1. Abstract

Volatile oils are products isolated from plants or their organs through a physical process that have a certain volatility (higher or lower) and have a pleasant smell characteristic of the source from which they come. They are also known as ethereal or essential oils, and usually their name is given by the popular name of the plant from which they are extracted. The most important characteristic of these mixtures, which also confers special economic value, is the specific smell. It is the basis of uses in perfumery, in cosmetics and in the food industry. Many volatile oils have special therapeutic qualities, some of which have been known and used since antiquity. Essential or volatile oils are products of plant secondary metabolism, extracted from flowers, bark, stem, leaves, roots, fruits and other parts of the plant, through different methods. They are complex, heterogeneous mixtures of mono- and sesquiterpenic constituents, but also aromatic compounds.

2. Introduction

There is a wide variety of plants of different shapes, sizes, colors and flavors. Many such plants contain compounds that typically cannot be seen with the naked eye—they are present in the roots, flowers, seeds, bark, or other areas of the plant. These compounds are known as volatile oils (VOs) or essential oils (EOs). They are extremely concentrated, their action being extremely powerful. Also called volatile aromatic compounds, EOs give the plant its own aroma, protect it from environmental conditions and harmful insects, and play an important role in plant pollination [1]. EOs are aromatic extracts from plants or fruit peels that have been used for centuries in traditional medicine for their therapeutic benefits. EOs help to stimulate the nerve centers and the central nervous system, especially having beneficial effects on headaches, to relieve problems with insomnia and to combat fatigue. EOs are these volatile substances that help the body function optimally and improve emotional well-being [2]. Today, EOs are widely used in aromatherapy and natural health care products.

3. Characteristics

VOs are also called EOs or essential oils. These are complex mixtures of aliphatic and aromatic hydrocarbons, acids, aldehydes and alcohols, esters and other constituents, predominating compounds from the terpenoid class. These oils constitute a class of active principles very valuable for the perfumery, food, cosmetic and food industries. The most representative action is the antiseptic one, in addition to the action of being a special natural odorant or aromatizer [3]. Most EOs have a broad spectrum of activity against gram-positive or gram-negative bacteria. In addition to these, VOs have an antiviral, collagen-choleretic, decongestive, cicatrizing, circulation and breathing stimulating action. The most important VOs compounds are terpenes and their derivatives, such as: geraniol in rose and eucalyptus flowers, linalool in lilies of the valley, orange blossoms, citral in orange peel, coriander, borneol and camphor [4]. The composition of EOs, the proportion in which different terpenes are found, depends on the nature of the species, the plant organs, pedoclimatic and agrotechnical factors and the development phase of the respective plant.

3.1. Spread of Volatile Oil-Containing Plant Families

Usually, VOs are found in higher plants (about 50 families) belonging to some orders of angiosperms (Asterales, Apiales, Arales, Laurales, Lamiales, Magnoliidaes, Poales, Rutales, Sapindales, Zingiberales) or gymnosperms (Pinales), but they also know fungi
that produce azulenogenic sesquiterpene lactones (Baziodiomy-
cetes), volatile sesquiterpenes (Ascormycete), or algae that elabo-
rate halogenated sesquiterpenes and Bryophytae specialized in the
biosynthesis of sesquiterpene lactones compounds [5]. Although
terpenic compounds are characteristic of the plant kingdom, some
monoterpenes biosynthesized by soil bacteria (bornyl acetate, geo-
smina), by insects, as well as some sesqui- and diterpenes of animal
origin (Celentera, Spongierae) have been reported. Aromatic plants
are those species that contain a larger amount of VOs (at least 0.1-
0.2%), which have a sufficiently perceptible smell or which lend
themselves to profitable economic exploitation. Apart from these,
there are other species that, although they do not have a character-
istic smell, loved perfumes and scented oils, which they used in
massage or to perfume their hair or clothes [6]. Their knowledge of
the healing properties of the slopes spread throughout the empire.
In the Middle Ages, lavender and other herbs, caught in a bouquet,
were used as protection against the plague.

