

Freshwater *Cladophora glomerata* as a new potential cosmetic raw material

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Introduction

Currently, algae and their extracts are one of the most commonly used natural cosmetic raw materials [1]. This is due to the presence of biologically active compounds in their thalli such as carbohydrates, fatty acids, and polyphenols, which determines the multidirectional algae cosmetics to the skin. The cosmetic market is dominated by preparations containing marine algae. Generally, there are produced only cosmetics with marine species of algae, such as: *Laminaria ochroleuca*, *Fucus vesiculosus*, *Ulva lactuca*, *Chondrus crispus*, *Corallina officinalis*. This algae are applied to almost every types of cosmetic products: creams, masks, balms, shampoos, shower gels, as well as make-up cosmetics and make-up removers [2].

Cladophora glomerata is a filamentous green macroalga with a typically branched thalli (Photo 1) [3]. Algae from the genus *Cladophora* occur both in marine and in freshwater habitat. *Cladophora glomerata* is a cosmopolitan species mass occurring in Polish inland waters in the form of free-floating mats on the water [4]. So far, researchers have mainly focused on studies on marine species of the genus *Cladophora* to determine biologically active compounds in them [5 – 7]. It turned out, that these algae contain such bioactives as: saturated and unsaturated fatty acids [5], sterols, terpenoids [6], as well as phenolic compounds [7]. On the other hand, a few research have been conducted on the freshwater *Cladophora* and its application as a natural source of bioactive substances [8 – 10]. Hence, it is worth to continue studies on the new direction of research on freshwater algae as a potential cosmetic raw materials.

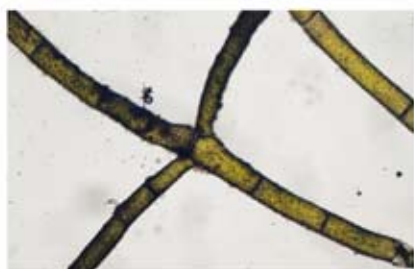


Photo 1. Branched thallus of *Cladophora glomerata* (photography made with a light microscope Zeiss Axioskop 2 MOT; author: Marta Pikosz)

Bioactive compounds in freshwater *Cladophora glomerata*

It turns out, that also freshwater algae may be a source of bioactive compounds next to marine algae commonly used in cosmetology. The freshwater algae from the genus *Cladophora* are characterized by a high amount of such macroelements as: calcium, potassium and phosphorus, as well as the following microelements: magnesium, iron and zinc [8]. Each of these elements function in separate way in cosmetics and is responsible for the proper conduct of metabolic processes in the skin. Calcium is an element of antiallergic and anti-inflammatory activity. Potassium is involved in water management body, in maintenance

of normal osmotic pressure and acid-base balance. Afterwards, the phosphorus is a component of coenzymes, phospholipids and nucleic acids. Of these macroelements magnesium is a dominant element in freshwater *Cladophora*, which strengthens the walls of blood vessels, activates numerous enzymes and is involved in the biosynthesis of urea. Magnesium deficiency accelerates skin aging. Iron in cosmetics regenerates the skin, detoxifies the skin cells, strengthens hair and nails. The presence of zinc in algae determines the anti-inflammatory, antiseborrhoeic and anti-virus activities. Zinc is used to treat acne, herpes, and various types of skin irritation [11, 12].

One important group of biologically active compounds occurring in the freshwater *Cladophora glomerata* are saturated and unsaturated fatty acids included in the group of lipids or lipophilic substances. They are aliphatic lipophilic monocarboxylic acids containing respectively saturated bonds (saturated fatty acids) or at least one double bond in the carbon chain (unsaturated fatty acids) [13]. The dominant saturated fatty acid in the freshwater *Cladophora glomerata* is palmitic acid (C16:0), and between others saturated fatty acids there have been detected such acids as: miristic (C14:0), pentadecanoic (C15:0), stearic (C18:0) and arachidic (C20:0). It turned out, that *Cladophora glomerata* is also a source of a number of unsaturated acids, such as: tetradecatrienoic (C14:3), tetradecatetraenoic (C14:4), 9-hexadecaenoic (C16:1), hexadecadienoic (C16:2), 6,10,14-hexadecatrienoic (C16:3), heptadecatrienoic (C17:3), linoleic (C18:2) and eicosahexaenoic (C20:6) [14]. Fatty acids have many important functions in cosmetics. In particular unsaturated fatty acids, and among them essential fatty acids (EFAs), are characterized by good effects on the skin. They act as emollients, or substance covering the skin with a thin hydrophobic layer (they create hydro-lipid coat of the epidermis), which protects against excessive loss of water, and thus protects against dehydration and exfoliation of the skin, loss of elasticity and hydration. Moreover, fatty acids have antiallergic and anti-inflammatory properties, they regulate the metabolism of the skin, they are involved in the production of sebum and eicosanoids. These compounds also have building functions, because they are a part of cell membranes, intercellular cement and ceramides. Various properties of saturated and unsaturated fatty acids cause that they are used both as components of cosmetics for dry and sensitive skin as they protect the skin against infection and loss of moisture, as well as they are used in preparations for oily and combination skin because they can normalize skin metabolism by improving the lipid barrier of the epidermis keratinization and regulation processes. In addition, fatty acids by protecting skin from drying out and from unfavorable external factors ensure an adequate level of hydration and elasticity, and therefore act as anti-aging and anti-wrinkle ingredients. Palmitic acid present in large quantities in *Cladophora glomerata* is used in cosmetics as emulsifier, and its derivative – ascorbyl palmitate is a common antioxidant. Very valuable acid present in the algae is linoleic acid (Fig. 1) that belongs to the group of EFAs. It plays an important role in blocking hormones (eicosanoids) involved in inflammation of the skin, and also in the synthesis of ceramides. Furthermore, linoleic acid as a natural sebum component regulates sebaceous glands of the skin and unclogs pores [11, 14]. According to some studies, the fatty acids

