THE CHEMICAL PROFILE OF ESSENTIAL OILS OBTAINED FROM FENNEL FRUITS (*FOENICULUM VULGARE* MILL.)

ANA CLARA APROTOSOAIE[1], ADRIAN ŞPAC[1], MONICA HĂNCIANU[1], ANCA MIRON[1], VIOLETA FLORIA TĂNĂSESCU, VASILE DORNEANU[1], URSULA STĂNESCU[1]

[1]*Faculty of Pharmacy, "Gr.T.Popa" University of Medicine and Pharmacy, Iasi, Romania*
[2"]*Anastasie Fătu" Botanical Gardens, Iasi, Romania*
**corresponding author: anaclara70@yahoo.com*

Abstract

Fennel (*Foeniculum vulgare* Mill., *Apiaceae*) is a well-known aromatic and medicinal plant. Essential oils obtained by hydrodistillation from fresh ripe fruits of fennel collected during three different years (2001-2003) from experimental cultures were investigated in order to evaluate their chemical profile related to climatic conditions. The constituents of the essential oils have been characterized using gas chromatography and mass spectroscopy analysis (GC-MS). The main compounds in all fennel volatile oils were: t-anethole, estragole, fenchone and limonene. The essential oil of fennel fruits showed a characteristic chemical profile from year to year. The essential oil content and its monoterpenes components were the most susceptible features to be affected by climatic conditions (temperature and rainfall).

Rezumat

Uleiurile volatile obținute prin hidrodistilare din fructele mature şi proaspete de fenicul, recoltate din culturi experimentale în 3 ani diferiți (2001, 2002, 2003), au fost analizate în scopul evaluării profilului lor chimic raportat la condițiile climatice caracteristice anilor de cultură. Constituenții uleiurilor volatile au fost caracterizați prin gaz cromatografie cuplată cu spectrometrie de masă. Compuşii majori identificați în toate uleiurile volatile de fenicul au fost trans-anetolul, estragolul, fencona şi limonenul. Conținutul în ulei volatil şi cel al fracției monoterpenice sunt cele mai afectate de acțiunea factorilor climatici (în special, temperatură şi precipitațiile).

Keywords: *Foeniculum vulgare,* essential oil*,* GC-MS*,* meteorological data

Introduction

Fennel (*Foeniculum vulgare* Mill., *Apiaceae*) is a well known medicinal and aromatic plant spread in Mediterranean area and Central Europe. It is widely cultivated throughout the temperate and tropical regions of the world for its aromatic fruits which are used as a culinary spice.

Herbal drugs and essential oil of fennel have antispasmodic, diuretic, anti-inflammatory, analgesic and antioxidant effects [3, 4, 7]. They

are active for dyspeptic complaints, flatulence and bloating. The volatile oil showed antioxidant, antimicrobial and hepatoprotective activity [5, 6].

Mature fruit and essential oil of fennel are used as a constituent of pharmaceutical and cosmetic products. They are also used as flavoring agents in food products.

Essential oil composition depends upon external and internal factors affecting the plant such as: environmental and climate conditions, season of collection, age of plants, the stage of ripening of the fruits or genetic data [1, 2, 8].

Plasticity in the chemical composition of fennel essential oil in response to climate factors, either in nature or under controlled conditions, is less known.

This research was conducted in order to determine the variation of content and essential oil chemical composition of fennel fruits collected during three different years (2001-2003).

Materials and methods

Plant material

The ripe fruits were harvested in September of each year (2001-2003) from *Foeniculum vulgare* Mill. cultures from the experimental lots in "Anastasie Fătu" Botanical Gardens, Iasi. In this experimental area, cultures of *Foeniculum vulgare* (Mill.) were made in 2001-2003 period. The type of soil was cambic chernozems and clay-illuvial chernozems.

Isolation of essential oil

The volatile oils were obtained from fresh fruits by hydrodistillation in Clevenger apparatus (3 hours). The oil was separated, dried over anhydrous sodium sulfate and kept in a dark glass bottle at 4°C for the analysis.

GC-MS analysis

An analytical system, consisting of HP 5890 Series II GC and HP 5971 MSD, was used. GC/MS analysis of the essential oil was performed on HP-5MS capillary column (30 m x 0.25 mm diameter x 0.25 μm thick) coated with cross-linked methyl silicone gum. Carrier gas was helium with 1ml/min flow rate. Temperature program: 35°C held for 5 min, then heated up to 260°C at 10°C per min, and maintained for 3 additional minutes at this temperature. The temperature of injector was 250°C and of the MS interface was 280°C. Injection volume was 0.1 μl essential oil.

