

# Phenolic acids used in the cosmetics industry as natural antioxidants

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## Abstract

The aim of the work was to collect and systematize information available in the literature on the important role of phenolic acids in industry and to present their basic properties.

The growing interest in bioactive compounds is related to the possibility of their use, including in the pharmaceutical, cosmetics, dermatology and aesthetic medicine. Bioactive substances can be obtained from natural sources such as fruits, vegetables, cereals and medicinal herbs. They have strong antioxidant properties. Phenolic acids are synthesized in plant cells under the influence of oxidative stress. This stress causes the destruction of the skin cells in which the oxidation of the components takes place, i.e. DNA, lipid membranes and structural proteins. As a result of these processes, the skin becomes dehydrated, there is a loss of elasticity, sagging, appearance of wrinkles and furrows, discoloration and vascular spider veins. A beneficial feature of phenolic acids is limiting the formation of free radicals and protecting the cell against their harmful effects. In connection with the above, cosmetic preparations and treatments with phenolic acids counteract photoageing of the skin, and also show depigmenting properties, controlling tyrosinase activity. Preparations containing phenolic acids are used in cosmetics in the form of: creams, face masks and serums. These acids are recommended because of their antibacterial, anti-inflammatory and antioxidant properties in the regeneration of acne, seborrheic and atopic skin.

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## Introduction

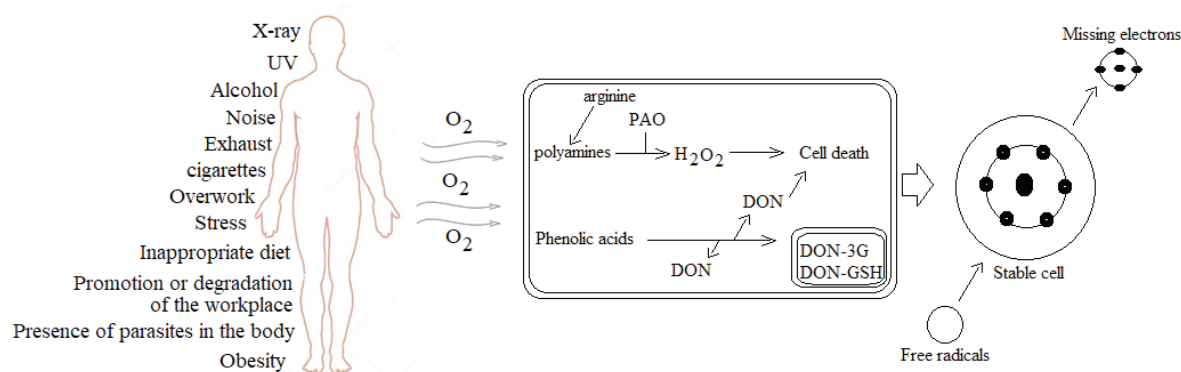
Increasing interest in bioactive compounds is related to the possibility of their use in the different industries. Bioactive compounds are used in medicine, pharmacy, dietetics, dermatology, cosmetology and aesthetic medicine. The cosmetics industry meets the requirements of consumers suffering from various type of dermatitis. Establishing the amount of artificial ingredients in cosmetics by replacing them with natural components fits in with modern pro-ecological trends.

The aim of the work was to collect information available in the literature on the important role of phenolic acids in the cosmetics industry and to present their basic properties. The work includes the chemical structure of phenolic acids, the mechanism of antioxidant activity, properties and natural sources of these compounds.

The impact of stressors on humans, such as pathogenic microorganisms and abiotic factors (Fig. 1) (ROS) and disorders of homeostasis. ROS are products of the next oxygen reduction stages [1,2]. This reduction can take place by transferring electrons to oxygen. Oxygen reduction and excitation products such as hydrogen peroxide, superoxide anion radical, hydroxyl radical, and triplet state. Free radicals have a positive molecule and are oxidizing with a positive molecule, oxidizing. ROS contribute to the destruction of cell membranes and tissues. Oxidation of biological molecules, their inactivation and destruction of cellular organelles by ROS leads to abnormal cell

