10

The Natural and Anthropogenic Processes Responsible for the Presence of Methoxyphenols in Ecosystems and Human Surrounding

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1. Introduction

Phenols form one of the largest group of compounds present in the environment. These substances are characterized by strong noxious activity, they are also mutagenic and carcinogenic. Due to their toxicity, the persistence to degradation and accumulation in the environment including living organisms they present a real danger for humans and ecosystems.

Guaiacol and syringol belong to a group of methoxyphenols. These compounds commonly exist in the environment [1] and in trace concentrations are contained in edibles and drinking water [2]. The presence of methoxyphenols in the environment is related to transformation processes that proceed in the result of microbes activity [3]. The most important group of microbes that are responsible for formation of methoxyphenols including guaiacol and syringol are fungi. These organisms are capable to biodegrade natural polymers contained in organic matter and wood what results in formation of low molecular weight compounds of phenolic structures [4]. Another group is bacteria that may form 2-methoxyphenol from vanillic and ferulic acids abundantly present in terrestrial environments.

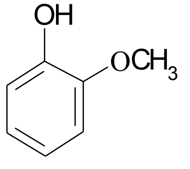
The excessive release of methoxyphenols and their chlorinated derivatives to the environment is related with human activity. The processes including combustion of wood and plant wastes lead to formation of methoxyphenols and their methylated derivatives [5]. Methoxyphenols are also used in chemical and pharmaceutical industries. 2-methoxyphenol and

2,6-dimethoxyphenol are used as components and precursors of azo dyes, pesticides and medicines of antiseptic properties [6]. Moreover, these compounds are used in production of vanillin [7]. The most important source of chlorinated methoxyphenols introduced into surface waters are sewages produced in wood pulp bleaching process. The performed investigations have revealed high concentrations of chloroguaiacols and chlorosyringols contained in these effluents [8] that polluted aqueous ecosystems and thus changed their ecological balance. Chlorinated methoxyphenols penetrate water organisms and bioaccumulate in their tissues even in the concentrations exceeding 1000-fold of amounts of these compounds present in water [9].

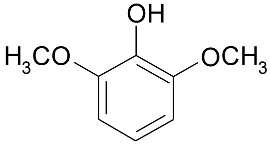
Methoxyphenols and particularly their chlorinated derivatives exert strong toxic capacities. In human and animals these compounds may disturb function of reproductive system, cause strong skin irritation and even death [10]. Besides, the investigations revealed that discussed compounds are mutagenic [11], genotoxic and inhibit synthesis of DNA, RNA and proteins.

2. Structure

Guaiacol and syringol belong to a group of methoxyphenols. Guaiacol is 2-methoxyphenol and it is also termed as 1-hydroxy-2-methoxybenzene and 2-methyl-catechol. Syringol is 2,6-dimethoxyphenol.

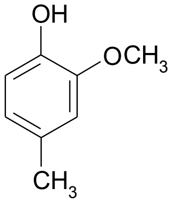


guaiacol

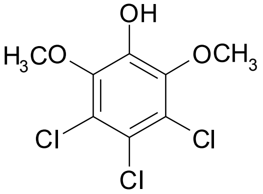


syringol

Chlorinated and methylated derivatives of these compounds are formed in the results of substitution of hydrogen atoms with methyl residue and chlorines atoms in aromatic ring.



4 - methylguaiacol



trichlorosyringol

Guaiacol forms white or slightly yellow crystalline mass or colourless to yellowish liquid. It is characterized by slightly phenolic, sweet odour and their melting and boiling points are 25°C and 204°C respectively. It is poorly soluble in water – 18.7 g/L and much soluble better in organic solvents like ether or alcohol. Chloroguaiacols are almost water-insoluble, 4,5-dichloroguaiacol and tetrachloroguaiacol may be dissolved only in the amounts of 78 mg and 4.7 mg in one litre of water respectively.

3. Natural sources

Methoxyphenols are formed in the result of numerous processes leaded by microorganisms; they are also the natural components of some biopolymers present in plants and terrestrial environment. 2-methoxyphenol and 2,6-dimethoxyphenol are contained in lignin, that with cellulose and hemicellulose is a biological matrix of plants' tissues. High concentrations of methoxyphenols are contained in resins, bark and wood of pine, spruce and willow and some species of grasses. The species like *Phanerochaete crassa, Pleurotus eryngii* and *Phlebia sp.* can degrade complex structures of lignin to low molecular weight compounds including methoxyphenols. Pyrolysis, a combustion of wood derived from oak, willow and birch leads to emission of syringol, 4-methylsyringol, 4-allylsyringol and propylsyringol to the atmosphere [12, 13]. Methoxyphenols were also determined in oils from flowers of pandanus (P*andanus odoratissimus)*, dogwood (*Cornus controversa*) and *Plantago asiatica.*

Fungi participate in transformation of ferulic acid (phenolic acid abundantly present in soil) to guaiacol. This process is mainly leaded by yeasts like *Rhodotorula rubra* and *Sporotrichum thermophile* [14]. These microbes transform trans-ferulic acid to 4-vinyguaiacol in a carboxylation process. Next, 4-vinylguaiacol is transformed to vanillic acid that is finally converted to guaiacol during decarboxylation (Fig 1.).