Evaluation of the results was performed using ChemStation Software and Wiley mass spectral library. The identification of the components, was

based on comparison of their mass spectra in the apex of each peak with those of analytical standards from Willey Mass Spectral Library.

Meteorological data

Meteorological data covering March to October intervals of each year (2001-2003) were obtained from Moldova Regional Weather Station (Iasi, Romania). The average values for surface soil temperature (°C), atmospheric temperature (°C), sunlight duration (hours), rainfall (mm/m^2), relative humidity (%) are reported in table I.

Results and discussion

The essential oil content (%) of fennel fruits is presented in table II and figure 1.

Table II

The content of *Foeniculum vulgare* essential oils

ml essential oil/100 g fresh vegetal material	2001 year	2002 year	2003 year
	11.00	12.60	2.00

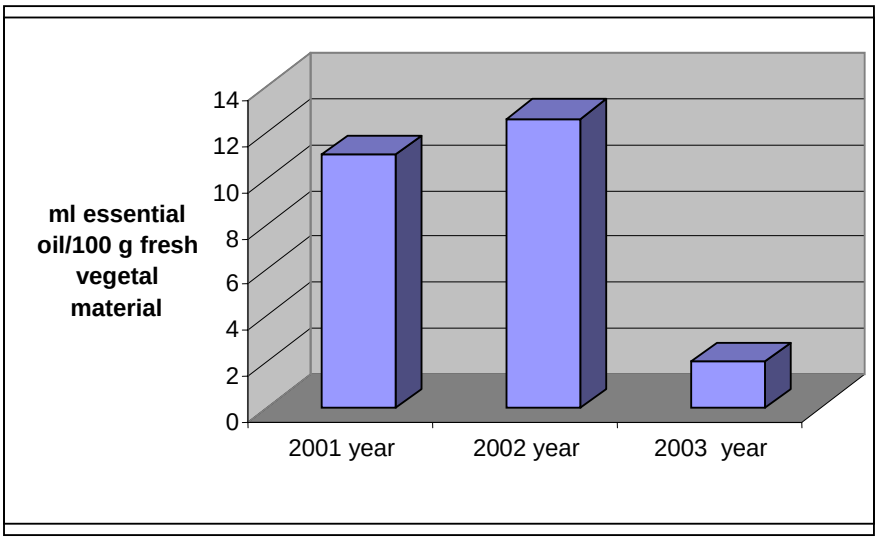

Figure 1

The fennel essential oil yield

A large variation in the volatile oil content was observed (2.0-12.6%). The lowest value was obtained in 2003, while the values for 2001 and 2002 were close (11.0 and 12.6%, respectively).

The results of the GC-MS analysis are showed in table III.

Table I

Meteorological data of 2001-2003 years, March-October intervals – monthly average

Meteorological parameter	MARCH			APRIL			MAY		
	2001	2002	2003	2001	2002	2003	2001	2002	2003
Surface soil temperature (°C)	6.6	7.3	0.3	13.9	12.8	6.9	20.5	24.9	26.7
Atmospheric temperature (°C)	6.6	6.6	0.7	11.2	9.9	9.2	15.8	18.4	20.7
Sunlight duration (hours)	123	190.6	125	237.8	175.2	203.3	297.2	304.8	340.8
Rainfall (mm/m^2)	35	31.9	139	54.6	15.3	173	54.2	31.1	39.8
Relative humidity (%)	70	59	76	66	69	55	62	53	50

Meteorological parameter	JUNE			JULY			AUGUST		
	2001	2002	2003	2001	2002	2003	2001	2002	2003
Surface soil temperature (°C)	22.3	25.2	28.3	30.1	28.2	26.0	28.60	25.2	26.5
Atmospheric temperature (°C)	18.1	20.1	21.3	23.7	23.3	21.2	22.70	20.6	21.5
Sunlight duration (hours)	208	268.2	320.2	309.2	271.6	247.3	289.90	253.8	312.1
Rainfall (mm/m^2)	114.6	42.0	14.4	40.6	171.8	115.7	16.20	33.2	31
Relative humidity (%)	70	66	51	67	67	69	59	72	63

Meteorological parameter	SEPTEMBER			OCTOBER		
	2001	2002	2003	2001	2002	2003
Surface soil temperature (°C)	17	18.1	17.4	12.50	10	9.5
Atmospheric temperature (°C)	15.90	15.2	15.3	11.60	9.6	8.9
Sunlight duration (hours)	172.40	143.4	202.5	180.20	134.2	139.9
Rainfall (mm/m^2)	179	29.8	42.8	30.5	60.5	76.5
Relative humidity (%)	74	76	66	77	75	72