3.2. Location

The synthesis and accumulation of VOs either outside the plant,
in glandular hairs (Asteraceae, Geraniaceae, Lamiaceae, Moraceae)
and papillae (Rosa sp.), or inside it, in secretory cells (Araceae,
Lauraceae, Magnoliaceae, Pieperaceae, Zingiberaceae), in inter-
cellular spaces of schizogenous or schizolysigenous origin, respec-
tively in secretory channels (Abietaceae, Apiaceae) or in secretory
bags. VOs can accumulate in all plant organs, but in different quan-
tities [7]. Thus, we find them in: roots, rhizomes, leaves, flowers,
seeds, in the wood of the stems or in the bark. Although all organs
of a species may contain VOs, its composition varies according to
the organ in which it is found [8]. For example, from Citrus
aurantium L. Ssp. Aurantium known under the popular name of
bitter orange (Rutaceae) can be obtained three kinds of VOs: the
essence of Curacao (Aurantii aetheroleum), by pressing the fresh
pericarp; Neroli essence (Neroli aetheroleum), by steam distilla-
tion of immature flowers; bitter orange essence, by steam distilla-
tion of leaves, branches and fresh unripe fruits. The VOs content of
plants is mostly below 1%, rarely reaching 15% or even more [9].

4. Physical-Chemical Properties

4.1. Physical Properties

VOs are liquid substances with an aromatic and pleasant smell.
Due to the rising vapor pressure, they give azeotropic mixtures
with water vapor and distill at much lower temperatures. They are
generally colorless, but there are also colored VOs: in reddish (cin-
namon VOs), in blue (chamomile VOs), in green (absinthe VOs).
VOs boil at temperatures between 150-300°C and are lighter than
water. Exceptions to this are cinnamon, bitter almond and clove
oils, which are heavier than water [10].

They are soluble in organic solvents, in alcohol, in fixed oils, insolu-
ble in water, soluble in 60% hydrochloride solution, but are good
lipophilic solvents. VOs are flammable substances, their smell is
sometimes irritating, although aromatic, and the taste is burning.
VOs penetrate through the skin. Being soluble in the lipid layer of
the skin, they very quickly cross the external layers and quickly
enter the blood. For example, by applying them in large doses to
the skin of mice or rats, they immediately cause their death. In
smaller doses, they cause depression or excitement [11].

In the Romanian Pharmacopoeia 10th edition, VOs are described
as clear liquids, in most cases, colorless or colored with an aromatic
smell, usually characteristic of the main component and with a
burning taste. At low temperatures, certain VOs deposit crystals,
which redissolve with slight heating and in air and light change
their physical properties.

4.2. Chemical Properties

Depending on its components, each essential oil has specific
dehuming properties. Oils stored in the light generally brown due
to photo-chemical oxidation reactions. Their oxidizability is ex-
plained by the existence of double bonds as well as oxydryl and
carbonyl functions grafted on the chain or on the basic nucleus.
As a result, some of the oil components easily pass into macromo-
elar condensation compounds. Due to the concentrated sulfuric
acid, intense colors appear.

The composition of VOs is influenced by several factors, such as:
harvest period, demographic region, climate, storage period, ex-
traction method, drying conditions, analysis methods. Most stud-
ies have shown that it is the geographical region that influences the
VOs content [12].

4.3. Chemical Composition

Almost all VOs belong to the terpenoid class. For certain particu-
larities represented by each substance included in this group, they
are all called terpenoids, but the term terpene is usually given only
to compounds with 10 carbon atoms.

A series of terpenoids, such as carotenoids, resinic acids, triterp-
enic acids or saponosides, are not included in the group of VOs
due to their high molecular weight, solid state of aggregation and
therefore lack of volatility [13].

Only monoterpenes and some sesquiterpenes are constituents of
VOs. Apart from this, the category of VOs also includes a series of
aromatic combinations, trainable with water vapors, with a pleas-
ant smell, of biogenetic origin either from acetyl coenzyme A, but
also of phenyl-propanoic origin.

Monoterpenes are the most quantitatively representative com-
ounds in the composition of all VOs, constituting secondary
products resulting from the activity of secondary metabolism [14].

