Clove Oil - Properties and Applications

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Introduction

Both, cloves and clove oil have been known and used in Babylon, Assyria, Egypt, Greece and China, for centuries. Cloves were imported to Europe from Maluku Island (historically known as *The Spice Island* already in the fourth century. Because of the price, they were kept in golden basket, like treasures. In Poland in cosmetic recipes included in so-called *Zielnik Falimirza,* which was first published in 16th century, they are called Goździki. The Latin name of carnations, cariophyllum, comes from Greek and means " a flake of coconut" [1].

Clove *Eugenia Caryophyllata*

Plants of the genus Eugenia (Syzygium), comprising of about 100 species, grow in tropical climate. Clove (*Eugenia caryophyllata*) is a high (up to 15 m), evergreen tree of the family Myrtacae. It blooms twice a year, it yields for 60 years, and bears first fruits at the 6÷10 years of age. Its fruits are edible and are used frequently to make spices. From the fifteen -year -old plants about 2 up to 4 kg of cloves can be obtained annually. Large spreading plants provide even 50 kg of dry cloves. Carnations, used as spices, are undeveloped buds. Cloves are harvested just before blooming, during the period from August to February, because at that time they contain the most considerable amount of oil. Buds reach the length of 10-18 mm, after drying they become dark brown. Whole cloves can be stored up to 24 months. Annual production of cloves in the world can reach several thousand tons [2, 3].

Cloves have a strong, kind, pleasant aroma, similar to the flower of the same name, and an urgently - biting taste very often causing numbness of the lips.

The raw material is rich in essential oil obtained from flower –buds. Under the skin there are ellipsoidal oil tanks. When squeezed the clove stem oil is released , while rubbing on a paper sheet an oily stain is formed, that disappears after heating up [2,3].

Carnations not only consist of volatile oil. They also contain 12-14% of tannin, mucous compounds, caryophyllene (natural bicyclic sesquiterpene), oleanolic acid and eugenin [3, 4].

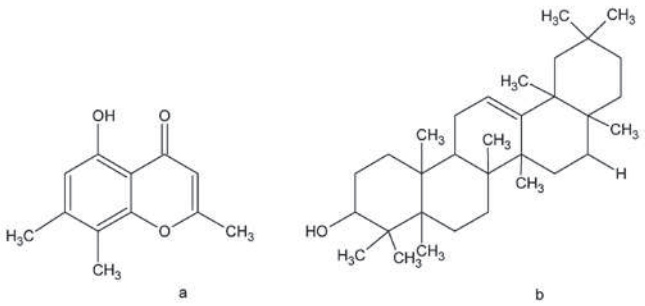

Fig. 1. a– Eugenin, b - Oleanolic Acid

Preparation of Clove Oil

Clove oil (Oleum caryophylli) was initially received by a German chemist Cordus Valerius, who lived in the first half of the sixteenth century. Since that time, it can be purchased at pharmacies [5].

Clove oil is extracted from the *Syzygium aromaticum*. The raw material includes leaves and buds of plants. The quality of the oil depends on the origin and maturity of the buds, and the method of preparation. To produce the clove oil less valuable, contaminated or damaged cloves are needed. The best raw material is derived from cloves Maluku Islands, then to Zanzibar, Singapore, and the worst are those derived from Antilles and Guyana. After fragmentation Caryophyllales buds are carried out by steam distillation, which lasts from 8 to 24 hours. Cohobation and re-distillation of water increases the efficiency of the process, which is about 18% [2, 6]. Clove oil is also obtained by the hydrodistillation using the *Clevenger* apparatus. Within 4 hours of distillation efficiency reaches 5%. The obtained oil is dried with anhydrous sodium sulfate [7].

Clove oil can also be obtained by extraction with ethanol and carbon dioxide in a supercritical fluid state. Supercritical Fluid Extraction (SFE) leads to the receipt high-quality essential oils, where the maximum content of the main ingredient, eugenol is 58.77% [8]. The yield of this process is 19.56% [8].

Oil which is extracted from the twigs is relatively cheaper than oil produced from buds, leaves and shoots Caryophyllales, which are more accessible. As a result of steam distillation of (18÷24h), twigs, leaves and shoots Caryophyllales clove oil is obtained with a yield of 1.5 - 3%. The oil is dark brown, has a less pleasant odor than the oil from buds and has a woody spicy fragrance [2, 9].