Table III
Compounds identified in fennel volatile oils

RT (min.)	Compound	Area (%)		
		2001	**2002**	**2003**
4.30	1,8-cineole	4.29	-	-
5.04	α-pinen	0.34	-	1.88
5.13	β-pinen	0.59	-	0.33
7.74	limonene	0.34	-	-
6.34	cymene	1.36	-	-
8.65	**limonene**	**0.34**	**1.04**	**1.85**
9.11	γ-terpinene	-	0.36	-
9.35	camphene	-	-	0.16
10.18	myrcene	-	-	0.72
10.46	α-felandrene	-	-	0.34
10.69	α-terpinene	-	-	0.03
11.08	**fenchone**	**8.56**	**10.56**	**13.12**
11.48	γ-terpinene	-	-	0.36
13.08	camfor	-	-	0.41
13.78	terpinen-4-ol	0.20	-	0.08
14.62	**estragole**	**2.53**	**8.28**	**2.99**
14.93	α-terpineol	0.23	-	-
16.82	**t-anethole**	**60.42**	**75.81**	77.61
19.24	p-anisaldehide	-	-	0.05
19.77	2,3,4,6-tetramethyl-phenol	-	1.72	-
20.22	timol	7.41	-	-
20.59	carvacrol	12.09	-	-

RT= retention time (min.)

The number of compounds identified in the three oils was different: thirteen (13), six (6) and fourteen (14) were identified, representing 97.77% (2001), 98.36% (2002) and 99.79% (2003) of the fruit volatile oil. Trans-anethole, a phenylpropanoid derivative was the main compound in all oils; other major components were fenchone, estragole (methyl chavicol) and limonene.

Although all volatile oils consisted of monoterpenes and aromatic compounds, differences were observed in their qualitative and quantitative composition (tables III and IV).

Table IV
Percentual composition of *Foeniculum* volatile oils on major component types

Nr.	Compounds category (%)	2001	2002	2003
1.	Monoterpenes	13.96	12.55	19.29
2.	Aromatic compounds	83.81	85.81	80.50

We noticed a discret variation in the aromatic fraction content from 80.50% (2003) to 83.81% (2001) and 85.81% (2002). On the other hand a

significant increase of the monoterpenes level from 12.55% (2002), 13.96% (2001) to 19.29% (2003). Generally, the decrease of the aromatic fraction content was accompanied by an increase in the monoterpene levels.

The amount and composition of the oils seem to correlate with the meteorological data. Colder atmospheric and surface soil temperature (figures 2, 3) and abundant rainfall (figure 4) at the beginning of the vegetation period determined lower volatile oil yield and higher level of monoterpene for 2003 (2%; 19.29%, respectively) compared to 2002 (12.6%; 12.55%) and 2001 (11%; 13.96%) years.The effect of the meteorological factors on the oil composition is also determined by the plant development phase.

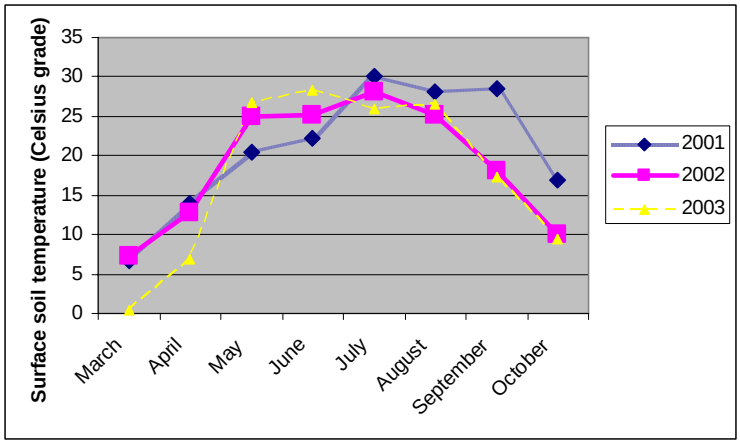

Figure 2
Surface temperature soil (°C) of 2001-2003 years, March-October intervals (monthly average data)