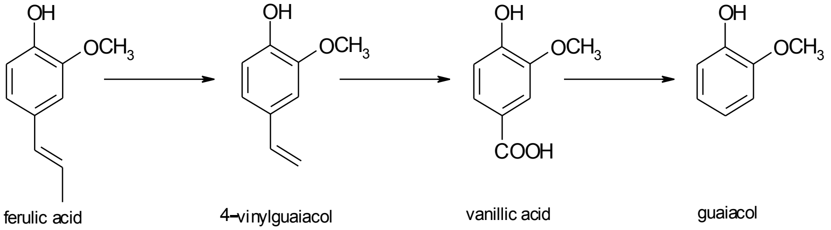


Fig. 1. Transformation of (trans-)ferulic acid by *Sporotrichum thermophile* [14]
Rys. 1. Transformacja kwasu (trans-)ferulowego przez Sporotrichum thermophile [14]

The important effect on formation of methoxyphenols in the environment is related with fungi that belong to *Basidiomycetes* and *Ascomycetes*. These species are capable to form chlorinated derivatives of methoxyphenols like 4,6-dichloroguaiacol and 4,5,6-trichloroguaiacol from other aromatic structures and inorganic chlorine present in soil [3].

Degradation of humic substances (the main organic component of soil) leads to formation of phenolic derivatives including syringol alcohol. Guaiacol is also present in faeces of animals that consume high quantities of plant material. Moreover, guaiacols and syringols are produced in the result of O-methylation of catechols under the influence of O-methyltransferase (EC 2.1.1.6) (Fig. 2).

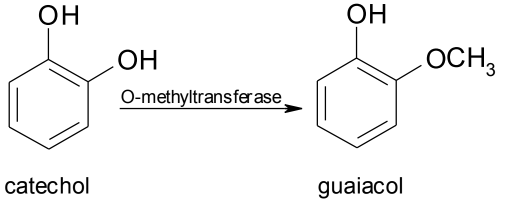


Fig. 2. O-methylation of catechol
Rys. 2. Proces O-metylacji katecholu

3.1. Lignin

After cellulose lignin is the most abundant natural polymer being the main aromatic chemical compound of vegetal tissue [15]. Its content in wood is of 18 – 40 % what depends on the species of the plant [16]. The structure of lignin is very complex and contains both aliphatic and aromatic fragments including phenolic and methoxy-phenolic groups (Fig. 3). The recent investigations revealed that there is some consistency in the structure of discussing biopolymer. Regularity of the lignin is related with three precursors like p-cumaric alcohol, coniferyl alcohol and sinapic alcohol that are responsible for formation of its structure. These alcohols may be converted by laccase (EC. 1.10.3.2.), multicoppers blue oxidase [17] and other oxidases to radical forms by elimination of hydrogen atoms in their hydroxyl residues. As radicals reveal high reactivity they react themselves to form dimmers and finally complex structures that represent lignin.

The structure formed in the results of these reactions is characterized by repeated fragments like guaiacol, syringol and p-hydroxyphenolic residues [4]. Lignin may be degraded under the influence both of natural (microorganisms) and anthropogenic factors. The investigations on the chemical stability of lignin that is related to the kinds of bounds that cement its structure let predict the formation of specified compounds during degradation of this biopolymer. It was evidenced that the bound of β-O-4 is the weakest and thus is the most susceptible for disruption. Therefore, during degradation of lignin mainly methoxyphenols including guaiacol are released to the environment. These suggestions were confirmed by Japanese scientists which analyzed the products of lignin decomposition in a temperature of 270°C.

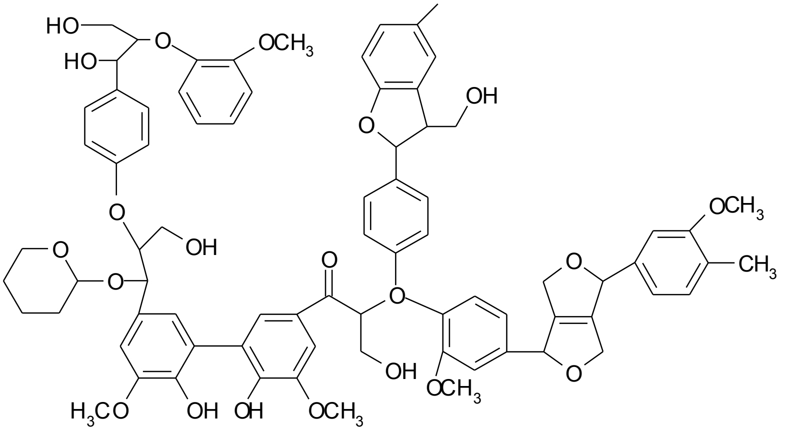


Fig. 3. The fragment of lignin structure
Rys. 3. Fragment struktury ligniny

3.1.1. Pyrolysis of lignin

Pyrolysis is the thermo-chemical process of decomposition of high molecular weight organic biopolymers like lignin contained in plant matter. Natural processes like fires of forests or other plant communities are responsible for thermal degradation of biopolymer and releasing of different substances to the environment. However, plant matter combustion has very important industrial significance as high amounts of solid biomass and wastes may be readily converted into liquid products like crude bio-oils or slurry of charcoal oil. Conventional pyrolysis may be also termed slow pyrolysis. Fast pyrolysis is a high-temperature process in which biomass is rapidly heated in the absence of oxygen. In the result of thermal wood biomass conversion numerous of low molecular weight aromatic compounds are released to the environment including 2-methoxyphenol (guaiacol), alkylguaiacol, 4-methylguaiacol, 4-vinylguaiacol, 1-propylguaiacol, 2,6-dimethoxyphenol (syringol), 2,3-dimethoxyphenol, 2,5-dimethoxyphenol, vanillin, phenol and catechol [5]. Also pyrolysis of grass material derived from four species of *Lolium* and eleventh species of *Festuca* genera leaded to formation of different methoxyphenols like phenol, guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, syringol, 4-methylsyringol, 4-ethylsyringol and vanillin [18]. As it was noticed burning of non-wooden biomass more often leads to formation of some methylated and alkylated methoxyphenols The mechanism of pyrolysis is related with free radical reactions. First step is related with elimination of hydrogen atoms in hydroxyl residues in lignin precursors and then the impact of formed free radicals on lignin fragments and formation of dimers (Fig. 4) [16].

