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SECTION 3
PHARMACEUTICAL CHEMISTRY AND PHARMACOGNOSY

3.1 The components content of essential oil of *cirsium arvense* (l.) scop. herbs

The urgent problem of modern pharmacy is the phytochemical study of perspective species of medicinal plants, identification and determination of the content of biologically active substances, standardization of plant raw materials.

The influence of the chemical composition of plant materials on its pharmacological activity a is intensively studied. Hundreds of groups of biologically active substances in a large number of plants were studied, which became the basis for the creation of many herbal remedies. In this time, about 500,000 plant species are known, many of which are used in official medicine.

Asteraceae is a very large and widespread family of flowering angiosperms. The family includes over 32,000 currently accepted species, in over 1,900 genera (list) in 13 subfamilies [153, 154, 155, 156].

Nearly all *Asteraceae* bear their flowers in dense heads (capitula or pseudanthia) surrounded by involucral brasts. The name *Asteraceae* comes from the type genus *Aster*, from the ancient Greek "ἀστήρ", meaning star, and refers to the star-like form of the inflorescence.

Most members of *Asteraceae* family are annual or perennial herbs, but a significant number are also shrubs, vines, or trees. The family has a cosmopolitan distribution, with species ranging from subpolar to tropical regions, colonizing a wide variety of habitats.

The largest proportion of the species occur in the arid and semiarid regions of subtropical and lower temperate latitudes. The *Asteraceae* may represent as much as 10% of autochthonous flora in many regions of the world. Prospective plants for obtaining highly effective plant remedies are species of the genus *Cirsium* L. (*Asteraceae*), which has up to 481 species of perennial herbaceous flora. Distributed in Europe, North Africa, North and Central America. With about 60 species from

North America(although several species have been introduced outside their native ranges) [19, 23].

The Biology of Canadian Weeds: *Cirsium arvense* list four varieties:

– *Cirsium arvense* var. vestitum (Wimm. & Grab). Leaves gray-tomentose below; *Cirsium arvense* var. integrifolium (Wimm. & Grab). Leaves all entire or the upper leaves entire and the lower stem leaves shallowly and regularly pinnatifid or undulating; *Cirsium arvense* var. arvense. Leaves shallowly to deeply pinnatifid, often asymmetrical; *Cirsium arvense* var. horridum (Wimm. & Grab). Leaves thick, subcoriaceous, surface wavy, marginal spines long and stout [179].

According to recent in the Ukraine, *Cirsium* Mill. genus is represented by 30 species [154, 155, 156].

Cirsium is a genus of perennial and biennial flowering plants in the *Asteraceae*, one of several genera known commonly as thistles. These differ from other thistle genera (*Carduus*, *Silybum* and *Onopordum*) in having feathered hairs to their achenes. The other genera have a pappus of simple unbranched hairs. The flowering period includes period for April to August [168, 182, 175].

The most popular species of *Cirsium* Mill. genus are: *Cirsium vulgare* (Savi) Ten., *C. arvense* (L). Scop.,*C.* acaule (L.)Weber.ex F.H. Wing., *C.* adjaricum Sommier & Levier, C. aduncum Fisch. & C. A. Mey. ex DC.,*C.* ageratum Ledeb., *C.* alatum (S. G. Gmel.) Bobrov, *C.* alberti Regel. & Schmalh., *C.* albowianum Sommier & Levier, *C.* arachnoideum (M. Bieb.) M. Bieb., *C.* argillosum Petrov ex Kharadze, *C.* badakhschanicum Kharadze, *C.* balkharicum Kharadze, *C.* bornmuelleri Sint. ex Bornm.,*C.* bracteosum DC., *C.* brevipapposum Czerniak,*C.* buschianum Kharadze, *C.* canum (L.) All., *C.* caput-medusae Sommier. & Levier, *C.* caucasicus Petr., *C.* cephalotes Boiss., *C.* charkeviczi Barkalov, *C.* chlorocomos Sommier. & Levier, *C.* ciliatum (Murray) Moench., *C.* coryletorum Kom., *C.* czerkessicum Kharadze, *C.* daghestanicum Kharadze, *C.* dealbatum M. Bieb., *C.* decussatum Janka, *C.* (M. Bieb.) Hand-Mazz., *C.* echinus (M. Bieb.) Hand-Mazz., *C.* erisithales (Jacq.) Scop., *C.* erythrolepis K. Koch, *C.* esculentum (Siev.) C. A. Mey., *C.* euxinum Kharadze, *C.* fomini Petr., *C.* gagnidzei Kharadze, *C.* glabifolium (C.

