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CONTRIBUTIONS TO THE STUDIES ON THE ESSENTIAL OILS ISOLATED FROM *CORIANDRUM SATIVUM* L. AND *FOENICULUM VULGARE* MILL.

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Introduction

Foeniculum vulgare Mill. and *Coriandrum sativum* L. are medicinal and culinary plants belonging to *Apiaceae* Lindl. family, native to the Mediterranean region and cultivated worldwide.

Coriander (*Ccoriandrum sativum L.*) is a glabrous, herbaceous, annual plant with pronounced taproot and slender branching stems up to 20-60 cm tall. The leaves are variable in shape. The lowest leaves are stalked and pinnate, the leaflets roundish or oval, slightly lobed. The segments of the upper leaves are linear and more divided. White or pale pink flowers are in small 5-10 rayed umbels. Fruits are rounded, ribbed, 3-5 mm in diameter.

Coriander has quite favorable climatic conditions within the Republic of Moldova, where plants rich up to 50cm (Photo1).

Fennel (*Foeniculum vulgare Mill.*) is an herbaceous, perennial, with all parts strongly aromatic. Stems erect, slim, reaching a height of 1,5 meters, bearing soft, lacy, dark green leaves with thread-like lobes and swollen bases. Umbels compound, terminal and lateral, 5-9 cm across; rays 6-20, unequal. Calyx teeth obsolete. Petals yellow, obovate. Fruit oblong, glabrous, 4-6(-10) mm long and 1,5-2,5 mm wide.

In our conditions the growth rhythm of the plants is being observed at normal rate, reaching a height of 1,2-1,5 m (Pfoto 2).

Photo 1. C. sativum L. (flowering period)

Photo 2. F. vulgare Mill.

The importance of these species as a spice-aromatic and medicinal plant is well known. They were used as vegetable and flavour for hundreds of years in many parts of the world.

At the present time, the mature seeds, leaves and young tender shoots of fennel are used as an expensive and extravagant spice and vegetable in many countries (Bulgaria, Romania, Hungary, Greece, Turkey, France, Germany, Egypt, India, China etc.). The aromatic seeds are widely used in the food and flavour industry for addition to meats, fish and sea-food, soups, salad dressing, cakes, bread, teas and alcoholic beverages. Soft growing tips are used to flavour and garnish fish dishes, soups and baked foods. The young leaves often used as a garnish on raw or cooked dishes and make a very pleasant addition to salads [6]. As well as, the coriander is often added to salads, meat dishes, soups, stews, marinades. Young leaves are also consumed fresh as a constituent

of salads. Coriander seeds used as a flavoring in meat products, bakery goods, tobacco, gin and curry powder. Coriander roots have more intense flavor than the leaves and are often cooked as a vegetable.

The therapeutical properties of coriander and fennel essential oil isolated from seeds are carminative, digestive, stomachic, laxative [7], diuretic, depurative, analgesic, stimulant, aphrodisiac, aromatic, expectorant, and antispasmodic [3, 13, 15, 17, 18]. In modern medicine the essential oil and various extracts from coriander have been reported to have antioxidant [16], antibacterial [10, 11], anti-fertility [1], anti-diabetic [8], hypotensive [12], anti-cancerous and hypolipidemic [5] properties. Today these species are highly appreciated in perfumery and cosmetic industry for soups, detergents, toothpastes, creams, perfumes, air fresheners and emulsifiers.

Numerous studies have been conducted on these species, grown in different world regions, particularly on their volatile oil compounds [2, 4, 9, 14]. The aim of this work is to reveal the chemical composition of coriander and fennel essential oil cultivated in Republic of Moldova.

Material and methods

The seed material was received from Germany (Duisburg Botanical Garden) in 2004. The experiment was carried out in 2007 at the experimental fields in Botanical Garden (Laboratory Vegetal Resources) of Academy of Sciences of Moldova. Soil fertilizer wasn't applied. Coriander seeds were collected manually at full maturity in the second decade of July. For the purpose of obtaining fennel essential oil the fruiting umbels were cut promptly when they turned brown and the seed ridges become greyish.

To obtain essential oil was used 100g of thoroughly crushed mature seeds. The distillation apparatus consists of heating cap, a 1L extraction flask, a 3 ml graduated receiver (Dean and Stark) and condenser (jacketed coil). The weighted plant material and 0.7L H_2O were used and the distillation was carried out for 4h after reaching the boiling point. The essential oil content was recalculated for 100 g of dried material.