These are compounds with 10 carbon atoms in the molecule and
are made up of the following groups:

- Hydrocarbons: acyclic (myrcene, ocimene), monocyclic (cy-
mene), bicyclic (pinene);
- Alcohols: linalool (lavender, coriander), geraniol (orange), farne-
sol (ylang-ylang), menthol (mint), borneol (rosemary, pine);
• Aldehydes: citronellal (cinnamon, lemon);
• Ketones: carvone (cumin, anise, mint), camphor (camphor, cinnamon, sage), menthona (mint);
• Esters: terpenyl acetate (pine), bornyl acetate (rosemary);
• Ethers: anethole (dill, anise), apiol (parsley);
• Peroxides: ascaridol;
• Phenols: thymol (thyme), carvacrol (mint, raindrop) [15].

Sesquiterpenes are made up of 3 isoprene units (15 carbon atoms). The increase in the chain also causes an increase in the number of chemical structures. They are made up of functional groups similar to monoterpenes:
• Azulene: guaiazulene (guaiacol), camazulene (chamomile, mouse tail);
• Alcohols: bisabolol (chamomile), farnesol (lemon, rose);
• Ketones: turmerone (turmeric) [16].

4.4. Aromatic Components
In the composition of VOs, there are also some substances with an aromatic structure, which, in addition to their pleasant smell, also have the property of being entrainable with water vapor. From a biogenetic point of view, VOs are of terpenoid or phenyl-propanic origin. The aromatic components comprise the following functional groups:
• Aldehydes: cinnamic aldehyde (cinnamon);
• Phenols: eugenol (cinnamon, dill);
• Alcohols: cinnamic alcohol (cinnamon) [17].

Due to the diversity of substances that make up VOs, there are several classification criteria that reflect the structure and property of the components, namely:
• According to the number of carbon atoms in the molecule: terpenes 10C, sesquiterpenes 15C, diterpenes 20C, triterpenes 30C;
• By the functions grafted onto the basic nucleus: hydrocarbons, alcohols, aldehydes, ketones, acids, compounds with mixed functions;
• According to the shape of the molecule: acyclic, monocyclic, bicyclic and tricyclic [18].

4.5. Classification of Volatile Oils
According to the degree of volatility, oils are classified as follows:
• Highly volatile - they evaporate the fastest, have a stimulating effect, are quickly absorbed, have a strong smell, are not persistent;
• Medium volatile - they last about 2-3 hours before evaporating, they have an effect on the organs;
• Weakly volatile- have the lowest degree of volatility, evaporate very hard, have a relaxing effect, are persistent [19].

4.6. Obtaining Volatile Oils
Like vegetable oils, VOs are extracted from those parts of the plant where large amounts are present, for example:
• Flowers - roses, tuberoses, jasmine;
• Flowers and leaves - mint, geranium, violets;
• Fruits - coriander, fennel, anise;
• Seeds - ambrette, nutmeg;
• Fruit peel - orange, lemons;
• Roots - ginger, angelica;
• Wood or bark - canthal, cinnamon, cedar;
• Flower buds and buds - currant, poplar, cloves;
• Whole plant - sage, basil, thyme;
• Needles and branches - fir, pine [20].

In certain cases, the odorous substances are extracted from the natural or pathological exudates of plants (balms, resins, oleogumiresins, gumiresins). In general, all the organs of the plant contain the same oil, but there are small exceptions. For example, in this sense, the cinnamon tree and the bitter orange. The cinnamon tree produces three types of VOs: an oil rich in eugenol (in the leaves), an oil whose major component is cinnamic aldehyde (in the bark), and an oil rich in camphor (in the root). From the bitter orange are extracted: neroli oil and absolute (from the flowers), orange oil (from the peel of the fruit), and petitgrain bigarde oil (from leaves, young branches and unripe fruit) [21].