Oil from the dried stalks Caryophyllales is also commercially available. Obtained with a yield of about 5%. Clove oil is colorless or pale yellow and darkens during storage. It is heavier than water and is characterized by persistent intense spicy scent and bitter, burning taste. Its composition is similar to the composition of the oil from the leaves. Eugenol and eugenol acetate are responsible for the smell of cloves (spicy, sweet with a hint of balsamic-fruit). Vanillin (deepening spicy character), caryophyllene and its derivatives (note of the wood and green) and trace amounts of cresols, guaiacol and methyl guaiacol (phenolic pungent odor) also affect the smell of clove oil [2].

Physic-chemical properties of clove oil, depending on the place of origin and plant parts from which it was obtained are given in the Table 1 [2].

Table 1

Physic-chemical properties of clove oil [2]

Parameter	Oil from buds (Zanzibar)	Oil from the buds (Madagascar)	Oil from the stalks	Oil from the leaves (Madagascar)
Density d_{20}, g/cm³	1.05	1.05	1.040 – 1.067	1.046 – 1.053
Refraction coeff. n_D^{20}	1.53	1.53	1.531 – 1.538	1.533 – 1.535
Rotation α_D^{20}	–0°32'	–0°25'	–1°30'	–1°20' do –0°49'
Content of phenols, %	91	93	83 – 95	86 – 90

The annual world production amounts to tens of tons of oil. It is obtained in Indonesia, Madagascar, Brazil, Tanzania, Sri Lanka, UK and USA.

Clove oil from the buds may be distorted by the addition of the terpenes obtained during the isolation of eugenol from oil or other oils.

The greater number of these compounds increases the optical rotation of the test substance, lowers specific gravity, refraction coefficient and eugenol content. The value of clove oil can be checked by examining the content of phenols - especially eugenol [10].

Composition of Clove Oil

Composition of clove oil altogether with its properties, depends on the origin of the plant, its growing season, the weather, time of day and air humidity. Another essential factor is the time which passes between the moment of picking up the raw material, and the production of oil. There are more than 100 components of clove oil worldwide.

Table 2 shows the composition of clove oil, depending on country of origin of raw material [2].

Table 2

Composition of clove oil, depending on the origin of raw material [2]

Component	Content, %					
	Madagascar	Zanzibar	Indonesia	Indie	Comores	Europe*
Heptan-2-one	0.01	0.01	0.05	0.05	0.03	tr
α-Kopean + α-Ilangen	0.08	0.29	1.70	0.84	0.08	tr
Caryophyllene	0.08	0.29	1.70	0.84	0.08	tr
α-Humulen	0.47	0.52	2.10	1.06	0.44	1.40
δ-Kadinen	0.19	0.33	5.30	0.54	0.18	tr
Kalamenen	0.30	0.20	0.49	tr	1.14	tr
Eugenol	73.80	70.00	36.00	77.13	63.80	84.80
Eugenol acetate	14.20	11.00	11.70	5.04	21.80	0.30

* = commercial
tr = trace amounts only

The main component of clove oil - eugenol was identified by Bonastre in 1826. Eugenol in essential oil reaches from 30 to 95%, whereas eugenol acetate content amounts up to 22%. Oil from the growing leaves contains the smallest amount of eugenol (28%). The amount of eugenol increases to 95% as the leaves ripen, and content of eugenol acetate decreases from 51 to 1%.

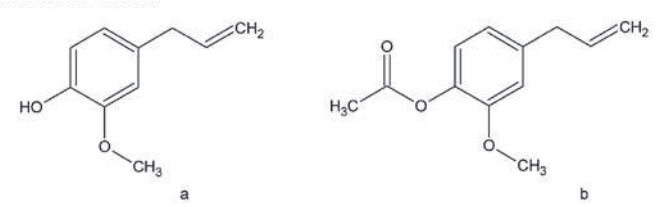

Fig. 2. Eugenol and eugenol acetate

Caryophyllene, α-Kopan, α-ilangen, humulen, kalamenen and heptane-2-one are present in smaller amounts in the oil.

Table 3 shows how the amounts of the major components of oil change, depending on

Table 3

Composition of clove oil, depending on the part of the plant and its growing period [2]

Component	Content, %				
	Oil from buds – development of plants			Oil from stalks	Oil from leaves
	2 months	3 months	4 months		
Heptan-2-one	0.13	0.09	0.05	0.05	0.03
Caryophyllene	7.22	7.59	6.18	6.57	6.42
α-Humulen	1.24	1.44	1.06	1.53	1.39
δ-Kadinen	0.31	0.44	0.54	0.63	śl.
Eugenol	59.14	60.82	77.13	80.19	80.97
Eugenol acetate	24.59	16.71	5.04	0.44	śl.