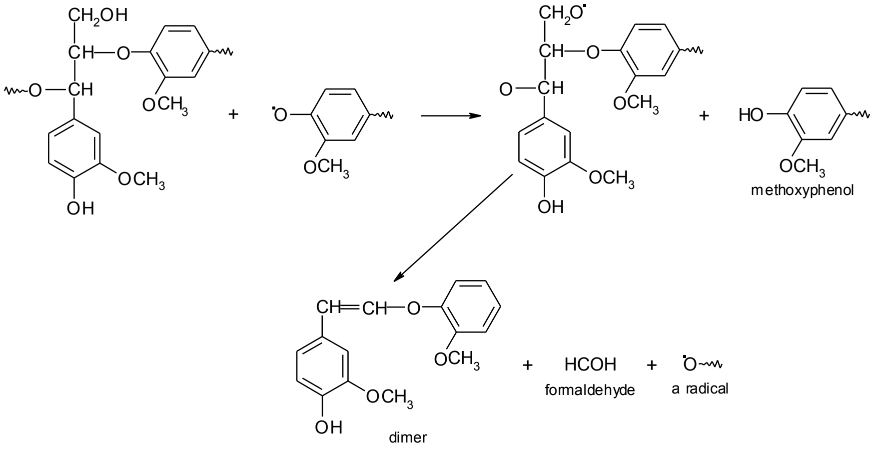


Fig. 4. Radical mechanism of lignin pyrolysis [16]
Rys. 4. Mechanizm rodnikowy pirolizy ligniny [16]

The amount of free radicals formed in these reactions depends on several factors like reaction time, temperature, the presence of catalysts and kind of plant material. High concentrations of methoxyphenols and dimethoxyphenols are released during high temperature and short time of pyrolysis.

3.2. Humic substances

The transformations of organic compounds derived from organic matter like lignin, pectin, proteins, carbohydrates and tannins leads to formation of high molecular weight structures like humic acids. This process is named as humification and formed substances are usually termed as humus. Humic substances constitute the mixture of different chemical compounds, which structures has not been yet completely described. In the structure of humus we may find methoxy and hydroxyl residues substituted to benzene ring derived from lignin and also hydroxybenzoic acids, aromatic aldehydes, ketones and other aromatic derivatives (Fig. 5).

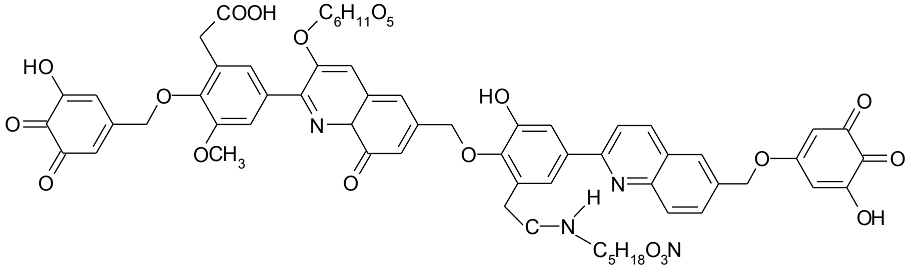


Fig. 5. The fragment of humic acid structure
Rys. 5. Fragment struktury kwasu humusowego

Not long ago, it was considered that humic substances are not noxious for people. These substances were eliminated in a process of purification of raw water to drinking purposes due to esthetical regards. However, the investigations have revealed that they are the cause of undesired smell of water and are also the precursors of trihalomethanes and chlorophenols that reveal toxicity and carcinogenicity. It is worth noting that humic substances actively accumulate xenobiotics including pesticides and their transformation products and also chlorinated compounds derived from sewages produced by cellulose-paper plants [19]. It was observed that about 60% of chloroguaiacols and 90% of chlorocatechols introduced into ecosystems are accumulated in deposits [20].

So that, during decomposition of humus, for example in the result of resuspension of sediments present in lakes or rivers the accumulated xenobiotics like phenols, catechols, methoxyphenols and their chlorinated derivatives may be released in considerable amounts to aqueous environment.

4. Anthropogenic sources

4.1. Application in industry

Guaiacol and syringol and their derivatives are commonly used in chemical, pharmaceutical and food industries. Investigations carried out by Italian scientists showed antibacterial properties of 2-methoxyphenol. They observed that guaiacol dissolved in water revealed toxic influence towards *Pseudomonas savastanoi* [21]. Potassium sulphoguaiacol is usually used in syrups. In organism it is degraded to guaiacol, which during inhalation irritates mucous membrane causing expectorant reflex. Guaiacol stimulates organism to production of increased amount of mucus, which decreases its density and viscosity. Sulphoguaiacol is used in permanent catarrh of respiratory tract, bronchi inflammation, pertussis and asthma [22].