The methods of extracting VOs from vegetable products are based on their physico-chemical properties, especially the high vapor pressure and solubility in non-aqueous volatile solvents and fatty substances. Like vegetable oils, VOs are extracted from the parts of the plant that present larger amounts. Obtaining VOs requires compliance with a number of conditions without which the oil quality required by the regulations cannot be reached. The harvesting of plant material must be done with great care so as not to be contaminated with parts or remains of other species. Plant material that undergoes hydrodistillation is not always processed immediately after harvesting. Due to some chemical and morphological changes, as a result of the action of air and heating due to settling in piles, which favors fermentation, a lower quality oil is obtained. In the case of drying the plant material before processing, it can cause the appearance of some interested olfactory constituents under certain conditions. The process of obtaining VOs (technological process) has a decisive influence on their quality and composition. The products subject to extraction can be both fresh and dry, whole or fragmented (leaves, herbs), crushed (underground organs) or in the form of sawdust (wood) [22].

The choice of the appropriate extraction method is made depending on the amount of VOs in the vegetable product, its location and its physico-chemical properties. For example, vegetable products
with a high content of VOs (pericarp of citrus fruits) can undergo pressing.

For vegetable products with medium content of VOs, distillation or entrainment with water vapor is preferred, and for those with low content of VOs, extraction with volatile solvent or lipophilic substances is used. VOs containing easily degradable principles are extracted cold.

Heating (especially direct heating) favors the carbonization of the vegetable product and the formation of volatile compounds, which reduce the quality of the oil [23].

The main extraction processes are:

• Distillation with water vapor in an open circuit;
• Distillation in a closed circuit;
• Water vapor training;
• Extraction with apolar volatile solvents.

4.7. Open Circuit Steam Distillation

It is the simplest method of extracting VOs. The principle of the method consists in boiling the chopped vegetable product with water (brought to the distillation vessel together with the water) and distilling the VOs together with it. From the hydrodistillate (VOs/water dispersion), the VOs separates either by itself, sometimes requiring a rest of 24-48 hours, the collection being carried out in Florentine vessels, or by salting with sodium chloride (which increases the density of the medium of dispersion and accelerates the separation of the VOs), followed by extraction with apolar solvent. Florentine vessels are containers with a side tube in the lower or upper part, as the oils have a supra- or sub-unit density. Although it is a simple method, it presents a series of disadvantages, which negatively influence the quality of the VOs. In addition to the volatile compounds formed through possible carbonization, due to the high temperature, esters can hydrolyze, hydrocarbons can cyclize, alcohols, aldehydes and ketones can oxidize. Also, isomerizations and racemizations can occur or other volatile compounds (coumarins) can be produced, which are not among the constituents of the VOs [24].

4.8. Closed Circuit Distillation (Neo-Clevenger apparatus)

This process allows the direct obtaining of the VOs. In the case of VOs that are viscous or denser than water, their collection can be done in a non-volatile non-polar solvent with low density (xylene, toluene). The method can also be used to determine the VOs content of vegetable products.

Entrainment with water vapor consists in passing the water vapor obtained in a generator, over the chopped plant product, placed in a heated container.

A hydrodistillate is obtained, from which the VOs (higher in quality than that obtained by distillation) is separated according to the techniques presented for steam distillation or by centrifugation or by other processes (cohabation). The cohabation consists in the repeated distillation of the hydrodistillates until the separation of the VOs. Other times the hydrodistillates can be brought into the steam generator to be used in a new steam drive [25]. Extraction with non-polar volatile solvents is used in the case of vegetable products with low content of VOs or when it is easily altered. The solvents currently used are aliphatic hydrocarbons (petroleum ether, hexane, but also propane or liquid butane) or aromatic (benzene), sometimes halogenated (chlorinated or fluorinated) derivatives of methane and ethane. Ethanol is used for purification. The choice of the solvent is made according to the technical and economic parameters: selectivity, stability, chemical inertness, boiling temperature (it should not be too high, to be easily removed from the oil, nor too low, to avoid losses and high costs), safe handling (non-toxic and non-flammable as possible). The use of solvents with a low boiling point avoids the degradation induced by the presence of water and acidic pH, or other possible changes in the constituents of the VOs that harm the quality. The disadvantage of these processes is the lack of selectivity, along with the VOs, other lipophilic compounds are extracted (fatty substances, phospholipids, carotenoids, resins, alkaloids, aglycones, etc.). Soxhlet apparatus or reflux apparatus can be used as laboratory apparatus. In the industry, stainless steel extractors equipped with a heating mantle, an extract exhaust valve, a cover for the access of the plant material, a basket made of wire mesh where the plant product packed in cloth bags are brought, a system for introducing and distributing the solvent are used and another for exhausting the vapors towards the refrigerant. Extraction can be simple, multiple or countercurrent [26].