All RP-HPLC experiments were performed with Agilent 1100 HPLC system (USA) with diode-array detector. The analytic column was a Zorbax XDB C-18 (4.6 x 75), with guard column Extend C-18. Mobile phase was a mixture of MeCN : H_2O (in gradient), flow rate – from 0.4 up to 1.2 ml/min. Maximal pressure – 300 Bar, temperature + 40^0C, analyze time 43 min. Components were detected at UV wavelengths 195, 200 and 210 nm.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance DRX 400 MHz (400.13 and 100.61 MHz) spectrometer. Chemical shifts are given in parts per million values in δ scale with $CDCl_3$ as reference (set δ_H at 7.27 ppm and δ_C at 77.02 ppm) and coupling constants in Hertz. Carbon substitution degrees were established by DEPT pulse sequence and the correlations between hydrogen and carbon atoms with bi-dimensional experiments such as COSY, HMQC and HMBC.

Results and discussions

The obtained results of quantitative analyzes has demonstrated a content of coriander essential oil – 0,72%, that of fennel – 5,2%. The main constituents of the fennel essential oil were anethole (34,70%), fenchone (11,06%), carvone (4,66%), ocimene

(4,25%), α-pinene (2,94%), *p*-cymen (1.42%) and camphene (1%) (Tab.1, fig. 1).

The main components of coriander oil according to RP-HPLC analysis are: geraniol – 16,91%, thymol – 2,52%, verbenone – 1,39%, camphor – 1,35%, camphene – 1,32%, linalyl-acetate – 0,92%, linalool – 36,86% and *p*-cymene – 0,53% (Tab.1).

The NMR analysis of coriander oil evidenced the presence of two main chemical components: linalool and camphor. The ^{1}H-NMR signals of linalool are: 1.21(s) ppm, 1.5(m) ppm, 1.53 (s) ppm, 1.62 (s) ppm, 1.95 (m) ppm, the region 4.95-5.20 ppm is a linalool region with 2 doublet of doublets and triplet of triplets and 5.8 ppm doublet of doublets. The camphor ^{1}H- signals from 1.61-1.69 ppm are overlap with linalool signals, and the same case of overlapping is met for the multiplet from 1.9 ppm. Others camphor signals are 0.77 (s), 0.84 (s), 0.89 (s) of three CH_3 groups. Also the followed signals are from camphor, 1.262-1.372 (m) ppm, 1.75 (s) ppm, 1.80(s) and 2.24-2.31 ppm. The correlations between ^{1}H-NMR (X-axis) and ^{13}C-NMR (Y-axis) signals were attributed with the help of HMQC (**H**eteronuclear **M**ultiple **Q**uantum **C**oherence)-experiment. The HMQC technique is selective for direct C-H coupling. (Fig. 2).

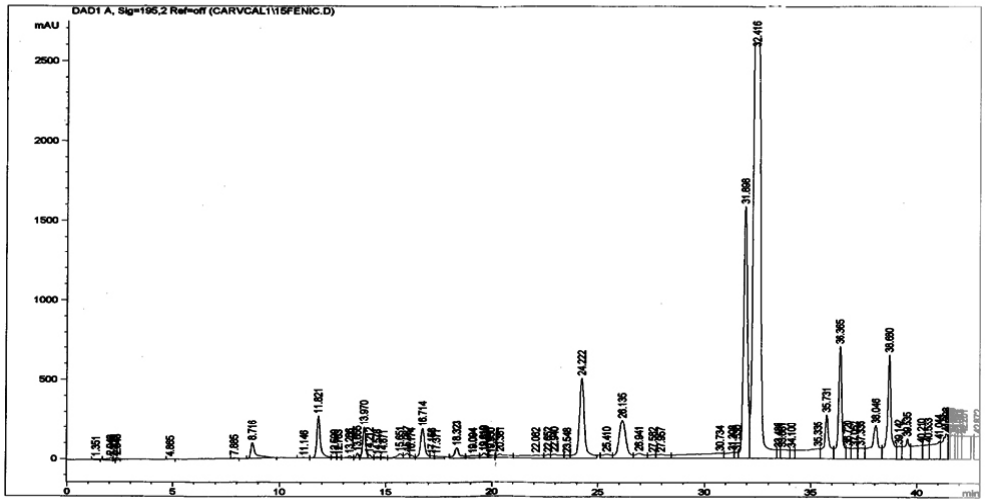

Fig. 1. Chromatogramma of essential oil of *Foeniculum vulgare* **Mill.**
OX – retention times, OY – intensity of peaks

Table 1. The chemical composition of essential oil of *Coriandrum sativum* L. and *Foeniculum vulgare* Mill.