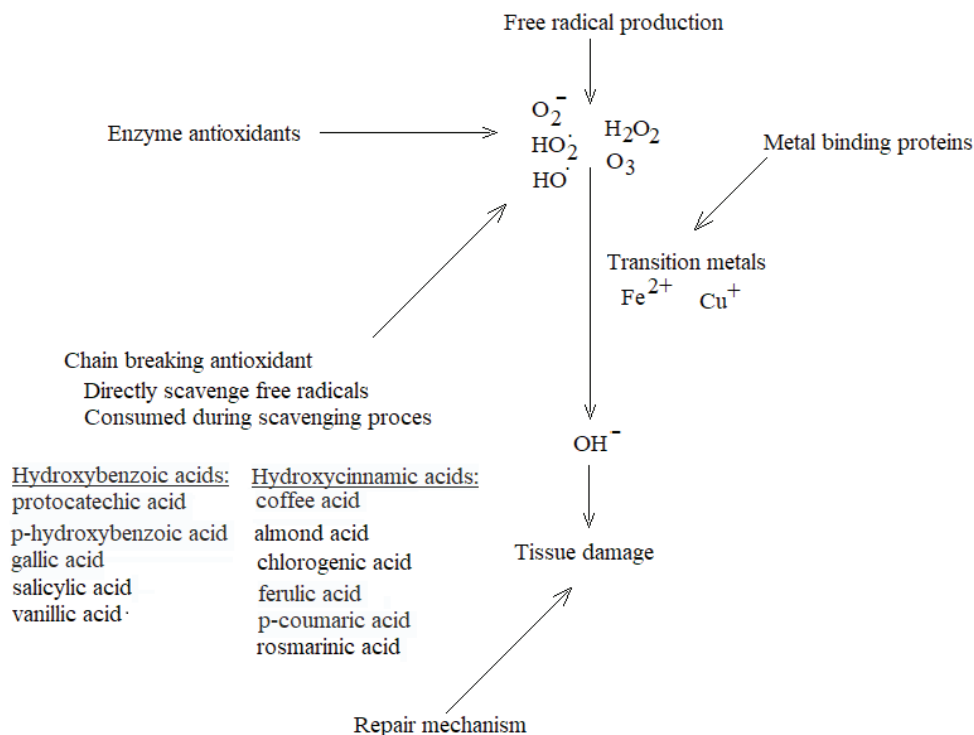
function. As a result of oxidative stress, ROS and oxidative damage. Because radicals have the capacity to react in an indiscriminate manner leading to damage to almost any cellular component, an extensive range of antioxidant defences, both endogenous and exogenous, are present to protect cellular components from free radical induced damage. These can be divided into three main groups: antioxidant enzymes (catalase, glutathione peroxidase, superoxide dismutase), chain breaking antioxidants, and transition metal binding proteins (Fig. 2). These compounds have antioxidant activity and are called antioxidants [2-4]. Antioxidant enzymes catalyse the breakdown of free radical species, in the intracellular environment. Transition metal binding proteins prevent the interaction of transition metals such as iron and copper with hydrogen peroxide and superoxide producing highly reactive hydroxyl radicals. Chain breaking antioxidants are electron donors and react with free radicals before target molecules are damaged.

Bioactive compounds are among the basic nutrients or non-nutrients found naturally in plant material and they can strengthen, weaken or modify the body's physiological and metabolic functions. The compounds with antioxidant properties include, among others, phenolic acids (Fig. 3). Chemically, phenolic acids have structure of phenols compounds with substituent. Phenolic acids may be formed in plants via two metabolic pathways, i.e. the shikimate pathway and the acetic acid metabolic pathway. Phenolic acids are derivatives of benzoic or cinnamic acid present in free or bound form in the form of

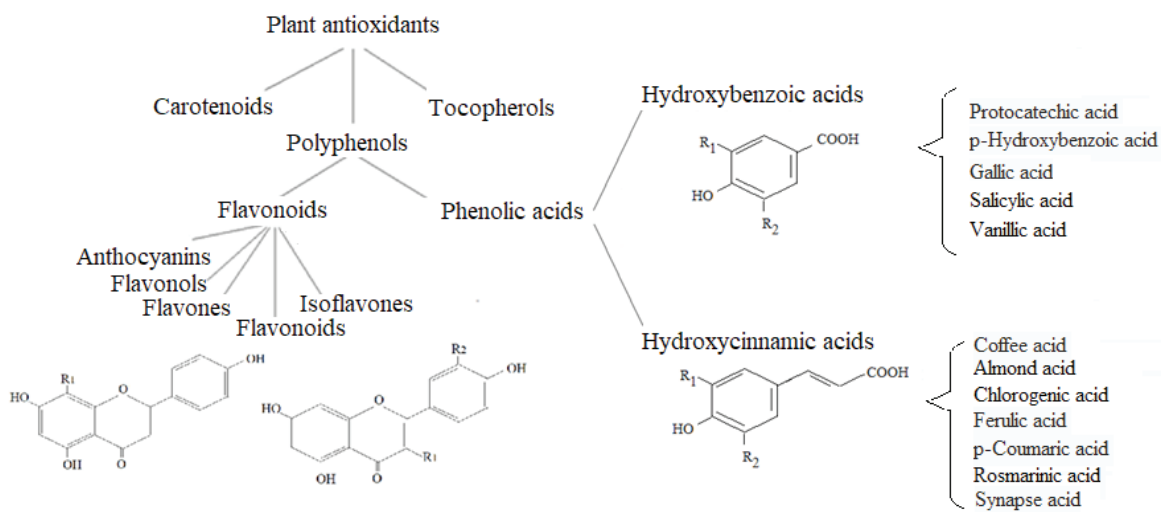


**Fig. 1.**

The process of capturing free radicals [5]