Winkl.) O. Ferdsch.. & B. Ferdsch.., *C.* helenioides (L.) Hill, *C.* heterophyllum (L.) Hill., *C.* hypoleucum DC., *C.* imereticum Boiss., *C.* isophyllum (Petr.) Grossh., *C.* kamtschaticum Ledeb. ex DC., *C.* komarovii Schischk., *C.* kosmelii (Adams) Fisch. ex Hohen., *C.* lamyroides Tamamsch., *C.* lanceolatum (L.) Hill., *C.* laniforum (M. Bieb.) Fisch., *C.* macrobotrys (K. Koch.) Boiss., *C.* macrocephalum C. A. Mey., *C.* oblongifolium K. Koch., *C.* obvailatum (M. Bieb.) Fisch., *C.* oleraceum (L.) Scop., *C.* osseticum (Adams.) Petr., *C.* palustre (L.) Coss. ex Scop., *C.* pannonicum (L. f.) Linik., *C.* pectinellum A. Gray., *C.* pendium Fisch. ex DC., *C.* pseudolappaceum Kharadze., *C.* pubigerum (Desf.) DC., *C.* rhizocephalum C. A.Mey., *C.* rigidum DC., *C.* rivulare (Jacq.) All., *C.* roseolum Gorl., *C.* sairamense (C. Winkl.) O. Fedtsch.& Fedtsch., *C.* schantarense Trautv. & C. A. Mey., *C.* semenovii Regel., *C.* serratuloides (L.) Hill, *C.* serrulatum (M. Bieb.) Fisch., *C.* simplex C. A. Mey, *C.* sosnowskyi Kharadze, *C.* strigosum (M. Bieb.) Fisch., *C.* svaneticum Sommier & Levier, *C.* svchnosanthum Petr., *C.* turcestanicum (Regel) Petr., *C.* ukrainicum Besser ex DC., *C.* uliginosum (M. Bieb.) Fisch.,*C.* vlassovianum Fisch. ex DC., *C.* waldsteinii Rouy [153, 154, 156, 157, 167, 169, 180, 181, 172, 177].

Cirsium arvense (L.) Scop. (Image 1) is a species of flowering plant in the daisy Asteraceae family, native throughout Europe and northern Asia, and widely introduced elsewhere. The standard English name in its native area is creeping thistle. *Cirsium arvense* (L.) Scop.is an invasive, non-native plant in many terrestrial systems, often dominating plant communities, particularly in agricultural systems. Its invasion into forest systems is not well understood.

As a subclassification of the "Eudicot" monophyletic group, *Cirsium* is a "true dicotyledon". The number of Pollen grain furrows or pores helps classify the flowering plants, with eudicots having three colpi (tricolpate).

Creeping thistle is a herbaceous perennial plant growing up to 150 cm, forming extensive clonal colonies from thickened roots that send up numerous erect shoots during the growing season. It is a ruderal species.

Stems 30–150 cm, slender green and freely branched, smooth and glabrous (having no trichomes or glaucousness), mostly without spiny wings. Leaves alternate on the stem with their base sessile and clasping or shortly decurrent.

The leaves are very spiny, lobed, up to 15–20 cm long and 2–3 cm broad (smaller on the upper part of the flower stem).

The inflorescence is 10–22 mm diameter, pink-purple, with all the florets of similar form (no division into disc and ray florets). The flowers are usually dioecious, but not invariably so, with some plants bearing hermaphrodite flowers. The seeds are 4–5 mm long, with a feathery pappus which assists in wind dispersal. 1–5 flower heads per branch, with plants in very favourable conditions producing up 100 heads per shoot. Each head contains an average of 100 florets. Average seed production per plant has been estimated to 1530. More seeds are produced when male and female plants are closer together as flowers are primarily insect-pollinated.Variation in leaf characters (texture, vestiture, segmentation, spininess) is the basis for determining creeping thistle varieties [153, 154, 156, 170, 171, 176].

According to Flora of Northwest Europe there are two varieties: *Cirsium arvense* var. arvense (Most of Europe. Leaves hairless or thinly hairy beneath), Cirsium arvense var. incanum (Fisch.) Ledeb. (Southern Europe. Leaves thickly hairy beneath) [168, 179].

The study of the chemical composition of plant essential oil and accumulation during the growing season allows us to expand the range of herbal raw material exhibiting antimicrobial, wound healing and immune-stimulating activities.

