Application and characteristics of Achillea millefolium and its oil

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Introduction

Increased interest in products of natural origin has been noticed within recent years. It concerns the cosmetics, pharmaceutical and food industry. *Achillea millefolium* L. (yarrow) and its oil play an important role in a wide range of substances of natural origin, used in our everyday life. The goal of this article is to characterize these two products and underline their role in small-scale production.

Yarrow (Achillea millefolium L.)

Yarrow herb [other common names of a common yarrow, depending on the place of occurrence are: gordaldo, nosebleed plant, old man's pepper, devil's nettle, sanguinary, milfoil, soldier's woundwort, thousand-leaf (as its binomial name affirms), thousand-seal]

Latin name of Achillea comes from the name of Achilles, who at the time of the Trojan War healed the wounds by means of Achillea herb. It was immortalized in the Iliad by Homer. Species' name refers to the characteristic shape of its leaf and comes from a Latin word millefolium – of thousand leaves.

Yarrow herb is a perennial or an undershrub from the Asteraceae family, very common in Poland and whole Europe, Central Asia or in North America. It grows on meadows, roadsides and grass-lands, sunny places and fertile soils. The plant is strongly aromatic, its stem is abundantly covered with moss and produces many leaves. It grows up to 80 cm, it has *umbel-shaped* inflorescence which consists of white or pale pink tongue-shaped flowers. It blossoms from June to October. The plant itself and its flowers are picked only in sunny places and always when they are freshly bloomed.

Achillea species include many types of this cosmopolitan plant. On Northern hemisphere there are over 120 species of perennials. There are types that differ in azulene content level, called chemotaxones. Within species there can be differentiated two types of plants: those containing or not containing azulene. The difference depends on the region the plant comes from, but they do not differ in terms of morphology.[1].

Therapeutic action is assigned both to a herb (*Herba Millefolii*) and to its flower (Flos Milleffolii). They both contain the same ingredients.

Curative properties can be explained by properties of various compounds the plant consists of, particularly etheric oil and its content (mono- and sesquiterpens, dicavoiloquinoic acid (DCQAs) [2].

Etheric yarrow oil

The oil is derived mainly from a flower. Fresh flowers contain up to 0.25% and dry up to 0.6% oil. Its content in other parts of the plant ranges only within 0.1-0.3% [3]. Crop plants are richer in oil. In herbs grown in Austria the content reaches up to 5.88%, in Germany up to 5.65%, in Italy up to 2.25% and in Poland up to 2% [2]. Polish Pharmacopoea Part IV specifies requirements for oil content as 0.25% [4].

Oil from *Millefolii (Oleum Millefolii)* is produced in a steam distillation process of flower heads. Distillation residue is used as a compost [3].

The oil could also be isolated by extraction with CO_2 at supercritical condition (40-60°C, 10 MPa) [5].

Oil has a form of dark blue or greenish liquid. It has an irritating

and bitter taste. Its density ranges within 0.896-0.932, it dissolves in 90% ethanol (1:1 volumetric ratio). 50% azulene content gives it characteristic colour. 0.1 g of oil dissolved in 20 cm³ of ethanol gives blue solution. The colour comes from azulene. Oil from *Millefolii* is cheaper alternative for camomile oil [3]. Its physicochemical parameters are shown in table 1.

Table I

Phisicochemical constans of Achillea millefolium oils [6]

Parameter	Walue
Specific gravity	0,900-0,936
Optical rotation	do -1,65°
Optical rotation	1-12
Saponification value	19-27

Main ingredients of *Millefolii's* oil are mono- and sesquiterpenes that are characterised by various pharmacological activities, assured by clinical trials [7].