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may also exhibit antibacterial and antifungal properties, which points to a new use of freshwater algae *Cladophora glomerata* as a source of natural preservatives [9].

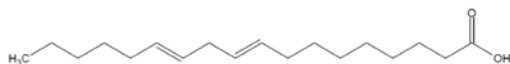


Fig. 1. Linoleic acid

Among other compounds of a lipids found in freshwater *Cladophora glomerata* steroids are noteworthy. These substances include in their construction tetracyclic carbon skeleton derived from 1,2-cyclopentanoperhydrophenanthrene [13]. In freshwater *Cladophora glomerata* there were detected such steroids as ergosterol, β -sitosterol, decortinol, and a derivative of cholesterol – 22-dehydro-24-izopropylcholesterol [9]. Ergosterol belongs to mycoesterols, i.e. sterols isolated mainly from fungi. The compound is prepared on an industrial scale with yeast, and then is used to produce vitamin D₂ [13]. The β -sitosterol (Fig. 2) is a typical phytosterol, or plant steroid alcohol having an anti-inflammatory, antibacterial, antiviral and strengthening the skin's resistance activity [11]. Furthermore, phytosterols have the ability to supplement the shortage within the intercellular cement, thereby they enhance the epidermal lipid barrier and protect the skin from excessive loss of water [12]. Cholesterol and its derivatives act on the skin softening and firming, moreover, they are good emulsifiers of water-in-oil type and regulators of creams consistency [11]. Steroids derived from algae *Cladophora glomerata* may be therefore used in various types of cosmetic products: purifying and anti-acne gels and creams, anti-aging emulsions or protective creams for dry, sensitive and allergic skin.

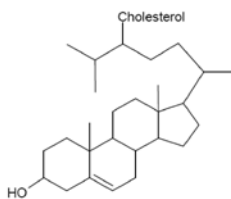


Fig. 2. β -sitosterol

A very important group of bioactive substances in the modern cosmetic industry are antioxidants. These compounds protect skin against destructive effects of free radicals on skin cells, and as a result – prevent aging of the skin. Many substances with different chemical structure are included to antioxidants, e.g. carotenoids and polyphenolic compounds. It turns out that the freshwater *Cladophora glomerata* is a rich source of such antioxidants as carotenoids: β -carotene (Fig. 3), lutein and zeaxanthin [8]. These compounds are tetraterpenes, namely ionones derivatives which contain conjugated polyene chain [13]. Carotenoids are precursors of vitamin A and they are fat soluble. β -carotene and other carotenoids primarily act as antioxidants in cosmetics, thus they are a popular ingredients in anti-aging and anti-wrinkle preparations. Furthermore, they are involved in the process of keratinization of the epidermis adjusting its exfoliation. Carotenoids deficiency may result in excessive dryness and exfoliation of the skin. They are also used as a natural UV filters and pigments to production of lipsticks, powders, nail polish and other make-up cosmetics. Carotenoids derived from freshwater algae *Cladophora glomerata* can be therefore used in products for dry, mature and aging skin, as well as in the manufacture of color cosmetics [14].

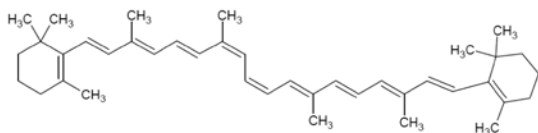


Fig. 3. β -carotene

Other important substances acting as antioxidants are polyphenols – compounds containing at least two hydroxyl groups attached to the aromatic ring (example: eckol (Fig. 4)). The presence of the conjugated double bonds in the aromatic ring determines the antioxidant properties of polyphenols. This group includes: flavonoids (including isoflavones, catechins, anthocyanins), polyphenolic acids, coumarin and the others [11]. A particular group of polyphenols are flavonoids. They are plant dyes, usually yellow coloured, being 1,4-benzopyrone derivatives. They show multidirectional effect on skin: antioxidant, anti-free radical, anti-inflammatory, sealing blood vessels and protective against UV radiation. Moreover, flavonoids inhibit the action of hyaluronidase – enzyme degrading hyaluronic acid, and elastase – enzyme hydrolyzing elastin [12, 14]. As a result, flavonoids protect skin against the effects of aging, strength connective tissue and act anti-wrinkle in anti-aging preparations. They are also desirable cosmetic ingredients for vascula, allergic and sensitive skin. In studies on the freshwater macroalga *Cladophora glomerata* it was found that it is a raw material rich in polyphenolic compounds. Within the group flavonoids have also been detected in the freshwater species [15]. In the same research there have been confirmed the high antioxidant and antitumor activity of this species [16].

