables 2 and 3. The components having the value of > 5 % were evaluated as the major ones.

TABLE-2
ESSENTIAL OIL CONSTITUENTS OF FRUIT AND STEM IN BITTER FENNEL

Compounds	RT	Fruit	Stem
α-Pinene	8.58	1.75	1.81
Camphene	9.15	-	-
β-Pinene	10.30	-	-
Myrcene	11.01	0.59	-
α-Phellandrene	11.53	0.29	18.24
p-Cymene	12.45	-	2.26
Limonene	12.61	1.42	-
Sabinene	12.63	-	3.58
3,7-Dimethyl-1,3,6-octatriene	13.12	-	-
γ-Terpinene	14.02	0.32	-
L-Fenchone	15.34	15.10	-
Camphor	17.94	0.19	-
Estragole	20.54	5.20	3.41
Fenchyl acetate	21.53	-	-
Bicyclo [2.2.1] heptane	22.15	-	1.39
trans-Anethole	24.48	75.05	64.09
Thymol	24.87	-	-
Phenol	25.27	-	-
Copaene	28.40	-	-
Germacrene	32.77	-	3.90
Naphthalene	34.49	-	-
Neophytadiene	42.84	-	-
Total		99.91	98.68

Fruit: In the fennel fruit, 9 compounds representing 99.91 % of the oil were identified, with major compounds being: *trans*-anethole (75.05 %), fenchone (15.0 %) and estragole (5.20 %). Estragole was followed by relative small amounts of α- pinene (1.75 %) and limonene (1.42 %). The other four components were also found below 1 %.

Stem: Eight compounds representing 98.68 % of the stem oil of bitter fennel were identified, among which *trans*-anethole (64.09 %) and α-phellandrene (18.24 %) were the major ones. The minor constituents accounted for 1.39 to 3.90 % of the total essential oil of stem and included: *p*-cymene, sabinene, estragole, bicyclo[2.2.1]-heptane and germacrene (listed in order of elution).

Leaf stalk: The leaf stalk oil showed a total 20 components of which the first two components (*trans*-anethole and α-phellandrene) representing 83.02 % of the oil (75.64 and 7.38 %) were identified. The percentage amounts of estragole, α- pinene, neophytadiene, germacrene, fenchone and sabinene were recorded 3.93, 2.36, 2.09, 1.95, 1.67 and 1.57 %, respectively. On the other hand, thymol, *p*-cymene, myrcene, β-pinene, camphene, bicyclo[2.2.1]heptane, naphthalene and fenchyl acetate contents did not exceed 1 %. The camphor, phenol, 3,7-dimethyl-1,3,6-octatriene and γ-terpinene were also found trace amounts (< 0.1 %).

TABLE-3
ESSENTIAL OIL CONSTITUENTS OF LEAF STALK AND LEAF IN BITTER FENNEL

Compounds	RT	Leaf stalk	Leaf
α-Pinene	8.58	2.36	31.79
Camphene	9.15	–	0.09
β-Pinene	10.30	0.37	2.97
Myrcene	11.01	0.57	2.84
α-Phellandrene	11.53	7.38	38.23
p-Cymene	12.45	0.58	1.96
Limonene	12.61	–	–
Sabinene	12.63	1.57	6.30
3,7-Dimethyl-1,3,6-octatriene	13.12	0.06	0.25
γ-Terpinene	14.02	0.05	0.06
L-Fenchone	15.34	1.67	1.00
Camphor	17.94	0.09	–
Estragole	20.54	3.93	0.42
Fenchyl acetate	21.53	0.12	0.20
Bicyclo[2.2.1]heptane	22.15	0.15	–
trans-Anethole	24.48	75.64	7.40
Thymol	24.87	0.72	0.23
Phenol	25.27	0.06	–
Copaene	28.40	0.15	0.13
Germacrene	32.77	1.95	2.02
Naphthalene	34.49	0.12	0.13
Neophytadiene	42.84	2.09	3.07
TOTAL		99.63	99.09

Leaf: Eighteen constituents comprising 90.09 % of the leaf oil were characterized. α-Phellandrene (38.23 %), α-pinene (31.79 %), *trans*-anethole (7.40 %) and sabinene (6.30 %) were predominant components in this oil. The percentage amounts of neophytadiene, β-pinene, myrcene, germacrene, *p*-cymene and fenchone in the leaf oil were 3.07, 2.97, 2.84, 2.02, 1.96 and 1.00 %, respectively. In addition, camphene and γ-terpinene were reported trace amounts and the others components identified were found below 1 %.

The proportions of the major components within total essential oil varied between average 80 % (in stem, leaf stalk and leaf) and 90 % (in fruit) in the each samples investigated (Tables 2 and 3). It was recorded that essential oil was obtained from crushed fennel seeds by hydrodistillation and GC-MS analysis revealed 20 components, of which 18 (comprising > 96 % of the oil) were identified[9]. On the contrary, only two components comprised average 90 % of the essential oil in present work (Table-2, Fig. 1). While we characterized the 18 constituents comprising 90.09 % of the leaf oil (Table-3), that the 29 constituents constituting 92.1 % of the leaf oil were identified was reported[10]. As seen in Fig. 2, the number of minor components was found higher in leaf stalk and leaf essential oil than the others.