Table 2

The most popular pharmacological effects of mono- and sesquiterpenes

Effect	Monoterpenes	Sesquiterpenes
Stimulant	+	+
Stimulant	+	+
Anthelmintic	+	+
Disinfectants	+	+
Irritant	+	+
Sedative	+	+

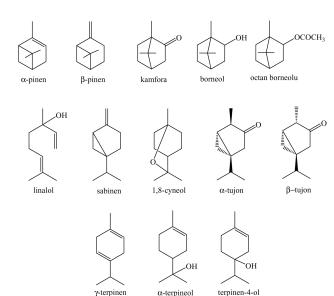
Within monoterpenes ingredients, the most important are α - i β -pinene, thujone, cineole, borneol and its acetate. Pinens represent bicyclic monoterpenes. á-pinene is liquid that has characteristic smell and boiling point of 156°C, whereas β -pinene's boiling point is 162°C. Separation of these two isomers is difficult. The process is conducted using fractionating distillation on efficient columns. á-pinene is one of the most important monoterpenes. It occurs in almost every etheric oil. The highest amount of β -pinene was found in white inflorescence of a plant (19.3%), the lowest is in strongly pink inflorescence. Pinens are cosmetic aromatizing substances (13.1%) [8,9].

Thojone, in the past called "tanacetone," is a liquid having characteristic odour. It is strongly toxic and has anti maggot properties. Cineole is a terpene oxide. It is an antichocking disinfecting and spasmolytic agent. It has a pleasant smell.

Borneol is a saturated alcohol, having a characteristic camphoric smell. It occurs in a free or esteric form. It has practical application in perfume industry $[8 \div 10]$.

The separate stages of plant development have also an impact on substances forming the yarrow herb. Studies were conducted in Norway that related to monoterpenes content change accompanying vegetative growth. Initially, vegetative and complete growth of a plant has been tested. The following monoterpenes were identified in the test:

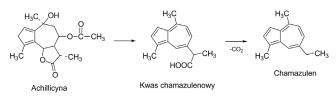
At the initial stage of development, the highest content of cam-



phor, 1.8-cineole and α -thujone was found. During vegetative development, amounts of sabinene, 4- terpineol, borneol and its acetate were increasing. At the complete growth of a plant, the highest amounts of β -pinene, α -thujone and 1.8-cineole, and α -pinene were found in etheric oil. At the same time, the lowest amount of β -thujone and γ -terpinene were determined. While growing, the plant is poorer in sabinene, camphor, 4- terpineol and borneol and its acetate [11]. Sesquiterpenes present in etheric oil, form acyclic and bicyclic structures. Usually, they are lactones of sasquiterpenes. The most important sesquiterpene of the oil is one of the azulenes – chamazulene (content up to 50%). Its forerunner, called proazulene is achillicine (8-acetoxy-artabsine), a lactone of sesquiterpene, matricin stereoisomer. It is colourless and not bitter. Azulene has a fundamental configuration for this group of substances.

Chamazulene is derived from achillicine through chamazulenic acid.

Chamazulene (1.4-dimethyl-7-ethyl azulene, dimethyl hulene) is a



blue oil having boiling point of $tw_{12} = 161 \text{ °C}$ and $tw_{11} = 145 \text{ °C}$ and density $d\frac{D}{4} = 0.9883$. LD₅₀ determined for white mice is 3g/kg [12].

Amount of chamazulene in oil determines its colour. Table 3 presents relation between colour of oil and chamazulene content [13].

Changes in content, particularly in amount of azulene that gives the colour are characteristic feature for the oil (Tab. 3).

Chamazulene has anti-inflammatory characteristics [14]. Its de-Table 3

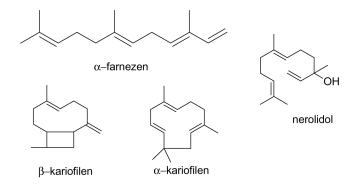
The scale of the oil changes the color depending on the chamazulene content

oil coloration	chamazulene content
Colorless	lack
Pale blue	lack
Green blue	traces
Slightly blue	poor content
Blue	average content
Dark blue	high content

rivatives are acetyl balchanolide and millefoide [9].

According to studies performed by Norwegian scientists, during

maturation of the plant, the content of sesquiterpenes changes and within complete growth phase there is the highest amount of trans nerolidol, β -cariofilene and its oxide. In a preliminary and vegetative growth period of a plant, there is relatively high content of α -farnesene, 10 and 8% respectively, but at complete growth stage the amount decreases to 2%. At this stage of growth, the highest content of trans nerolidol occurs (about 6%). Moreover, oil contains α -cariofilene, cariofilene oxide and cis nerolidol [15].