Components	Coriander essential oil		Fennel essential oil	
	Content (%)	Retention indices (min.)	Content (%)	Retention indices (min.)
camphene	1,32	13,76	1,0	13,97
***p*-cymene**	0,53	16,23	1,42	16,71
verbenone	1,39	19,66	-	-
linalyl-acetate	0,92	20,37	-	-

carvone	-	-	4,66	24,22
camphor	1,35	23,95	-	-
***α*-pinene**	-	-	2,94	26,14
fenchone	-	-	11,06	31,90
anethole	-	-	34,70	32,42
geraniol	16,91	25,91	-	-
lynalool	36,86	26,67	-	-
ocimene	-	-	4,25	36,37
thymol	2,52	28,06	-	-

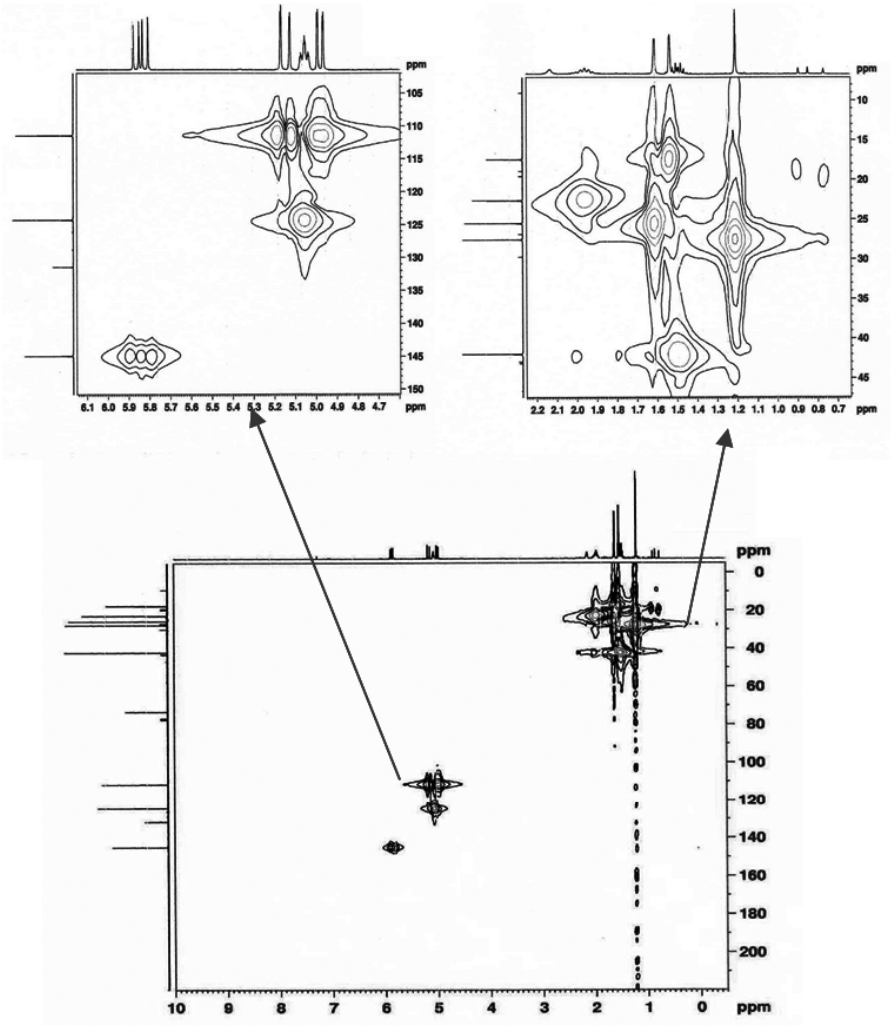

Fig. 2. The HMQC spectrum of coriander oil.

Conclusions

The content of essential oil isolated from the seeds of Coriandrum sativum L. and Foeniculum vulgare Mill. cultivated at experimental fields in Botanical Garden (I) of ASM is 0,72% and 5,2% correspondingly.

Using NMR and RP-HPLC methods we could distinguish as main components of coriander essential oil: linalool (36,86%), geraniol (16,91%), thymol (2,52%), camphor (1,35%), verbenone (1,39%), linalyl-acetate (0,92%), camphene (1,32%).

The main components of fennel essential oil are anethole (34,70%), fenchone (11,06%), carvone (4,66%), ocimene (4,25%), α-pinene (2,94%), *p*-cimen (1,42%), camphene (1%).

The low content of linalool (36,86%) from coriander essential oil and anethole (34,70%) isolated from fennel seeds can be linked with severe drought conditions during the summer of 2007.

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