Glycerol ether of guaiacol may be also used as an assist medicine in hypercholestero-lemia treatment. The experiments performed on rats confirmed that discussing compound increases solubility of cholesterol in blood and thus prevents its deposition in blood-vessels. 2-methoxyphenol is used in cosmetic industry in fragrances. 4-vinylguaiacol possesses a spicy clove-like aroma and is an appreciable flavour constituent in beers, wine and soy sauces. It is also used in fragrance and perfume industry [23]. Guaiacol may be also used to industrial production of some chemical compounds like vanillin.

Vanillin is the major component of natural vanilla which is one the mostly widely used and important flavouring materials worldwide. The source of vanillin are beans and pods of the tropical *Vanilla* orchid (*Vanilla planifolia*), however, its receiving in natural manner is very expensive. That is why vanillin is mainly synthesised on industrial scale from guaiacol with 80% efficiency [7].

Allylation of guaiacol is commercially important reaction which gives products such as eugenol and o-eugenol used in perfumes, flavourings and essential oils, and also in medicine (local antiseptic and analgesic) [6]. Another compound that is obtained from 2-methoxyphenol is 4-allylguaiacol intensively used in pharmacy and stomatology. This compound reveals antioxidative and fungicidal activities.

Syringol also exhibits antioxidative, bactericidal and fungicidal properties. Fume that contains 2,6-dimethoxyphenol is used in smoking of meat, pork-butcher's products and cheeses. Syringol has been employed in production of some anaesthetic drugs like 2,6-dimethoxyphenyl-morpholinopropionic chloride. This compound is used as anaesthetic in rabbits, dogs cats and other animals. Syringol may be also used as inhibitor of the formation of some toxic substances. The experiments conducted on rats showed strong correlation between the content of syringol and N-nitrosomorpholine (NMOR) in organism [24], which is a heterocyclic compound characterized by carcinogenic properties. The investigations evidenced that supplementation of rats with 2,6-dimethoxyphenol may decrease NMOR concentration in blood and stomach even up to 89%.

Nowadays, almost half amount of pigments used in chemical industry is represented by azo-dyes. These substances in dependence on their structure are characterized by yellow, orange, red, blue or green colour. 2-methoxyphenol and 2,6-dimethoxyphenol are used as the substrates to synthesis of these compounds. The reactions of formation of azo-dyes are based on conjugation of methoxyphenols with di-azo-salts in alkaline conditions to produce eight different colour pigments [25].

4.2. Wood pulp bleaching

Production of paper from wood requires elimination of hemicelluloses, as only cellulose and wood pulp is used in this process. The wood is decorticated, crumbled and pounded. Then, obtained pulp is exposed to sodium hydroxide and sodium sulphide what results in formation of water-soluble sulphonic-lignin acids. These compounds are very persistent to biodegradation as they are decomposed in surface waters only in the amounts of 4 -15 % after 30 days and of 30 – 70% after 20 weeks respectively [26]. The obtained brown-yellow cellulose is contaminated with other compounds that have to be eliminated in a process of bleaching (chlorination). The compounds usually used in this process are sodium hypochlorite and chloride dioxide that are inexpensive, however they are responsible for releasing of high concentrations of chlorine and chlorinated aromatic compounds to the environment like chloroguaiacols, chlorosyringols and chlorinated phenols. These compounds are formed in the result of chlorination of low molecular weight aromatic compounds derived from lignin and also pesticides like fungicides, bactericides and insecticides accumulated in processed wood. It was evaluated that 10 to 100 g of chlorinate guaiacols like tetrachloroguaiacol, 3,4,5,-trichloroguaiacol, 4,5,6-trichloro-guaiacol 4,5-dichloroguaiacol, 4,6-dichloroguaiacol, 3-chlorosyringol and trichlorosyringol are discharged per ton of bleached kraft pulp with the spent bleach liquor into recipient waters [8].

These compounds constitute a real danger for aqueous ecosystems as they are very toxic and are characterized by mutagenic and carcinogenic properties. That is why, in recent years chlorinated oxidants are more and more frequently replaced by hydrogen peroxide to decrease concentrations of chlorinated aromatics formed in describing process [9].

High concentrations (1 - 100 μg/L) of chlorinated guaiacols and syringols were noted in effluents produced during wood pulp bleaching in a paper production process [19].

5. Occurrence in the environment

Guaiacols and syringols are present in all of the components of natural environment. The appearance of these compounds was noted in surface waters non-exposed to anthropogenic contamination. Guaiacol, syringol and their chlorinated derivatives were determined in the drainage of the Dzierżązna river (Central Poland), the range of the concentrations of these substances was of 0.0011 to 1.300 μg/L for individual compound [27]. High concentration of guaiacol exceeding 23 μg/L was noted in non-polluted surface waters of the Piasecznica River and water of reservoirs of Blue Springs Reserve near