5. Mechanical Methods of Obtaining Volatile Oils

5.1. By Squeezing

Fresh fruits, cut into two or three parts, are cored. The remaining peel is squeezed over a bowl containing a sponge. As the sponge soaks, it is squeezed into a collecting vessel. Along with the VOs, a part of the cell juice also passes during squeezing. After collection the aqueous liquid is allowed to separate and the oil is decanted [27].

5.2. By Erasing

Scrape the surface of the fruit with a needle grater or rotate one or two fruits in a spiked funnel, or in a cylindrical vessel whose bottom is covered with short spikes arranged in concentric circles. The spikes must be of adequate size so as to pierce only the oil glands, because penetrating too deeply into the pericarp of the fruit increases the amount of cell fluid, which will decrease the quality of the VOs [28].

5.3. By Pressing

In this case hand presses or hydraulic presses are used. The highest yield is given by hydraulic presses, but the best quality is given by the manual process [29].
5.4. Modern methods of Obtaining Volatile Oils

Ultrasound-assisted extraction includes two types of physical phenomena: diffusion through the cell wall and shedding of cell contents once the cell wall has been broken. Both phenomena are significantly influenced by ultrasound. Microwave Assisted Extraction: Microwaves are absorbed by the plant material, their energy causing a sudden increase in temperature within the glandular system.

The temperature is kept high until the internal pressure exceeds the expansion capacity of the cell wall, causing it to break and release or dissolve the odorant substances in the solvent. The plant material is separated by filtration and the filtered solution is pretreated to obtain the VOs [30].

The advantages of modern methods compared to traditional extraction procedures are:
- Short extraction time (30 min compared to 3-4 hours for hydrodistillation extraction);
- Lower energy consumption (0.25 KW compared to 4.5 KW in the case of hydrodistillation);
- The amount of CO2 removed into the atmosphere is lower (200 g CO2 per gram of VOs compared to 3600 g CO2 per gram of VOs in hydrodistillation) [31].

5.5. Fermentative Methods

These methods are applied to obtain unreformed VOs that are found in plants in the form of glycosides. The glycosides are first separated, by fermentation, with the help of enzymes that are usually found in the same plant. The plant material is shredded and mixed with water. A small part is kept and the rest is heated to 70-80°C to dissolve the glycosides when, at the same time, the enzymes are inactivated. To determine the fermentation, add the unheated part containing enzymes in an active state, then leave some time for fermentation. The VOs set free, by this enzymatic pathway, is trained by distilling the mixture, thus obtaining the essence of mustard, the essence of bitter almonds and the essence of wintergreen [32]. VOs are sensitive to the effects of light, heat, oxygen and moisture [33]. It is recommended that they be stored in dark bottles, out of direct sunlight and kept at or below room temperature. The cap of the bottle must be tightly closed, because VOs are substances that evaporate quickly [34]. Blends of VOs can be stored in similar bottles.

6. Conclusion

VOs constitute a class of active principles particularly valuable for the perfumery, cosmetic, pharmaceutical and food industries. Different studies have shown that VOs can have beneficial effects on the human body, but we must be careful what kind of VOs we use because not all oils are beneficial to our body, causing various health problems. VOs act strongly, directly on the target being true plant essences, they increase resistance to harmful factors in the environment and to epidemics. She retains their antimicrobial action even if they are administered repeatedly to the same person (we do not become resistant to their therapeutic action). If administered correctly according to the specialist’s recommendation, VOs are free from side effects.

References