An important component of the oil, although present in small quantities, is vanillin aldehyde 4-hydroxy-3-methoxybenzoic, one of the most popular fragrance compounds.

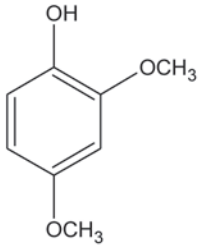

Fig. 3. Vanillin

Vanillin is a crystalline substance in the form of colorless needles or crystalline powder, white to yellowish, with a melting point 80-81°C and boiling point 284-285 ° C. Its strong aroma is perceptible at a concentration of 2x10-13 g/dm3 air. Both natural and synthetic vanillin is widely used in food industry. Vanillin can cause skin irritation especially among people with sensitive skin [6,11].

Use of Clove Oil

The use of clove oil is now similar to those centuries ago. Historically, carnations, as a spice, used to help overcome indigestion. The oil, on the other hand, was used to lessen the toothache. Saint Hildegard wrote in her work *Physica* about cloves: "Who has the pain that roars in his head as if he were deaf, should often eat the cloves ...". Cloves are also recommended for toothaches [12]. Their bactericidal activity was used in the Middle Ages during the prevailing diseases. It was believed that cloves prevent contagion during epidemics of plague [2].

Nowadays the clove oil, an important natural antibacterial drug, is used in many fields, including dentistry, pharmaceuticals, and aromatherapy. It is used as an analgesic, antiseptic, warming, disinfectant, and antibacterial because it inhibits the growth or kills most pathogens, such as: E.scherichia coli, Mycobacterium phlei, Bacillus substilis, Streptococcus aureus, Aspergillus niger, Penicillum chrysogenum. Oil is recommended for inhalation in the treatment of sore throat, colds, catarrh and inflammation of the mucous membranes of the mouth. It is also helps deal with any breathing problems, general weakness and neuralgia [2, 13, 14].

Clove oil also has antioxidant effects (2). Aqueous and alcoholic extract of Turkish clove has been studied. Aqueous extracts oil at concentrations of 20, 40 and 60 g / mol showed inhibition of lipid per oxidation of linoleic acid in emulsion within the limits of 93.3-97.9%, while alcoholic extracts of the same concentrations shows inhibition between 94.9-98.2%. The obtained results make it possible to use cloves as a convenient and accessible source of natural antioxidants in food supplements and pharmaceutical preparations [2, 15].

Clove oil has anticonvulsant effects as well, which were already known in Persian folk medicine. The cloves were there used as a cure for epilepsy. This has been described by an Arab physician Avicenna who lived in the late tenth and eleventh century. Research was carried out to evaluate anti-stress activity of eugenol, the main component of clove oil. It was performed on mice. Specified for oil LD50 = 0.64 (0.39-1.22) cm^3/kg [7].

Thanks to its characteristics, oil is an ingredient of many pharmaceutical preparations, ointments and painkillers. It is also a substrate for the production of dental analgesic preparations. In combination with zinc oxide is used to fill cavities in teeth. In addition, clove oil is included in mouthwash and gum liquids, toothpastes, and preparations for disinfection of hands. Eugenol is also widely used in dentistry. Zinc-eugenol paste is a good zinc-eugenol paste for the

filling of dental canals in treating periodontitis. Furthermore, the paste acts antiseptic, local anesthetic and is resistant to moisture [5,13,16].

Moreover, due to its activity the oil is widely used in aromatherapy. Massages and baths relieve various muscular and rheumatic pains, help with digestion problems, nausea and flatulence [2, 17]. However, clove oil can cause skin irritation and allergic reactions. It cannot be applied directly to the skin neither dissolved in vegetable oil nor in massage oil [13]. It is also an important component of perfume products, especially those with an oriental flavor. It is also used for perfuming soaps [2].

In aromatherapy there is a risk of undesirable side effects , such as irritation, contact allergy and phytotoxic reactions. Permissible concentration of the components (expressed in percent) of clove oil included in the products which are applied topically both in contact with human skin and removed from it are as follows [18]: isoeugenol -0.02 and eugenol - 0.50.