Tomaszów Mazowiecki in Poland (data not published). The concentrations of chlorinated methoxyphenols in sea waters are very low. The water of Baltic Sea contained concentrations of tetrachloroguaiacol of 1 to 5 ng/L [28]. Discussing compounds are present in industrial and municipal sewages and rivers exposed to human activity. The analysis of raw and purified sewages derived from Łódź town and the Ner River (Central Poland) revealed the presence of chloroguaiacols and chlorosyringols in the concentrations of some micrograms per litre of water. Moreover, it was evidenced that chlorinated methoxyphenols may be also formed in the result of biological purification of raw sewages [29]. The natural sources and human activity is also responsible for presence of chlorinated methoxyphenols in soil environment. The analysis performed in Tucholski Landscape Park (North-West Poland) revealed the presence of chlorinated guaiacols and syringols in a few forest and agricultural soils in concentrations up to 2 μg/kg of individual compound [1]. Atmospheric concentrations of chlorinated methoxyphenols in areas exposed to low industrial emissions are not considerable and amount of 0.020 to 0.068 ng/m^3 for individual substance (Georgetown, USA) [30]. The different situation showed the investigations of polluted air of New Delhi (India). In this case relatively high concentrations (23.34 – 36.95 ng/m^3) of determined syringol derivatives were correlated with intensive gaseous emission of coal-based power plants, industrial plants and domestic sources [31].

6. Biodegradation

Microorganisms perform an important role in degradation of natural compounds and xenobiotics including methoxyphenols and their derivatives. They are capable to degrade complex structures to simple organic and inorganic compounds and thus gain carbon and energy. The essential role in these transformations is played by enzymes that expression is the result of adaptation of prokaryotic and eukaryotic organisms to degradation (consumption) of organic substances.

6.1. Prokaryote

The very important enzymes produced by microbes are oxidases that participate in oxidation of phenols and phenol-related compounds with atmospheric oxygen. The species of bacteria that use these enzymes in degradation of 2,6-dimethoxyphenol are *Marinomonas mediterrane, Streptomyces antibioticus* and *Alteromonas sp.* [32]. The other bacteria - *Bacillus subtilis* and *Streptomyces cyaneus* transform guaiacol and syringol, and the efficiency of degradation process is enhanced with addition of Cu, Mn and Mg ions [33]. The investigations made on *Bacillus halodurans* revealed that this organism oxidases 2,6-dimethoxyphenol in pH of 7.5 to 8.0. In was observed that addition of chlorine stimulated enzyme activity what gives opportunity to use this bacteria in purification of sewages produced by cellulose-paper plants [34]. The another species from discussed genus – *Bacillus subtilis* is capable to degrade high concentration of 4,5,6-trichloroguaiacol [35].

Transformation of methoxyphenols often leads to their O-demethylation. This process was observed in bacteria - *Rhodococcus ruber* CA 16 that grew in cultures enriched with 4-chloroguaiacol, 5-chloroguaiacol and 4,5-dichloroguaiacol. Performed chromatographic analysis revealed formation of reaction products like 4-chlorocatechol and 4,5-dichloro-catechol (Fig. 6).

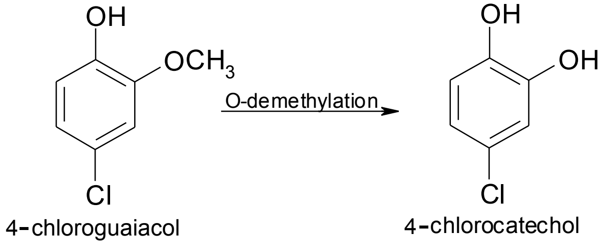


Fig. 6. Transformation of 4-chloroguaiacol in *Rhodococcus ruber*
Rys. 6. Transformacja 4-chlorogwajakolu przez Rhodococcus rubber

The investigations made on *Acinetobacter junii* confirmed formation of catechols from guaiacols. However, the scientists observed that bacteria couldn't transform 6-chloroguaiacol, 4,6-dichloroguaiacol, 4,5,6-trichloroguaiacol and tetrachloroguaiacol. The reason of the persistence of these compounds to degradation may be related with the presence of atom chlorine at sixth carbon position in aromatic ring, which seems to be recalcitrant to elimination [36]. The similar processes were observed in *Acetobacterium woodii* and *Eubacterium limosum* [37]. The beneath described microbes degrade (in anaerobic conditions) dichloroguaiacols, trichloroguaiacols and tetrachloroguaiacol to respective chlorinated catechols. It was ascertained that presence of atom chloride in the ortho position towards methoxy residue in aromatic ring decreased the rate of O-demethylation process.

Syringols may be also O-demethylated. The investigations leaded on *Agrobacterium tumefaciens* revealed that this bacterium is capable to O-demethylate methoxy residues in syringol [38]. Catechol and other dihydroxyphenols formed in these reactions may be further degraded by oxidative cleavage of the aromatic ring. This degradation process is mainly catalyzed by 1,2-dioxygenase (EC 1.13.1.1.) that cleavages benzene ring between the first and the second carbon atoms (intradiole cleavage) and 2,3-dioxygenase (EC 1.13.1.2.), which degrades aromatic structure between the second and the third carbon atoms (extradiole cleavage). The first process leads to formation of maleiloacetate and the second to production of muconolactone. These products are further degraded to inorganic compounds in a mineralization reaction (Fig 7.).