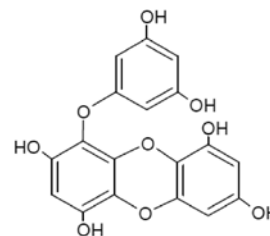


Fig. 4. Eckol

Terpenoids are another group of biologically active compounds isolated from freshwater macroalgae *Cladophora glomerata*. These are derivatives of terpenes, i.e. hydrocarbons which are oligomers of isoprene. Terpenoids are compounds mainly of plant origin, most often occurring as a volatile constituents of essential oils, characterized by a specific odor and biological activity [13]. For example, trans-phytol (Fig. 5) present in *Cladophora glomerata* [9] is a diterpene alcohol and chlorophylls component, regenerating and rejuvenating the skin [11].

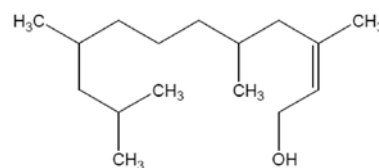


Fig. 5. Trans-phytol

Apart from the described chemical compounds, the freshwater green macroalga *Cladophora glomerata* are the source of many other bioactive substances. Carbohydrates are worth mentioning that serve important functions in cosmetology as a moisturizing, anti-aging agents and protecting skin against photo-aging [9, 14]. In the freshwater species *Cladophora glomerata* there have also been detected a presence of tannins [15], which act astringent, anti-inflammatory, antibacterial, deodorant and firming on the skin [11]. Tannins have been used in the manufacture of creams and masks for oily and acne skin, firming lotions and anti-dandruff shampoos [12]. *Cladophora glomerata* contains also vitamins: A (retinol), C (ascorbic acid), E (tocopherol), B₁ (thiamine) and B₂ (riboflavin) [8]. Each of these elements function in separate way in cosmetics: vitamin A is an antioxidant, it regenerates the skin and regulates the processes of keratinization of the epidermis, vitamin C is also a powerful antioxidant and is involved in the biosynthesis of collagen, vitamin E protects the skin lipids against oxidation and treats

seborrheic dermatitis, vitamin B₁ regulates the water management of the skin, and vitamin B₂ is involved in the proper functioning of the skin and epithelial cells of blood vessels [11].

Summarizing, the freshwater green macroalgae *Cladophora glomerata* is a natural raw material rich in various biologically active compounds. Examples of these substances, their properties and potential use in cosmetics are summarized in Table I.

Table I
Biologically active compounds contained in the freshwater alga *Cladophora glomerata*

Group of compounds	Example	Properties	Application
Fatty acids	Linoleic acid	Emollients Antiallergic Anti-inflammatory Anti-wrinkle	Creams to dry, sensitive skin Anti-acne cosmetics Antiallergic preparations
Steroids	β-sitosterol	Anti-inflammatory Antibacterial Firming Emollients	Anti-aging cosmetics Purifying gels Creams to dry, sensitive skin
Carotenoids	β-carotene	Antioxidants Regulating keratinization processes Photoprotective	Anti-aging cosmetics Anti-wrinkle creams Moisturizing creams Make-up cosmetics
Polyphenols	Eckol	Antioxidants Anti-inflammatory Photoprotective Sealing blood vessels	Creams for vascular skin Anti-aging cosmetics Creams to sensitive and allergic skin
Terpenoids	Trans-phytol	Regenerating Rejuvenating	Anti-aging cosmetics
Carbohydrates	Alginic acid	Moisturizing Anti-wrinkle	Moisturizing creams Anti-aging cosmetics
Tannins	Gallic acid	Astringent Firming Anti-inflammatory	Purifying gels Anti-acne cosmetics Firming balms Anti-dandruff shampoos
Vitamins	Ascorbic acid	Antioxidant Regenerating	Anti-aging cosmetics

Conclusion

Currently, freshwater macroalgae are not a common cosmetic raw material yet in contrast to marine algae, which have become one of the most widely used natural cosmetic ingredients in recent years [1, 2]. However, it turns out, that the freshwater algae can be also a source of bioactive substances about cosmetic importance. The results of preliminary tests are promising and they showed that a freshwater species *Cladophora glomerata* contains a variety of biologically active compounds, especially a large amount of fatty acids, polyphenols, as well as macro- and microelements. It determines a wide range of biological activities and potential use of algae as one of the ingredients in cosmetic preparations [8, 9, 15, 16].

Acknowledgements

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