Clove oil boosts concentration and efficiency of thinking. In addition, revitalizes, energizes, exhibits analgesic and acts as an "aphrodisiac" [19, 20]. It is also used as a good air refreshener. It is recommended to mix it with essential oils of basil, citrus and spices [21].

Both, cloves and clove oil have been applied to the food industry. For centuries, cloves were used in the kitchen and unsurprisingly it is one of the oldest spices in the world. The descriptions of the annual gala dinner the professors from the Jagiellonian University used to have in the sixteenth century report that various meats were richly seasoned with cloves, among others [22].

Carnations are valued for the original flavor, make the taste of food products spicy. They are in many herbal blends such as curry. Carnations are an addition to marinades, mulled wine, beer, fruit sauces and compotes. Sugar confectionery, liquors, meat, sauces, etc., are flavored with clove oil too [23].

Clove and cinnamon oil acts as a natural preservative. It is a harmless component of food products. The mixture of these oils (1:1) inhibits the growth of mold, yeast and microbes. Probably their ingredients such as cinnamic aldehyde and eugenol, damage the cell walls of bacteria. Such properties can be used for storage of food products. Clove oil can also be used as an antioxidant and antimicrobial addition to oils, such as cotton oil. Addition of oil does not affect the color and appearance of cotton seed oil, in concentrations of 50 - 1200 ppm does not change its smell either [14, 24].

Antifungal action of clove oil and eugenol were also used in the food industry. Products may be contaminated with microorganisms during harvesting, technological process and storage of food. Since ancient times, in order to inhibit the growth of fungi gaped and spices were used, they also including cloves [25]. Effects of oil on Aspergillus flavus (a kind of widespread fungi) which can produce potentially carcinogenic aflatoxin, has been studied. The medium was the tomato purée. Studies have shown that the use of oil in quantities necessary to achieve the antifungal effect has a bad influence on the organoleptic properties of tomato puree (taste). This disadvantage can be avoided by applying oil to products with a strong taste that camouflage a clove flavor or adding only the active ingredients of essential oil [26]. Fungus Penicillium Citrinum can produce mycotoxins (citrinin) causing kidney damage and bleeding [27]. Citrate may appear in dairy products. Therefore, oil and eugenol was tested as an inhibitor of the development of Penicillium citrinum, during the production of regional cheese manufactured in the Spanish province of Galicia from unpasteurized milk in the presence of animal rennet [28].

Isolated from the essential components of the so-called isolates are also used in the food industry. Eugenol and isoeugenol is derived from clove oil. Properties of the two isolates are shown in Table 4 [6].

Table 4

Properties of isolates obtained from clove oil

Isolat	Taste	Fragrance	Form	Refraction coeff. n_D^{20}
Eugenol	scorching	clove	colorless, yellowish liquid	1.5400*
Isoeugenol	-	clove	pale yellow viscous liquid	1.5745*

* approximate size

Anesthetic properties of clove oil may also find practical use as a substance blocking and reducing stress and pain of living organisms such as fish during their studies (including the measurement of length and weight). The use of oil in such studies is effective. There was no mortality of fish observed. In addition, oil is a local and not expensive product in countries such as Indonesia. For studies of coral reefs essential oil concentration should be carefully selected and solvent should be also reasonably used, since they may have a negative impact on corals (e.g. Pocillopora verrucosa) - fading, inhibition of growth. The measures used in biological research should be characterized by rapid and short duration of action of the body to return to the normal state. Furthermore, it should be characterized by lack of toxicity of both, the test organism and the investigator, no adverse effects with repeated use, ease of use and low price [30].

Clove oil is also used for production of deodorizing and preparations acting as a deterrent for mosquitoes [2, 13].

Another area in which essential oils were applied (including clove) is painting. They are used here to dilute the paint, as a binder in oil painting [31].

Studies on the clove oil with stalks as fuel additive for diesel engines were interesting. Oil decreased the ignition temperature of fuel, which allows for its safe storage and transport, but such modifications of fuel, due to the price of oil, are not profitable [32].

Summary

Cloves and clove oil are significant components of natural resources. Eugenol, the most important part of them, representing the largest quantities, determines their properties. A widespread interest in these materials has been observed worldwide for ages. Due to the well-known use and benefits of clove oil the major beneficiaries of it is the food, cosmetics and pharmaceutics industry which constantly uses it in technology of medicine production.

Translation into English by the Author

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