In this case, when using herbal remedies, pronounced therapeutic activity is manifested, which is especially important in the fight against infectious diseases. For obtaining high-quality medicinal plant material, it is important to study the chemical composition of essential oil, which is of great importance in the future for drying, storing, processing and using plants and herbal preparations.

The extracts from the species of *Cirsium* Mill. genus exhibit many biological activities, such as antimicrobial, anticancer, antioxidant, hepatoprotective, antifungal, and antibacterial. These plants are famous for their use in traditional and conventional medicine, cosmetology, and some species are used as additive to food because of the nutritional value [157, 158, 167, 169, 170, 171, 173, 176, 188].

The numerous publications are devoted to methods for determining the biologically active substances of the *Cirsium* L. genus herbs raw materials. The main compounds the species of *Cirsium* Mill. genus are flavonoids, hydroxycinnamic acids, phenolic acids, sterols, alkaloids, polyacetylenes, acetylenes, triterpenes, sesquiterpene lactones, lignans, hydrocarbons and minerals [157, 159, 167, 172, 173, 175].

Infusions and decoctions from the herb and root of the *Cirsium arvense* (L.) Scop. are used in medicine of many countries around the world as effective means of anti-inflammatory, antitutor and hepatoprotective actions. The biological activity of the plants are associated with the presence of flavonoids, hydroxycinnamic acids, fatty oils, polysaccharides, carotenoids. At the same time the chemical composition of biologically active essential oil has not been investigated.

The *Cirsium arvense* (L.) Scop. thistle

The most of the known essential oils are colored liquids depending on the content of the components: borax, yellow, blue, green, pink and other. They are easily soluble in ether, alcohols, organic solvents, almost insoluble in water.

It is known that the content of essential oils in the morphological organs of plants during vegetation, their component composition and physic-chemical properties are directly related to the place and conditions of growth of this species, the time of collection of herbal raw material, method of obtaining the substance during processing [159, 175].

Insignificant concentrations of biologically active substances from the essential oils are able to partially flow to infusions or decoctions of herbal raw materials in soluble state and exhibit pronounced pharmacological activity on the human organism.

The components of the essential oils are very easily oxidized by UV-rays, radiation, high temperature, oxidizing agents of a chemical nature and others.

At the same time observe the change in odor, texture, color of substances, their biological actions. In our time, studies of essential oils of the *Cirsium* L. genus species have not been conducted and their component state is almost unknown.

The purpose of this work is to determine by GLC-MS the qualitative composition and quantitative content of biologically active components of essential oil from herb of *Cirsium arvense* (L.) Scop. [150].

The subjects used for research were herbs of *Cirsium arvense* (L.) Scop. flora of Ukraine, namely: tips of shoots 10-15 cm long with adjoining inflorescences and leaves. The plant raw material was harvested during the phenological phase (June-August 2014-2019) during flovering in different regions of Ukraine in accordance with the general requirements of the State Pharmacopoeia of Ukraine(1.3) [151_]. The drying is carried out to temperature not exceeding 40° C for 12 hours.

Harvesting of herbal raw material was performed according to generally accepted methods. The drying process was carried out for 12 hours in the dryer «Termolab SNOL 24/350» at a temperature of 350^0C, a layer thickness of 1 sm. For the study of weight loss drying and photochemical analyzes, air-dried herbal raw materials, suspended and weighing on For the study of weight loss during drying and phytochemical analyzes, air-dried vegetable raw materials, suspended on and weighing on device «AXIS» ANG 2000.0001 200 / 0.01.

The relatively low content of essential oil in the investigated herbal raw materials does not allow the substance to be obtained in required volumes. Therefore, for laboratory conditions, this technique was upgraded by us. An analysis was conducted by physical and physical-chemical methods.

Methods: 500,0 g (precipion sample) pre-ground to a diameter of particles (d=0,3 mm), air-dry grass, made in 1 liter flask, was added 500,0 ml of purified water. Ultrasound was performed on a device «UZDN-A1200T» with a working frequency for 50 Hz and time 1 hour. Obtaining the essential oil was performed by Clevenger method on the device recommended by the State Pharmacopoeia of Ukraine when heated on a water heater «WB-4 Micromed» ($t=100^0C$) for 4 hours. The quantitative content of essential oil was calculated in volume-weight (%) [152].

Analysis of the component composition of the essential oil was performed by the GLC-MS method on Agilent Technology 6890/5973 N chromatograph on microcapillary colums in the programmed mode. The method is effective for the analysis of complex multicomponent mixtures of volatile substances containing up to several tens of different compounds. It is characterized by a relatively short duration of up to 35 minutes, a high sensitivity of determination (up to 10^{-13} g), a small amount of sample used (up to 0,1 μl) and a small relative error of studies [150].