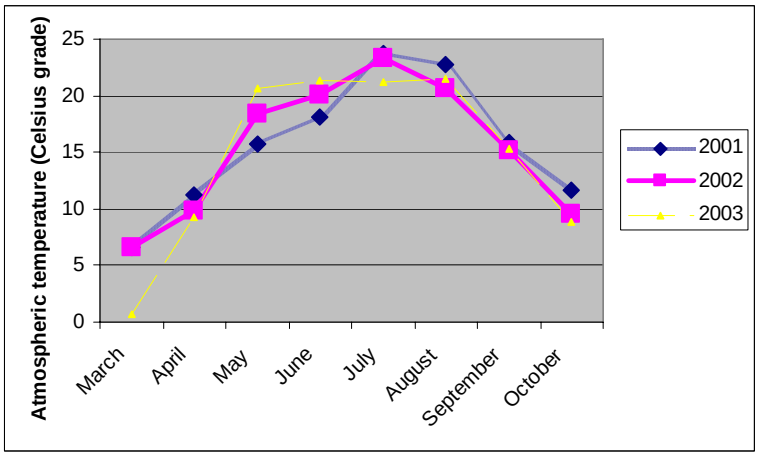

Figure 3
Atmospheric temperature (°C) of 2001-2003 years, March-October intervals (monthly average data)

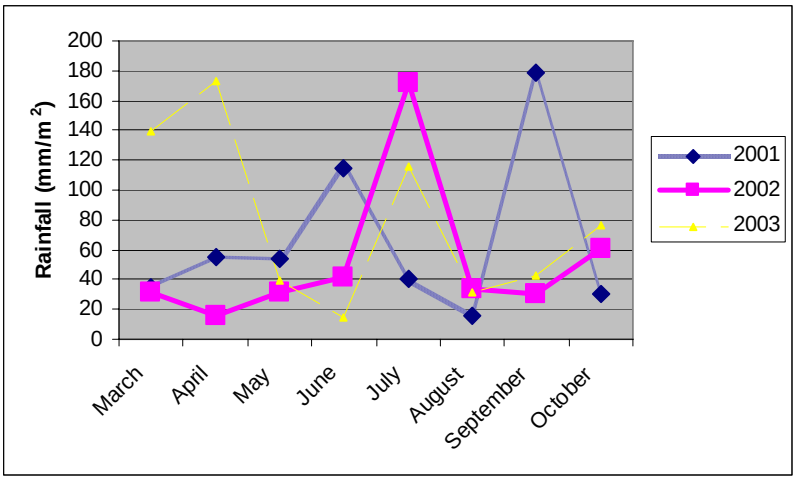

Figure 4
Rainfall (mm/m^2) of 2001-2003 years, March-October intervals
(monthly average data)

Conclusions

The essential oil of fennel fruits (*Foeniculum vulgare* Mill.) cultivated in Iasi (Romania) showed a characteristic chemical profile from year to year. While t-anethole, estragole, fenchone and limonene were the main components in all oils, qualitative and quantitative differences in composition were observed. The content and its monoterpenes components were the most susceptible features of fennel essential oil to be affected by climatic conditions (temperature and rainfall).

References

1. Bernath J., Nemeth E., Petheo F., Mihalik E., Kalman K., Franke R.- Regularities of the essential oil accumulation in developing fruits of fennel (Foeniculum vulgare Mill.) and its histological background, *J.Essent. Oil Res.*, 1999, 11, 431-438;
2. Rădulescu V., Pavel M., Teodor A., Tănase A., Ilieş D.C., Analysis of volatile compounds from infusion and hydrodistillate obtained from the species *Thymus pulegioides*, *Farmacia,* 2009, 57(3), 282-289
3. Choi E.M., Hwang J.K. - Antiinflammatory, analgesic and antioxidant activities of the fruit of Foeniculum vulgare*, Fitoterapia,* 2004, 75 (6), 557-565;
4. Misharina T. A., Polshkov A. N. - Antioxidant properties of essential oils: autooxidation of essential oils grom laurel and fennel and effects of mixing with essential oil from coriander, *Prikl Biokhim Mikrobiol.,* 2005, 41 (6), 693-702;
5. Toma C., Pancan I., Chiriță M., Zamfir A., Electrospray ionization tandem mass spectrometric investigation of M*elissa officinalis* oil, Farmacia 2008, 56(1), 92- 98

6. Ozbek H., Ugras S., Dulger H., Bavram I., Tuncer I., Ozturk G., Ozturk A. Hepatoprotective effect of *Foeniculum vulgare* essential oil, *Fitoterapia*, 2003, 74 (3), 317-319;
7. Parejo I., Viladomat F., Bastida J., Rosas-Romero A., Flerlage N., Burillo J., Codina C. - Comparison between the radical scavenging activity and antioxidant activity of six distilled and nondistilled mediterranean herbs and aromatic plants, *J. Agric Food Chem.,* 2002, 50 (23), 6882-680;
8. Piccaglia R., Marotti M.- Characterization of some Italian types of wild fennel (Foeniculum vulgare Mill.), *J. Agric Food Chem.,* 2001, 49 (1), 239-244.

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