**Fig. 2.** Antioxidant defences against free radical attack [4,6,7]



**Fig. 3.** Examples of bioactive compounds

esters and glycosides [7,8]. The rate of the antioxidant action of phenolic acids depends on their antioxidant activity, which increases considerably with the growing number of -OH groups in the -ortho or -para configuration. In view of the above the antioxidant activity of phenolic acids depends on the structure and polarity of a given compound, its stability in the reaction medium and the manner of isolation of these phenolic compounds. Acids of high antioxidant activity include e.g. caffeic and gallic acids.

Phenolic acids have a protective function in the plant and protect them from damage by the action of microorganisms and insects. They act as building blocks and in combination with polysaccharides they stiffen cell walls. In addition, phenolic acids have biological activity in the human body. They contribute to the removal of free radicals and the chelation of metal ions. In the literature on the subject there is information on the health-promoting effects of phenolic acids and that they can be used in medicine. Their antioxidant properties are used in the prevention of treatment of civilization diseases, including: coronary heart disease, cancer and diabetes. Phenolic acids are also used in cosmetology, they protect against photo-oxidative damage to the skin, with coffee acid being more active in this range than ferulic acid. Phenolic acids are widely used in dietetics, cosmetics as well as in dermatology and aesthetic medicine [9]. They have strong antioxidant properties that can delay the aging process of the skin. Phenolic acids are synthesized in plant cells under the influence of oxidative stress. This stress causes the destruction of the skin cells in which the oxidation of the components takes place, i.e. DNA, lipid membranes and structural proteins. As a result of these processes, the skin becomes dehydrated, there is a loss of elasticity, sagging, appearance of wrinkles and furrows, discoloration and vascular spider veins. The antioxidant effect of phenolic acids is even more effective thanks to the synergistic combination of acids with such compounds as: hyaluronic acid, freatit and vitamins C and E.

Phenolic acids are commonly found in plant tissues in bound form in the form of esters or glycosides, which are part of lignin and hydrolysing tannins. In addition, they combine with flavonoids, fatty acids, sterols and cell wall polymers.

Phenolic acids differ considerably in terms of their structure and physico-chemical properties, as well as the concentration, at which they are found in tested plant materials. These acids are in all plant parts, e.g. the pericarp, leaves, shoots and roots. They are accumulated in the vacuoles, guard and epidermal cells. In the literature can you found that the highest concentrations among phenolic acids were recorded for derivatives of hydroxycinnamic acid in red fruits and vegetables as well as green, green coffee beans and in green tea infusion. Cereal kernels are also rich sources of phenolic acids, with the highest concentrations of ferulic acid, followed by syringic and p-coumaric acids. Cereal germ contains esters of caffeic and ferulic acids (Table 1) [10-13].

The health-promoting effect of phenolic acids is based on their antioxidant, antimicrobial and anti-aging properties. Due to the above properties, phenolic acids are used in cosmetology and dermatology. You can find these compounds in generally available cosmetic preparations and during treatments in beauty salons. Treatments performed with these acids counteract the photoageing of the skin, and also show depigmenting properties, by controlling the activity of tyrosinase, which maintains even pigmentation of the skin. In addition, they alleviate the symptoms of acne and atopic dermatitis [9].

## Ferulic acid

Ferulic acid is a cinnamic acid derivative. This acid occurs naturally in grains, nuts, coffee beans and beets, as well as in conifers (bark, seeds and leaves). The antioxidant properties of the acid contribute to the inhibition of the skin photoaging process, regeneration and absorption of UVB and UVA radiation. It is used for the production of sunscreens. Ferulic acid moisturizes the skin and stimulates the synthesis of collagen and elastin fibers, rebuilding it, has a soothing and anti-inflammatory effect. Ferulic acid is used in cosmetics: anti-wrinkle creams, sun creams, body scrubs, seborrheic and acne preparations. Currently available and used creams, face masks and serums contain 1% ferulic acid. There are also preparations in the form of emulsions and alcohol solutions