Used HP 19091 S-433 (HP-5 MS) microcapillary chromatographic column, 30 m long, 0,32 mm in diameter. Injector: 7683 autoinjector, split (20:1). Detector temperature 250^0C. The temperature of the column thermostat is programmed from 50 to 320^0C (40^0C/min).

The sample was introduced into the chromatographic column in split less mode at a rate of 1,2 ml/min for 0,2 min. Continues flow of carrier gas (helium) 1,2 ml/min. The NIST05 and WILEY 2007 mass spectra libraries were used to identify the investigated essential oils, containing over 470000 components and programs for their identification. The interval standard method was used to calculate the quantitative content of the compounds. The concentrations of the components of essential oils were calculated by the sum of all areas of the respective chromatograms.

The results of the experiments were processed by the method of mathematical statistics under the license program “Statistica 6.0 for Windows” (Stat. Soft. Inc., №AXXR712D833214FANS). The reability of the obtained differences in the values of the State Pharmacopoeia of Ukraine was evaluated by Student’s t-criteria (p>95%).

The results of determining the composition of the essential oil in the herb *Cirsium arvense* (L.) Scop. from different growth sites are shown in Fig. 8 and in Tabl. 17.

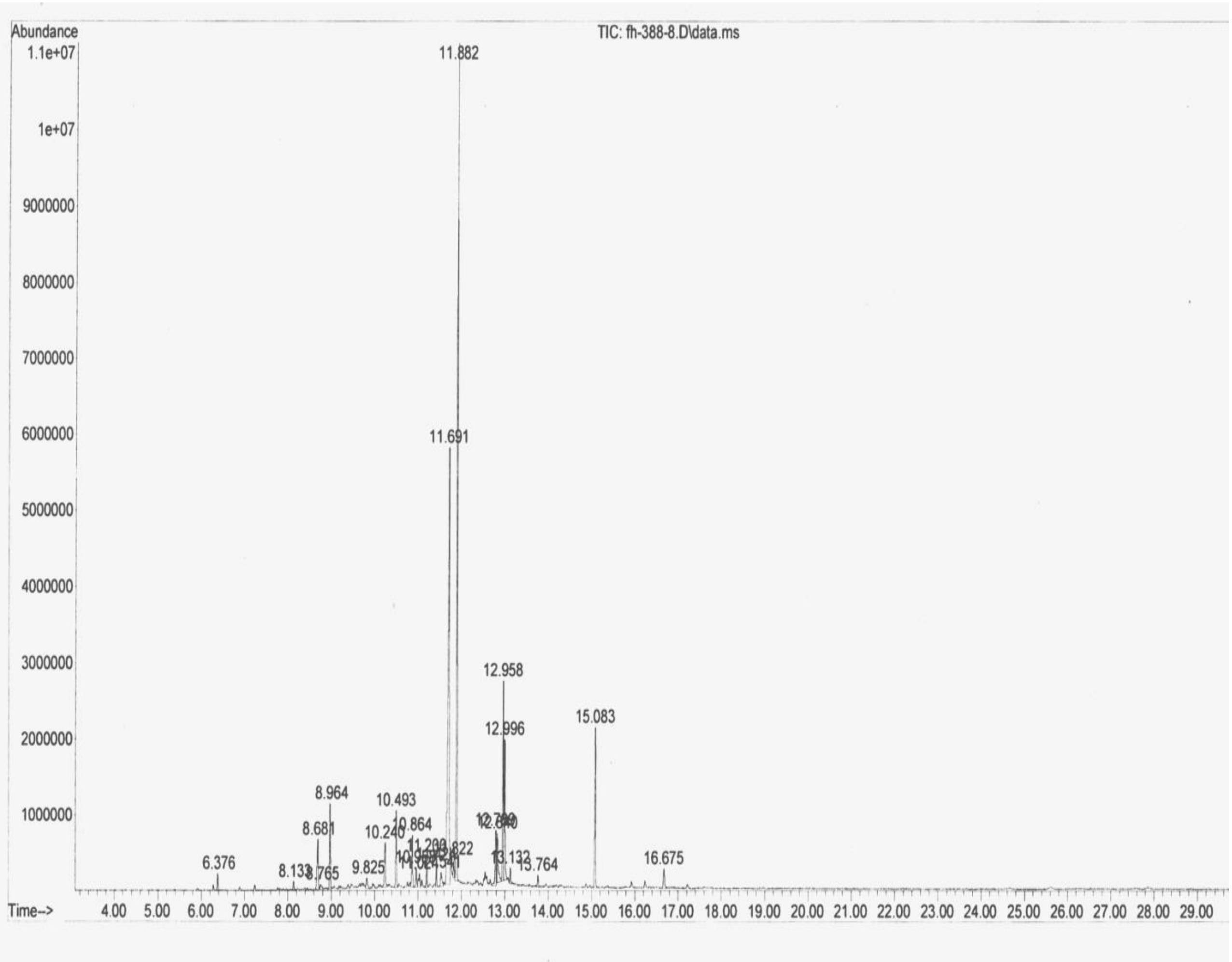

Fig. 6. GLC-MS of essential oil from *Cirsium arvense* (L.) Scop.

Table 17.

Composition and quantitative content of essential oil components from the herb of *Cirsium arvense* (L.) Scop., ($\bar{x} + \Delta \bar{x}$)%, μ=6, Zaporizhia region, Tokmok sity,(June-August) 2019 p.

№	Exit time (min.)	The name of compound	Quantitative content (%)
1	2	3	4
1.	5.00	2-Methyl-5-(1-methylethyl) - 3,4-diethyl-phenol	2,19±0,20
2.	6.57	Undecanoic acid 2, 8 dimethyl ester	0,98±0,09
3.	6.87	Dodecanoic acid ethyl ester	0,81±0,08
4.	7.09	Docahexadienoic acid methyl ester	1,05±0,11
5.	7.42	2-Hydroxy-2-methoxy-cinnamalaldehyde	2,01±0,19
6.	7.50	Tetradecanoic acid ethyl ester	8,84±0,89
7.	7.72	2-Pentadecanon-6,10,14-trimethyl octadecanal	1,53±0,16
8.	7.86	Pentadecanoic acid methyl ester	0,70±0,07