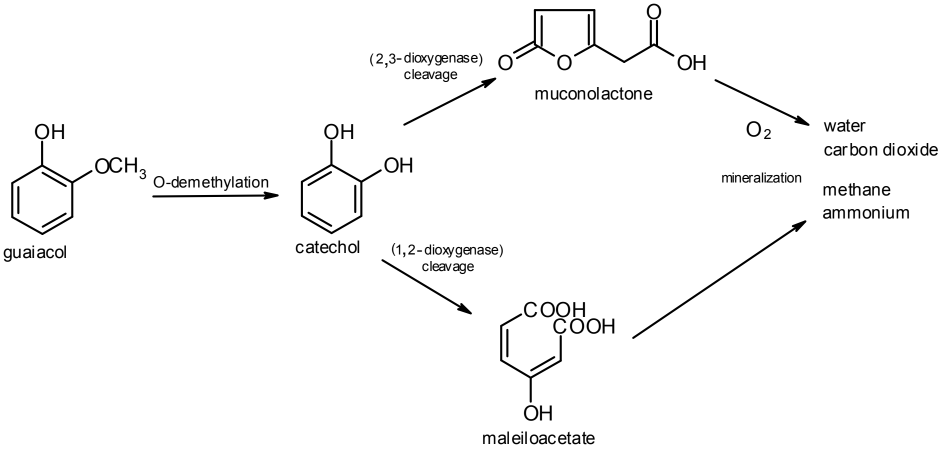


Fig. 7. Biodegradation and mineralization of guaiacol [38]
Rys. 7. Biodegradacja i mineralizacja gwajakolu [38]

Chloroguaiacols and chlorosyringols are also O-methylated to veratroles. These transformations are leaded by bacteria like *Arthrobacter* that metabolize chloro-, dichloro- and trichloroguaiacols and also tetrachloroguaiacol to respective veratroles (Fig. 8.) [39]. High concentrations of 4,5,6-trichloroguaiacol may be also degraded by *Bacillus subtilis* [35].

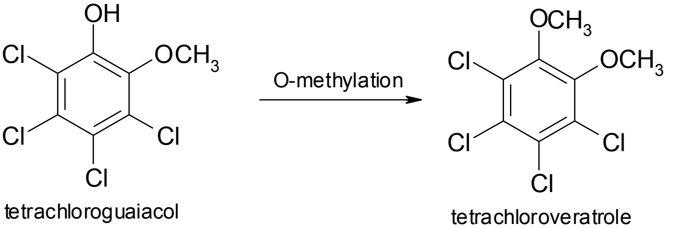


Fig. 8. O-methylation of tetrachloroguaiacol by *Arthrobacter sp.* [37]
Rys. 8. Proces O-metylacji tetrachlorogwajakolu przez Arthrobacter sp. [37]

6.2. Eukaryote

Eukaryotic organisms have also the ability to degrade methoxyphenols and their chlorinated derivatives. Fungi that belong to *Basidiomycetes* and *Ascomycetes* are capable to degrade lignin, mainly at the participation of laccase activity. The products that are formed in these reactions belong to low molecular weight aromatic compounds including methoxyphenols that are further incorporated into humic substances. 2-methoxyphenol and 2,6-dimethoxyphenol are degraded by the following species of fungi - *Gaeumannomyces graminis, Phanerochaete chrysosporium, Trametes pubescens, Chaetomium thermophilum, Pleurotus sajarcaju, Trametes trogii* and *Pleurotus ostreatus* POXC, POXA2 [40, 41]. Furthermore, syringol is biotransformed by fungi like *Botrytis cinerea* and *Pleurotus ostreatus* POXA1 [42]. Degradation of guaiacol and syringol was also observed in *Chaetomium thermophilum*. This organism usually exists in compost and decomposed organic matter. It metabolizes different substances in the temperatures of 50 to 60°C and in the range of pH values of 6.0 to 7.0. In the reaction, the elimination of hydrogen atoms from hydroxyl residues was observed what leaded to formation of radicals. As produced radicals revealed high reactivity they bound each other to form dimers, trimers and tetramers, that were incorporated into humic substances [43]. *Trametes sp.* converts 2,6-dimethoxyphenol to catechol that is than cleaved to form maleiloacetate used in tricarboxylic acids cycle [44]. Numerous yeasts are able to degrade aromatic compounds including guaiacol, even in low temperatures - not exceeding 10°C. The examples are: *Cryptococcus sp., Rhodosporidium sp., Rhodotorula sp., Mastigiobasidium sp.* and *Sporoblomyces sp*. [45].

O-methylation process was also observed in eukaryotic organisms like lower crustaceans. The exposition of *Daphnia magna* to 3,4,5-trichloroguaiacol in a period of 3 weeks leaded to conversion of this compound to 3,4,5-trichloroveratrole [46].

7. Environmental and occupational exposure

Guaiacol is present in bacon, butter, soy, tomatoes, maize, leaves of tea, cocoa beans, sesame, and honey. This compound was also determined in water and apple juice in which is formed during biotransformation processes leaded by bacteria *Alicyclobacillus acidoterrestris* [47]. 2-methoxyphenol is also produced in turned chocolate milk by bacteria *Rahnella aguatilis* [2]. Guaiacol is also found in beverages like rum, whisky and beer. In beer its derivative 4-vinylguaiacol is formed during enzymatic decarboxylation or thermal decomposition of ferulic acid. This process is performed by yeasts and some species of bacteria.

4-vinylguaiacol is characterized by strong smell that negatively affect on organoleptic properties of beer. A man is able to identify the change of taste caused by this compound in a concentration of 200 μg/dm^3.The presence of guaiacol in wine is related to the activity of bacteria *Bacillus subtilis* and actinomycetes like *Streptomyces sp.* A3, *Streptomyces sp.* A5 and *Streptomyces sp.* A13 [48].

