INVESTIGATION OF ISOLATION METHODS OF KEY COMPONENTS OUT OF ESSENTIAL OILS

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Annotation. *The results of theoretical and experimental researches concerning the development of the isolation method of key aromatic components out of essential oils are presented. High purity key components out of the essential oils of caraway and dill have been obtained.*

Key words*: essential oil, aromatic component, vacuum rectification, preparative chromatography.*

I. **Introduction.** Essential oils are the complex mixtures of aromatic substances that are isolated out of plants. The composition of essential oils depends on the type of plant, its chemotype, environmental and weather conditions, storage conditions of raw materials, methods of producing oils. Despite these factors, 2 - 3 key components form the typical and characteristic for plant species aroma. Their content is about 50…92% of essential oil. Dozens of other components that are in amount less than 5%, form shades and tones of the flavour [1].

II. **Statement of the problem.** One of the main directions of the essential oil processing in the world is an isolation of pure aromatic components. They are used in various aromatic compositions. Other aromatic substances are received out of them by chemical synthesis. For example, a key component of coriander essential oil is linalool with pleasant “lily of the valley” smell. It is transferred to citral (lemon smell) by an oxidation. Obtaining of pure components gives the possibility to investigate their aromatic, physical and chemical and pharmacological properties and to identify a naturalness of essential oil.

The main methods of the individual component isolation out of essential oils are distillation, vacuum rectification, fractional extraction, fractional condensation, stripping with inert gas [2-4].

However, it is impossible to isolate only specified substances by any of these methods. Other components are separated together with them.

The aim of research has been the development of an effective isolation method of key components out of essential oils.

The object of study has been chosen the method of vacuum rectification. It is used for the separation of multicomponent mixtures, including essential oils. But it is impossible to achieve the full and rational isolation because of the large number of components and technical features of the process.

The subjects of investigation have been chosen the essential oils of dill and caraway that consist of two key components such as limonene and carvone.

III. **Results.** The qualitative and quantitative composition of oils has been investigated by the gas chromatography (Table 1).

Table 1 **– Component composition of dill and caraway essential oils**

№	Components	Content,%	№	Components	Content, %
Dill essential oil			Caraway essential oil		
1	α-pinene	1,10	1	α-thujone	0,01
2	α-phellandrene	1,00	2	sabinene	0,04
3	limonene	42,00	3	β-myrcene	1,24
4	cineole	14,00	4	p-cymene	0,06
5	β-phellandrene	0,57	5	limonene	39,71
6	linalool	0,34	6	linalool	0,05
7	linalyl acetate	8,00	7	citral	0,16
8	dihydrocarvone	1,50	8	cis-limonene oxide	0,15
9	carvone	31,00	9	trans-limonene oxide	0,18
			10	α-terpineol	1,06
			11	dihydrocarvone	0,58
			12	cis-carveol	0,27
			13	carvone	56,39
			14	caryophyllene	0,10

Based on the basic laws of rectification, the essential oil components and their boiling points, the separation of each essential oil into fractions has been made. A fraction is a binary system of components that contains key components.

Dill essential oil was considered as the sum of such binary systems: α-pinene – α-phellandrene (fraction 1), limonene – β-phellandrene (fraction 2), linalool – linalyl acetate (fraction 3), dihydrocarvone – carvone (fraction 4). Caraway essential oil is the sum of such binary systems: α-thujone – limonene (fraction 1), linalool – cis-limonene oxide (fraction 2), α-terpineol – cis-carveol (fraction 3), carvone – caryophyllene (fraction 4).

The parameters of vacuum rectification of essential oils such as the optimal pressure, temperature and reflux ratio have been determined theoretically. The operating parameters have been worked out on an automated unit of fractional rectification (UFR with a capacity of 100 ml of essential oil per 1 cycle). With the aim of increasing the efficiency of the essential oil separation the unit has been improved:

1) Rectification column has been filled with nozzle – individual glass rings. The height of rectification column has been increased to 80 cm;

2) Insulation has been used. It is an infrared screen as a vacuum shirt. This allows the process in adiabatic mode.

The optimal parameters of the separation of essential oils of dill and caraway on the clean-cut fractions are presented in Table 2, 3.

Table 2 **– Optimal parameters of rectification of dill essential oil**

Steps	Temperature, ^{0}C		Pressure, kPa	Reflux ratio	Content,%
	reboiler	vapour			
The heating of column	50 …65	14…15	2,64	∞	–
Fraction 1	67…69	15…16	2,64	5:1	4,32
Fraction 2	115…121	62…69	2,64	6:1	30,34
Fraction 3	150…155	82…87	1,32	7:1	6,73
Fraction 4	-	-	0,92	-	55,11
Losses	-	-	-	-	3,50

It has been obtained the four fractions out of the dill and caraway essential oils. Its composition has been determined by the gas chromatography. It has been found

that limonene is part of the first and second fractions of the essential oils and carvone is in the fourth fractions of both oils.

Table 3 **– Optimal parameters of rectification of caraway essential oil**

Steps	Temperature, ^{0}C		Pressure, kPa	Reflux ratio	Content,%
	reboiler	reboiler			
The heating of column	50 …65	14…15	2,64	∞	–
Fraction 1	115…121	62…69	0,92	5:1	5,77
Fraction 2	161…168	82…87	0,92	5:1	36,44
Fraction 3	172…177	91…95	0,92	7:1	7,03
Fraction 4	-	-	0,92	-	47,26
Losses	-	-	-	-	3,50

The component compositions of the fractions are presented in Table 4.