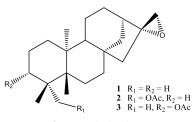


Farnesene is acyclic terpene having anti-inflammatory characteristics.

Cariofilenes are isomeric carbonates that have anti-cancer activity. α -cariofilene, called cumulene, has monocyclic structure. β -cariofilene that has dicyclic structure is one of the most common terpenes.

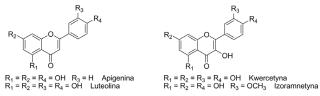
Nerolidol, 3-nonsaturated alcohol has a pleasant, balsamic smell [8].

Diterpenes, caurane derivatives (1-3), were isolated from a root of *Achillea Clypeolata* [16].

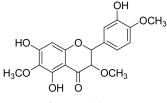


Caurane derivatives

Flavonoids, present in yarrow herb, have multiple biological (pharmacological) activities and play an important role in the plant. They are anti-oxidant agents. The most important from this group are: apigenin derivatives, luteolines, quercetines and isoramnetines, which occur in either free or glycosidic form [17].



Centaureidine (3',5,7-trihydroxy-3,4',6-trimetoxyflavone) was found in the species that grow in Hungary.

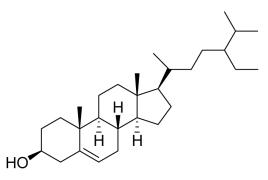


Centaureidine

 β -sitosterol and fitosterol were also identified in these types of a plant. Fitosterol is very common among plants. β -Sitosterol is used in hypercholesterolemia as an agent reducing cholesterol absorption in intenstines.

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Table 4



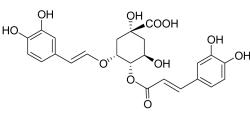
β -Sitosterol

Polyacetylenes, called also polyines, are an interesting group of substances identified in flower plants and microorganisms. They are made through aliphatic linkages having a number of triple bonds or compounds formed by their cyclisation. Polyacetals are lipophilic substances, their pharmacological characteristics are hardly known. From biogenetics point of view, they are linked to higher fatty acids, particularly with oleic acid. Matricaria ester is contained in yarrow herb [8].

Dicavoiloquinoic acid (DCQAs) is an interesting substance having an impact on medicinal activity of yarrow.

 $H_3C-C\equiv C-C\equiv C-C\equiv C-CH=CH-COOCH_3$

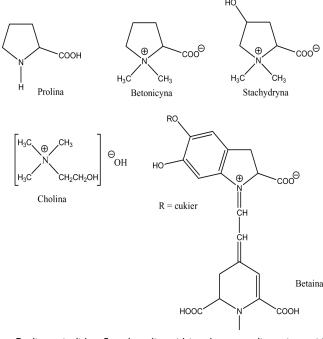




Dicavoiloquinoic acid

In vitro testing provided information that the compound has strong properties of HIV-1 inhibitor in tested cell lines [18].

In Achillea millefolium group, the following nitrium organic compounds have been identified [19].



Proline, pirolidon-5-carboxylic acid is a heterocyclic amino acid. Stahidrine is probably made through praline metisation. Betonicine is sometimes assigned to "protoalcaloids." Sweet taste characterizes both derivatives of proline [8].

Choline, hydroxide 2-hydroxy-ethyl-trimethylamonate, was isolated in crystalline form from bile (from Greek chole means bile). It is thought to have similar active properties as vitamins. It is acetylcholine forerunner, an important mediating agent that transmits nerve impulses in synapses.

Betaine, indol's derivative, called a colour alkaloid, was isolated from beetroots in 1957. About 10% of human population does not have the ability to reconstruct the agent to its colourless linkage. It is genetically driven feature that could be used in forensic medicine [8].

The most important mineral salts occurring in yarrow herb are magnesium and zinc compounds. Magnesium, called "the basic element of life," regulates muscles and nerves activity, has an anti-stress action, influences vascular system and heart, protects from heart attacks and heart arrhythmia.