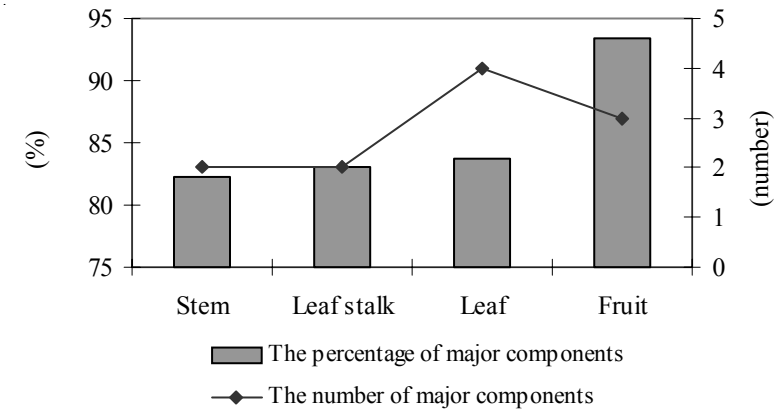

Fig. 1. Percentage and number of major components in some vegetative organs and fruit essential oils from bitter fennel

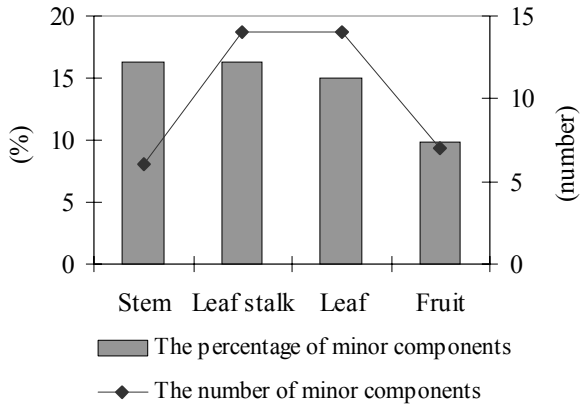

Fig. 2. Percentage and number of minor components in some vegetative organs and fruit essential oils from bitter fennel

The major differences among the chemical compositions of essential oils investigated were recorded. The fruit, steam and leaf stalk oils consisted mainly of *trans*-anethole (average 71.6 %). Contrary to that, *trans*-anethole content (7.4 %) of the leaf oil was found to be remarkably lower. The highest percentage (15.10 %) of fenchone was obtained in the fruit essential oil as well as small amounts (average 1.3 %) in the leaf and leaf stalk oils. This component was not occurred in the stem oil. The value of estragole in the four samples investigated varied between 0.42 % in the leaf oil and 5.20 % in the fruit oil. This value (average 3.5 %) was similar in the steam and leaf stalk oils.

Generally, it has been stated that the major compounds in essential oil of bitter fennel fruit were *trans*-anethole, fenchone and estragole (methyl-chavicol)[3,7,11-13]. That *trans*-anethole proportion in fruits ranged from 50 to 88 % was reported by

several researchers[14-17]. A remarkably different fenchone ratio of essential oil in fruits was found in the previous works in which the researchers obtained data between 2.5 and 20.0 %[12,14-16,18]. It was reported that the level of estragole in fruit was average 4.5 %[12,18]. Limonene was the component with the second highest value (average 11 %) after *trans*-anethole in fruit essential oil was recorded[9,18]. Contrary to these results, the ratio of limonene in fruit essential oil was very lower (1.42 %) in present study and similar results were found by JinMing *et al.*[19]. Correspondingly present findings confirmed that *trans*-anethole (73.6 %) was the major component in stem essential oil[17]. In addition, it is recorded that the limonene along with *trans*-anethole was found as a major component in stem[19]. The essential oil from stems was characterized by α-pinene (9.7-14.4 %), α-phellandrene (24.3-31.4 %), *p*-cymene (5.2-11.5 %), limonene (11.6-15 %) and fenchone (9.7-17.5 %) was reported[5]. However, limonene and fenchone was not found in essential oil from fennel stems and also α-pinene, α-phellandrene and *p*-cymene had lower values (1.81, 18.24 and 2.26 %, respectively) in present study.

The leaves essential oil contained mainly *trans*-anethole and limonene in the recent studies[10-19]. It is also reported that the ratio of *trans*-anethole in the leaf essential oil was 60.0 %[17], which is considerable higher than the value (7.40 %) obtained in present study. On the other hand, it was stated that the leaf essential oil contained estragole (12.3-12.1 %), α-phellandrene (9.4-27.2 %) and limonene (25.3-18 %) as major constituents[5]. As can be seen in Table-2, limonene was not found and also the value of estragole (0.42 %) was very low in the essential oil from present leaf sample.

Fennel essential oil is separated distinct chemical groups according to relative concentrations of chemical components in essential oil. That the presence of *trans*-anethole and estragole in essential oils were stable characteristics and also three distinct chemotypes were observed in the seed essential oil: fenchone-rich (31-42 % fenchone), estragole-rich (30-43 % estragole) and *trans*-anethole-rich (60-85 % anethole) chemotypes were emphasized[20]. When taken these findings into consideration, present essential oil from fruits belonging to *trans*-anethole-rich chemical group. Similarly, the 5 chemical groups (1. α-Phellandrene, estragole and *trans*-anethole, 2. α-Pinene, limonene and *trans*-anethole, 3. estragole and α-phellandrene, 4. estragole and α-pinene, 5. α-phellandrene) in fennel essential oil were characterized[21].

In conclusion, significant differences were observed in its chemical compositions and the essential oil ratio extracted from fruits and vegetative organs investigated of bitter fennel. The ratio of essential oil from fruits was the highest among the samples in this study. The essential oils from fruit, stem and leaf stalk consisted mainly of *trans*-anethole. The leaf essential oil contained lower *trans*-anethole and higher α-phellandrene and α-pinene concentrations compared to the other essential oils studied. In short, the chemical composition of the essential oils investigated was found both quantitatively and qualitatively different.

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