**Table 1.**

Examples of the source of phenolic acids

Group of phenolic acids	Name of acid	Occurrence
Hydroxybenzoic acids	Protocatechic acid	blackcurrant, red fruit (strawberries, raspberries), blackberries, red onion, radish, grapes, grapefruit, olive oil, carrots, east African satinwood, yellow leaf
	p-Hydroxybenzoic acid	tree, peroba, taheebo, red sandalwood
	Gallic acid	tea, strawberries, raspberries, blackberries, grapes, onions
	Salicylic acid	peaches, apples, blackberries, raspberries, nectarines, oranges, currants, plums, strawberries, grapes, cherries, broccoli, chicory, cucumbers, tomatoes, radishes, sweet corn, spinach, basil, dill, marjoram, mint, oregano, sage, rosemary and thyme, coffee, tea
	Vanillic acid	barbed oil, Spanish heath, upland cotton, Chinaberry, oriental ginseng, a Korean peroba, red sandalwood, luo shi, Shiitake mushroom, Eggplant
Hydroxycinnamic acids	Coffee acid	apples, pears, plums, leaves of Ginkgo biloba and Morus alba, tobacco leaves, coffee, potatoes, spinach, lettuce, cabbage, olive oil, wine, legumes, tomatoes, nuts, cereal grains, sunflower seeds
	Almond acid	bitter almonds, cherries, apricots
	Chlorogenic acid	apples, pears, berries, artichokes, eggplants
	Ferulic acid	grains of wheat, barley, rye and oats
	p-Coumaric acid	apples, blackcurrant, cereals, cereal bran
	Rosmarinic acid	herbaceous plants, rosemary ( <i>Rosmarinus officinalis</i> ), basil ( <i>Ocimum basilicum</i> ), oregano ( <i>Origanum vulgare</i> ), lemon balm ( <i>Melissa officinalis</i> ), marjoram ( <i>Origanum majorana</i> ), sage ( <i>Salvia officinalis</i> ) and thyme ( <i>Thymus vulgaris</i> )
	Synapic acid	vegetables from the Brassica family (broccoli, kale), citrus juices

containing 3-5% ferulic acid. From the medical point of view, ferulic acid has antibacterial, anti-inflammatory and antioxidant properties for the regeneration of acne, seborrheic and atopic skin. It is also used in cosmetic and aesthetic medicine. Preparads with a higher concentration of 8-12% (peels) are used there [9,14].

## Rosmarinic acid

Rosmarinic acid is a dimer of caffeic acid and 3,4-dihydroxyphenyl acid. Rosemary acid has antioxidant, antiallergic, anti-cancer and anti-inflammatory properties. In the literature on the subject one can find information about the local anti-inflammatory effect and inhibiting the development of cancer cells. In addition, it can have analgesic and anti-inflammatory

effects, also after internal use. Rosemary acid directly affects the cardiovascular system, preventing atherosclerosis and inhibiting the oxidation of LDL cholesterol. In elderly people, rosmarinic acid may reduce the symptoms of dementia and the development of Alzheimer's disease. This compound is responsible for maintaining proper skin hydration, as well as for maintaining its elasticity and firmness. Therefore, rosemary extract is also used cosmetically and can be found in many skin care products [9,15].

## Salicylic acid

Salicylic acid is a beta-hydroxy acid. As a chemical compound, it was isolated from the willow bark. Salicylic acid appearing in plants, regulating their growth. Its antibacterial, antifungal and anti-inflammatory properties are used in the production of antiseptics and cosmetics. In cosmetology, 2% alcoholic solutions of salicylic acid are used. In a higher concentration of 10-20% it has keratolytic properties. The more salicylic acid, the stronger the exfoliation, the acid can be used in places with a strong beard, e.g. Feet or elbows. It is available in the form of liquids, patches, ointments and gel with other medicinal substances. In turn, in combination with corticosteroids, it is used to treat skin diseases. Salicylic acid is used to treat onychomycosis. This acid regulates the secretion of sebum and for this reason is recommended for people with acne skin. With regular use it cleanses and narrows pores. Preparations with salicylic acid is recommended to combat dandruff on the head. This acid stimulates the renewal of the epidermis, reduces the visibility of scars, improves skin tone and forms the basis for the preparation of creams. After the cosmetic treatment with salicylic acid, sun exposure is not recommended [16,17].