Table 4 **– Content of limonene and carvone in essential oil fractions**

Fractions	Components	Content,%	Fractions	Components	Content,%
Dill essential oil			Caraway essential oil		
First	α-pinene	52,1	First	α- thujone	5,32
	α-phellandrene	39,2		sabinene	10,53
	limonene	7,1		β-myrcene	53,72
	cineole	1,6		p-cymene	13,4
Second	α-pinene	0,24		limonene	39,71
	α-phellandrene	0,44	Second	limonene	82,88
	limonene	69,47		linalool	3,81
	cineole	17,36		citral	5,85
	β-phellandrene	6,2		cis-limonene oxide	7,46
Thirthd	linalool	12,40	Thirthd	carvone	88,68
	linalyl acetate	3,68			
	dihydrocarvone	1,22		caryophyllene	11,32
	carvone	92,7			

The separation of the essential oils for several series of studies has shown the impossibility of the isolation of limonene or carvone in pure form. The vacuum rectification only allows concentrating them.

Therefore, the authors developed a schematic diagram of the isolation of components in pure form, shown in Figure 1.

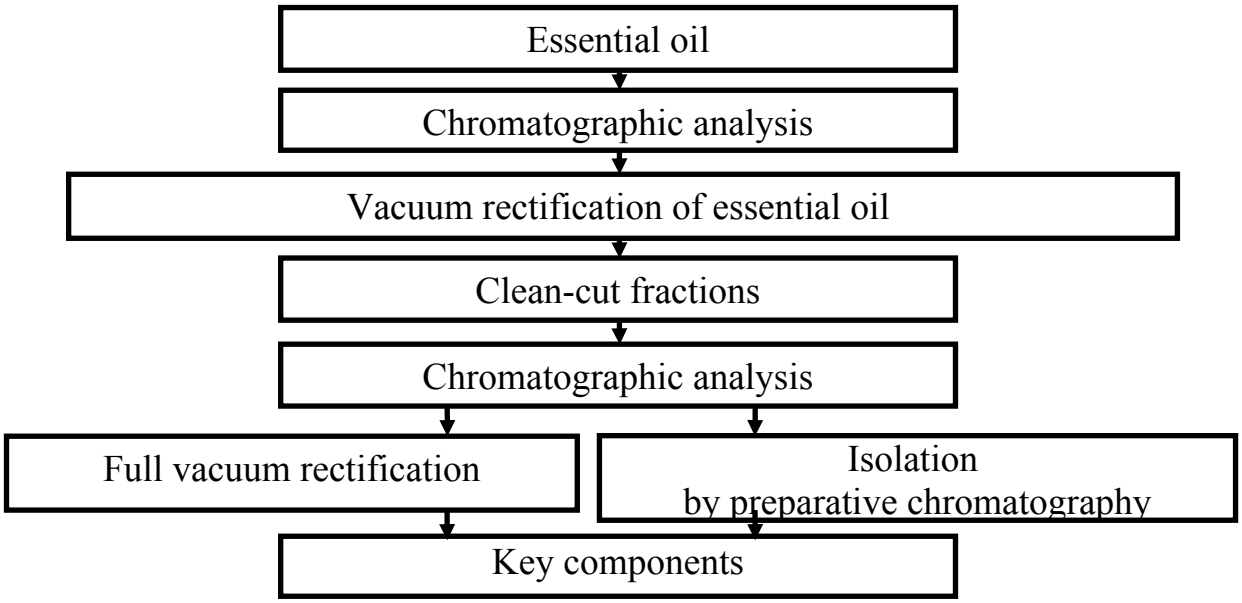

***Figure 1* – Isolation of aromatic components out of essential oils**

Using repeated vacuum rectification of the essential oil fractions requires theoretical calculations and multiple cycles to achieve the complete separation of fractions. So the preparative chromatography is the prospective method of isolation that has several advantages: 1) the high efficiency separation of the substances with similar properties, 2) the isolation of the target component with minimal losses to achievement a high degree of enrichment [2, 5].

The authors developed a method of the preparative isolation of components out of the essential oil fractions on "Chrome 31" preparative chromatograph.

Preparative column is very important. Solid Chromosorb A support of varying dispersion has been used in three sections. Its content in the first section is about 15 %, the particle size is 2 ... 3 mm, the second section – 25 %, the particle size – 1 ... 2 mm, and the third section – 60 %, the size of grains – 0.56 ... 1 mm. The stationary Carbowax 6000 phase has been chosen in the concentration to the solid support. It is about 25% in the first section, in the second section – 20%, in the third and fourth sections, respectively, 17% and 15%.

Using these parameters has allowed increasing the separation efficiency up to

520 theoretical plates for limonene.

The optimal isolation of limonene out of the first and second fractions has been made under conditions: column temperature – 150 ^{0}C, injector temperature – 250 ^{0}C, detector temperature – 250 ^{0}C, collection of fractions – 250^0 C, temperature of the Dewar vessel – 20 ^{0}C, the flow-rate of carrier gas – 80 ml/min, type of detector – katharometer.

The optimal isolation of carvone out of the fourth faction made under the chromatography conditions: column temperature – 170 ^{0}C, injector temperature – 250 ^{0}C, detector temperature – 250 ^{0}C, collection of fractions – 250^0 C, temperature of the Dewar vessel – 20 ^{0}C, the flow-rate of carrier gas – 90 ml/min, type of detector – katharometer.

IV. **Conclusions.** Thus, on the basis of experimental research the special method of analysis for isolation of the essential oil key components have been developed. It may be used to study the sources of natural flavours and in production of natural flavourings out of domestic plant material for food industry.

V. Literature

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