9.	7.92	Undecanoic acid2,8-dimethyl ester	2,32±0,24
10.	8.07	Pentadecanoic acid ethyl ester	0,79±008
11.	8.21	Hexadecanoic acid methyl ester	0,63±0,07

Continuation of table 17.

1	2	3	4
12.	8.24	Palmitoleic acid methyl ester	1,39±0,14
13.	8.33	Dodecanoic acid 2,8-dimethyl ester	51,03±5,10
14.	8.99	Linoleic acid ethyl ester	9,33±0,95
15.	9.08	Octadecanoic acid ethyl ester	2,09±0,19
16.	9.44	Tricosan	1,18±0,12
17.	9.77	3- Methyloctadecane	0,67±0,07
18.	10.10	11-Decyloctadecane	0,86±0,09
19.	10.29	Eikosan	8,75±0,88
20.	10.80	Heptacosan	0,98±0,09
21.	11.33	Nonakozan	0,66±0,07
22.	12.15	Nonadecan	0,85±0,09

For the first time in the composition of essential oil from the herb of *Cirsium arvense* (L.) Scop. the presence and quantitative content of 22 compounds, which are characterized by pronounced ant-inflammatory, antioxidant and antimicrobial activity, were determined. Organic fatty and their esters, terpene compounds, saturated carbohydrates of their acids and oxidized derivates were present to the greatest extent. The predominant components were: dodecanoic acid 2,8-dimethyl ester (51,03± 5,10%), linoleic acid ethyl ester (9,33± 0,95%), tetradecanoic acid ethyl ester (8,84±0,89%), eicosan (8,75±0,88%), undecanoic acid 2,8-dimethyl ester (2,32±0,24%); 2-methyl-5-(1-methylethyl)-3.4-diethylphenol (2,19±0,20%), octadecanoic acid ethyl ester (2,09±0,19%), 2-pentadecanon-6,10,14-trimethyl octadecanal (1,53±0,16%), palmitoleic acid methyl ester (1,39±0,14%), tricosan (1,18±0,12%). In the modern scientific literature does not describe 3 compounds: 2-methyl-5-(1-methylethyl)-3,4-diethylphenol, 2-hydroxy-2-methoxy-cinnam aldehyde, 2-pentadecanon-6,10,14-trimethyl octadenal. Most of the identified compounds from the student essential oil are quite well known and distributed in species of *Asteraceae* family. They are well soluble in fats, biological fluids of the human body, participate in biochemical metabolic processes. Show pronounced anti-inflammatory, antioxidant and antimicrobial activity [170, 171, 172, 175, 176].

The herb of *Cirsium arvense* (L.) Scop. promissing for obtaining highly effective fitotherapeutical preparations.