Micronutrients found in marjoram

Basic element	Biological activity
Mg	called "the basic element of life," regulates muscles and nerves activity, has an anti-stress action, influences vascular system and heart, decreases levels of toxic fraction of chole- sterol (LDL).
Zn	regulates processes occurring in an organism, accelerates wound healing, helps with lowering cholesterol levels, ensu- res proper brain activity, protects from prostate illnesses, strengthens immune system
Cr	lowers insulin demands, protects from diabetes, athero- sclerosis and drops of arterial blood pressure, helps with slimming by reducing excessive appetite
Fe	protects from anaemia, has an impact on muscles formation, increases organism's immunity, stimulates heart functioning as well as physical and mental condition
Cu	protects from anaemia, increases vitality, improves vitamin C activity, protects from stomach ulcers, is active in formation of myelin sheath
Pb	badly affects metabolic processes in organisms and activation processes of selected enzymes, causes lead- poisoning.
Cd	is claimed to be an industrial poisonous agent, with a healthy diet helps maintaining its controlled levels thanks to zinc activity, it is harmful especially for kidneys and liver and causes anaemia.

Yarrow application

Water and alcoholic extracts of yarrow were applied in traditional European medicine for centuries. In country medicine, *Achillea millefolium* was used in treatment of a stomach failure, particularly for long lasting stomach and intenstines' inflammations. It was known and recommended by Saint Hildegard, who wrote "... it prolongs life and brings back a good mood ..." [20]. Its fresh juice or chilled extracts from dried herb were applied to stanch blood release; whereas fresh chopped leaves were used to heal bruises, ulcers and wounds. It was thought that either juice or leaves infusion from this plant, mixed with milk and honey improves general strength. Baths containing herb infusions were advised as a cure for rheumatism and psychical exhaustion [21].

In vitro studies showed that an infusion from *Achillea santolina* has an antioxidant feature [22].

Tested n-hexane extracts from herbs and oils from Achillea gypsicola and *Achillea biebersteinni* showed anti-fungal and herbicidal activity [23].

Dr Czarnowski in his "Zielnik lekarski" (Medical herbarium), published at the beginning of the 20th century, wrote: "leaves before maturation are used usually in springs' treatments against liver, spleen, stomach and intestines failure. It is used also against women' problems, particularly chlorosis, and beginnings of tuberculosis" [24].

The plant could be found on the list of (registered) medicines used nowadays. It is defined as an inhibiting agent against minor bleeding from disrupted capillary vessels in mucosa of gastric tract. Moreover, infusion from the herb has ability to lose smooth muscles of intestines, bial and urine and improves secretion of stomach content. Also, it improves digestion and food acceptance [25].

The juice squeezed from a fresh herb was recommended to drink a few times per day in amount of two water spoons in order to "cleanup the blood" and to improve skin condition [26].

In Sweden young leaves were used as a hop or tobacco substitute [27].

Benedictines from Andechs recommend using leaves of a plant as an additive for salads, soups, sauces, cottage cheese and herbal butter [28].

The herb is used for production of liquor, which consisted of: 5 g of dried herb, 1 dm³ of pure vodka 50% and 20 g of sugar [29].

It is also used in households as food for cattle. Moreover, chopped leaves are mixed with poultry forage in order to remove bugs from their organisms [24]. It is a valuable element, food ingredient in animals' diet [27].

In addition, herbal extract and its oil are used in cosmetics formulas [30]. Zinc, as one of yarrow's microelements, plays a crucial role in a skin inflammation treatment, as lichens and acne. Yarrow herb can be also used in formulas of emulsions and creams for greasy and mixed skin and shampoos for greasy hair and against hair loss. Beauty mask made of the herb has a softening, cleaning, anti-oiling, bleaching and anti-inflammatory effect [31, 32].

Final remarks

Yarrow and its oil have important positions among products of natural origin. Chemical content of the oil makes it particularly useful in formulas of small-scale products. Pharmaceutical and cosmetics industries constantly increase their interest in this field.