## Almond acid

Almond acid is an alpha-hydroxyl compound. The solutions of mandelic acid are widely used in cosmetics. This is due to the numerous health-promoting properties of this substance. The effect of mandelic

acid on the skin is two-way: on the one hand it is exfoliating and the other disinfectant. The exfoliating properties of mandelic acid are proportional to its concentration. In the production of creams, it uses concentrations of 5-15% and these are usually mildly exfoliating creams for the night. Professional treatments of chemical peeling with almond acid, used in beauty salons, are made in 30-40% solutions. Almond acid exfoliates the outer layers of the epidermis, thus smoothing the skin tone and leaving it smooth, brightens blemishes and scars on the skin. In addition, mandelic acid has sebum secretion regulating properties. This acid has additional antibacterial properties. It inhibits the growth of bacteria such as *Staphylococcus aureus* (*Staphylococcus aureus*), *Proteus* sp. (*Stunts*), *Escherichia coli* (*coli bacillus*) and *Klebsiella aerogenes*. It is used for the care of acne skin and soothes inflammation of the skin. Almond acid is also used in skin softeners. It's a mild acid. It is usually well tolerated by the skin, without irritation and discoloration. Also suitable for sensitive skin capillaries [18,19].

## Chlorogenic acid

Chlorogenic acid is a hydroxycinnamic acid. It is a caffeic acid ester and acid (-) - poly (cyclic) [9,20]. Chlorogenic acid is used as various additives to beverages, cosmetics, and tea products and food, as well as medical substances [21]. Chlorogenic acid has an antibacterial and antiviral effect properties [22].

It is also a promising precursor relationship for the development of medicine that is resistant to HIV AIDS [23].

## Coffee acid

Coffee acid (3,4-dihydroxycinnamic acid) is one of the major hydroxycinnamic acids present in wine (Ilhami, 2006). The potential health effects of caffeic acids were tested in many animal models and in vitro tests [24]. This acid has antioxidant and anti-aging properties.

## p-Coumaric acid

p-Coumaric acid (4-hydroxycinnamic acid) is cinnamic acid derivative. P-coumaric acid is ubiquitous in plants. P-coumaric acid has antioxidant properties and it is believed to reduce the risk of stomach cancer [25] omitting the formation of carcinogens nitrosamines [9,26]. At the same time, dietary phenolysis looks differentiated intestinal absorption properties.

## Vanillic acid

Vanillic acid (4-Hydroxy-3-methoxybenzoic acid) occurs in many plants. In addition to anti-aging and anthelmintic, vanilla acid can inhibit liver fibrosis in chronic liver damage [27]. Vanillin acid is used as an analgesic and antipyretic [28].

Natural phenolic acids have extensive health and nurturing properties. They are characterized, inter alia, by strong antioxidant, antibacterial and antifungal activity. In the cosmetics and pharmaceutical industries, phenolic acids have an effect on various skin diseases. However, their antimicrobial properties have also been used for the preservation of cosmetics, medicinal products and food. Cosmetics can contain oils, emulsifiers, vitamins, minerals and plant extracts, which are the optimal environment for unwanted microorganisms. The development of microorganisms, such as bacteria or fungi, reduces the quality of the cosmetic. Therefore, preservatives are used to protect against microbial infections. Such preservatives may be esters of parahydroxybenzoic acid, otherwise called parabens (ethyl parabens, propyl parabens, butyl parabens, heptyl-arabenes and benzyl-arnenes). In comparison with benzoic acid, these substances act several times more strongly on microorganisms. They exhibit antibacterial activity over a wide pH range of 4-8. They are active antifungal and antibacterial. They show activity against Gram-positive and Gram-negative bacteria. These parabens are non-toxic, non-carcinogenic, non-terathogenic, hypoallergenic. The average concentration of paraben in cosmetic preparations is over 0.4%, while the maximum permissible content of the paraben mixture is

0.8%. The use of p-hydroxybenzoic acid esters in cosmetics may also result from other properties than antimicrobial activity, e.g. in soaps they are also used as antiperspirants, and in shampoos as a substance with anti-dandruff activity. 3-Hydroxybenzoic acid. 3-Hydroxybenzoic acid is in many plants (Tab. 1) [29-31]. It has antifungal, antimutagenic, antifungal and estrogenic activity [32] and antimicrobial activity [33]. The literature data show that p-hydroxybenzoic acid increases the impermeability of the cell wall, leading to increased resistance to pathogens [34]. That's why it can be used in the cosmetics industry as both an active and preservative substance.

In summary, phenolic acids are commonly found in plant tissues where they can be extracted and used for medicinal purposes. Their properties are based on antioxidant, anti-inflammatory and antimicrobial activity. As a result, phenolic acids can be widely used in cosmetic products as skin care products and in dermatology as therapeutic agents. The availability of phenolic acids in many plants and the ease of obtaining them is a stimulus for the industry to use them in cosmetic, pharmaceutical and food products.

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