The presence of 2-methoxyphenol is also undesirable as it negatively changes taste and smell of beverage. It is considered that this compound is found in 2-7% of all of wines. The formation of guaiacol starts in wooden cork in which a development of many species of microbes proceeds [49]. The microorganisms present in cork degrade vanillic acid in a anaerobic decarboxylation processes by the use of vanillin O-demethylase (EC 1.2.3.12) to form 2-methoxyphenol with efficiency of 50% that may be further degraded to catechol. 2-methoxyphenol may be also produced in edibles by *Nocardia sp* [50], *Bacillus megaterium* and *Paecilomyces variotti* [51].

The presence of some of discussing compounds like tetrachloroguaiacol and trichlorosyringol in the concentrations of 0,01 to 0,241 μg/L were noted in drinking water of Łódź, Warsaw and Wrocław in Poland [52]. The determined compounds were mainly formed from natural methoxyphenols present in surface (river) waters in the result of disinfection (chlorination) process.

The fume formed in the result of tobacco combustion contains relatively high concentrations of methoxyphenols including guaiacol and syringol. The smoke formed during combustion of wood is often used in smoking meat and cheeses. Unfortunately, this process negatively affects chemical composition (pollution) of processed food. This finding was confirmed by Spanish scientists that determined 320 new compounds including guaiacol and syringol in cheese that was smoked in fumes derived from pine needles [53]. The similar observation was performed during analysis of smoked herring fillets that contained considerable concentrations of toxic phenolic compounds like phenol, methylphenols, guaiacol, 4-methylguaiacol, 4-ethylguaiacol, syringol and eugenol [54].

Methoxyphenols comprise 20 -30 % of the carbon particulate weight in smoke from wood stoves and fireplaces in the inhalated fraction and are responsible for increased respiratory symptoms and diminished pulmonary function in children. The inhalation of wood smoke elevates 10 to 30-fold concentrations of these compounds including guaiacol, 4-methylguaiacol, 4-ethylguaiacol, syringol, 4-methylsyringol, eugenol and vanillin in urine [55].

Workers employed in production of vanillin, eugenol and azo-dyes are often heavily exposed to methoxyphenols activity. Another group is plant coke workers exposed to wood smoke that contains aromatic hydrocarbons and phenols. In the investigation performed by Bieniek the presence mainly of 2-methoxyphenol and also 2-methoxy-4-methylphenol and 2,6-dimethoxyphenol in urine of employees was observed. The analysed compounds were determined in considerable concentrations of 1.22 to 4.83 μg/ml of urine [56]. Moreover, workers employed at agricultural wastes combustion may be exposed to considerable concentrations of phenolic compounds like phenol, cresols, guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, syringol, 4-methylsyringol, 4-ethylsyringol, 4-allylsyringol and vanillin [57].

8. Noxious influence

Most of phenols are characterized by noxious activity. The scientists consider that two mechanisms are involved in this process, first is related to formation of free radicals and reactive oxygen species and the second is linked with the impact of phenoxy radicals on biochemical processes that occur in the cell [58]. The results of investigations have revealed that above mentioned properties are typical for phenol, chlorophenols, nitrophenols and also chloroguaiacols and chlorosyringols.

8.1. Acute toxicity

Guaiacol, syringol and their chlorinated derivatives reveal considerable toxicity towards human and animals. It is considered that guaiacol provokes similar undesirable changes in living organisms like phenol. 2-methoxyphenol easily penetrates skin and epithelium leading to their irritation and inflammation. The serious consequence is also related with contact of guaiacol solution with eyes. Guaiacol is bioaccumulated in blood, kidneys and respiratory tract. When swallowed in a dose not exceeding 2 grams it irritates epithelium of stomach, causes burning pain in oesophagus, provokes vomiting and bloody diarrhoea [10]. Administration of a dose above 2 grams leads to fast decrease of body temperature and weakness. The above mentioned dose may also lead to collapse, pause in heart action and paralysis of central motorial centre. In some cases intoxication with guaiacol may result in disturbance of respiratory processes and thus death of the organism. Clinical data describes death of nine years old child after administration of 5 ml of concentrated 2-methoxyphenol. Guaiacol may disrupt function of immune system as it strongly binds to human immunoglobin (HIgG) by a hydrophobic interaction. This interaction causes alterations of protein's secondary structure leading to conformational changes of HIgG (59). Moreover guaiacol strongly interacts with human serum albumin (HSA) inducing conformational changes of this protein and disturbance in microenvironment of HAS [60]. The investigations leaded on rabbits showed irritation and redness of skin after 24 hours treatment with guaiacol. Low value of LD_{50} = 3,74 mg of guaiacol per kg of body weight for rabbit after oral administration indicates on high toxicity of this compound. Lethal dose of 2-methoxyphenol for mice was evaluated for 400 mg/kg of body weight [10]. Guaiacol provokes hemolysis in cows and damage of epithelium and paralysis of heart muscle in mice. The experiments performed on rats revealed that guaiacol may penetrate and damage embryos of these animals and finally leads to their death. In adult rats it decreases the amount of leucocytes in blood and in a dose of 50 mg causes death of the exposed animals. The experiments performed on 1044 species of fungi isolated from soil confirmed considerable toxic properties of guaiacol. This compound caused inhibition of growth of 33% of investigated species and essential decrease of growth of 22% species [61]. In other investigation guaiacol caused inhibition of growth of 88 species of fungi revealing higher toxicity than phenol and catechol [62].