Literature

- I. Nemeth E., Essen J.: Oil. Res. 2005, 17, 501-512
- Benedyk B., Rothwangl-Wiltschingg K., Rozema E., Gjoncaj N., Rekinek G., Jurenitsch J., Kopp B. Glasl S.: Pharmazie 2008, 63, 1, 23-26
- 3. Muszyński J.: Farmakognozja. PZWL. Warszawa 1957
- Farmakopea Polska IV. Urząd rejestracji Produktów Leczniczych. Warszawa 1965
- 5. Bocevska M., Sovov´a H.: J. of Supercritical Fluids 2007, 40, 360-367
- Kordowski M., Wysocka-Rumińska A., Tałałaj S., Wiszniewski J.: Rośliny olejkowe i olejki naturalne. PWRiL. Warszawa 1955
- 7. Anton R.: Les Actualités pharmaceutiques 1979, 154, 23-30
- 8. Kohlműnzer S.: Farmakognozja. WL PZWL. Warszawa 1998
- 9. Malinka W.: Zarys chemii kosmetycznej. Volumed. Wrocław 1999.
- Kołodziejczyk A.: Naturalne związki organiczne. WN PWN. Warszawa, 2003
- Rohloff J., Skagen E.B., Steen A.H., Iversen T.-H.: J.Aggric Food Chem. 2000, 48, 6205-6209
- 12. The Merck Index 12th Edition, Whitehouse Stadion NJ, 1996
- 13. Špinarová Š., Petříková K.: Hort. Sci., Prague 2003, 30, 1, 7-13
- Wrzeciono U., Zapruto L.: Chemia związków naturalnych. Akademia Medyczna im. Karola Marcinkowskiego w Poznaniu. Poznań 2001
- Rohloff J., Skagen E.B., Steen A.H., Iversen T.-H.: J.Aggric Food Chem. 2000, 48, 6205-6209
- Aljančić I., Macura S., Juranić N., Andjelković S., Randjelović N., Milosavijević S.: Phytochemistry 1996, 43, 169-171
- Glasl S., Mucami P., Werner I., Presser A. Jurentsch J.: Z. Naturforsch 2002, 57c, 976-982
- Zhu K., Cordeiro M.L., Atienza J., Robinson W., Samson S.A., Jr., Chow A.: Journal of Virology 1999, 73, 3309-3316
- Mehlführer M., Troll K., Jurenitsch J., Auer H., Kubelka W.: Phytochemistry 1997, 44, 1067-1069
- 20. Zioła św. Hildegardy. Wydawnictwo M. Kraków 2000.
- 21. Kuźniewski E., Augustyn-Puziewicz J.: Przyroda apteką. Wyd. Dolnośląskie. Wrocław 2006
- 22. Ardestani A., Yazdanparast R.: Food Chemistry 2007, 104, 21-29
- Kordali S., Cakir A., Akcin T.A., Mete E., Akcin A., Aydin T., Kilic H.: Industrial crops and products 2009, 29, 562–57

- 24. Czarnowski A.: Zielnik lekarski. Wyd. Przewodnik Zdrowia. Berlin 1911
- Podlewski J.K., Chwalibogowska-Podlewska A.: Leki współczesnej terapii. Split Tradin Spółka z o.o. Warszawa 2005
- 26. Gumowska I.: Ziółka i my. Wydawnictwo PTTK "Kraj". Warszawa 1983
- 27. Nowiński M.: Dzieje upraw i roślin leczniczych. PWRiL. Warszawa 1983
- Bilgri A., Adam B.: Zioła w kuchni i aptece. Apteka benedyktynów z Andechs. Wydawnictwo M. Kraków 2004
- 29. Bielowski A.: Nalewki, które leczą. Wydawnictwo Diecezjalne i Drukarnia w Sandomierzu 2008
- 30. Nemeth E., Essent J.: Oil Res. 2005, 17, 501-512
- Jędrzejko K., Kowalczyk B., Balcer B.: Rośliny kosmetyczne. Śląska Akademia Medyczna. Katowice 2006
- Glinka R., Góra J.: Związki naturalne w kosmetyce. Warsaw Voice. Warszawa 2000

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