The toxic effect on organisms is also exerted by chlorinated methoxyphenols. These compounds are present in considerable concentrations in surface waters that are receivers of sewages produced by cellulose-paper plants. The performed analysis revealed toxic impact of 3-chloroguaiacol, 3,4-dichloroguaiacol, 3,4,5-trichloroguaiacol, tetrachloroguaiacol and 3-chlorosyringol on the activity of algae *Selenastrum capricornutum* [63]. The presence of these compounds in aqueous medium leaded to inhibition of growth of investigated species that was raised with increasing number of chlorine atoms substituted in methoxyphenol. The investigations confirmed that tetrachloroguaiacol (TeCG) is one of the most toxic phenols what is related to high number of chlorine atoms and also its persistence to degradation in the environment. Lethal dose of tetrachloroguaiacol for fish is established for 70 to 119 μg/L of water [64]. Tetrachloroguaiacol due to its high hydrophobocity may intensively bioaccumulate in nutritive chain. The content of TeCG in fish tissue is about 1000-fold higher in comparison to its amount in surface water. In physiological pH, tetrachloroguaiacol appears in blood mainly in ionized form (95%) and it is excreted by kidneys and liver. This process leads to accumulation of discussing substance in these organs where its concentration exceeds 10-fold of the amount of TeCG present in blood plasma. Considerably concentration of tetrachloroguaiacol in organs leads to their damage. Moreover, the presence of tetrachloroguaiacol in blood is responsible for accumulation of other xenobiotics by inhibition of organic anion transport even at a dose of 5 μM of TeCG and thus intensification of toxicity exerted by other organic compounds on fish organism [9]. Tetrachloroguaiacol also increases oxygen consumption up to 130% after exposure of rainbow trout (*Oncorhynchus mykiss*) to 96 h-LC_{50} of TeCG. The study showed that toxicity of tetrachloroguaiacol is similar to that exerted by pentachlorophenol [65]. Chlorinated methoxyphenols may also provoke disruptions in reproductive organs of fish, especially in a spawning-time. These findings were confirmed in investigations performed on fish living in river polluted with sewages derived from cellulose-paper plant. The females of the species of *Flexipenis vittatus* living in the water of the polluted river demonstrated changes in the features of morphology of anal fins characteristic to male individuals.

8.2. Genotoxicity and mutagenicity

Methoxyphenols also reveal negative impact on genetic structures. Guaiacol inhibits synthesis of proteins. The investigations performed on rats' hepatocytes showed strong (80%) inhibition of ribonucleic acid after application of water solution of 5 mM of guaiacol. In HeLa cells similar concentration of 2-methoxyphenol caused considerable (50 – 60%) inhibition of RNA synthesis. In another experiment guaiacol inhibited synthesis of deoxyribonucleic acid in embryo cells of hamster. In human lymphocytes guaiacol induced sister-chromatid exchanges (SCEs) and also chromosome aberration [66].In another experiment 2-methoxyphenol provoked sister chromatid exchanges in Syrian hamster embryo cells and its activity was higher than evaluated for 4-methylphenol [11]. Guaiacol is also one of the main compounds formed during tobacco combustion and it is supposed to be responsible for lung cancer development.

Methoxyphenols provoke mutagenesis in aqueous biota. These results were obtained in investigations performed on organisms living in the Baikal Lake (Russia). There were found damages in genetic material of fish and seals living in the areas polluted with effluents derived from cellulose-paper plant [65]. Strong mutagenic activity of chlorinated methoxyphenols was also observed in a bacterial test with *Salmonella typhimurium.*

9. Conclusions

1. Methoxyphenols are wide-spread aromatic substances present in surface waters, soil and atmospheric environment.
2. Those compounds are formed in numerous natural processes, mainly in the result of decomposition of humic substances present in soil and degradation of lignin which is the main component of plant cells' wall.
3. The anthropogenic pollution of the environment with methoxyphenols results from the usage of these substances in industry. Furthermore, the exceeding emission of methoxyphenols to ecosystems is linked to wood and plant wastes combustion (formation of guaiacol, syringol and methyl-methoxyphenols) and also paper and cellulose production (formation of chlorinated guaiacols and syringols).
4. Guaiacol and syringol, and in particularly chlorinated methoxyphenols due to their presence in edibles and drinking water and also exerting considerable toxicity may present the real danger for health of living organisms including human. The threat may be mainly related with chronic exposition of living organisms to low or moderate amounts of these compounds.

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Naturalne i antropogeniczne procesy odpowiedzialne za występowanie metoksyfenoli w ekosystemach i bezpośrednim otoczeniu człowieka

Streszczenie

Gwajakol i syringol należą do grupy metoksyfenoli. Gwajakol pod względem chemicznym jest 2-metoksyfenolem, a syringol 2,6-dimetoksyfenolem. Powszechność występowania metoksyfenoli w środowisku wiąże się z procesami degradacji biopolimerów, tj.: ligniny obecnej w tkankach roślin oraz substancji humusowych przy udziale bakterii oraz grzybów.

Mikroorganizmy i grzyby wyższe zdolne są także do wytworzenia gwajakolu, syringolu oraz chlorowanych metoksyfenoli z niskocząsteczkowych związków o charakterze naturalnym, np.: kwasu ferulowego lub wanilinowego.

W ostatnim kilkudziesięcioleciu, nadmierne przedostawanie się metoksyfenoli i ich pochodnych do środowiska związane jest głównie z aktywnością przemysłową oraz spalania drewna i odpadów. Przykładem może być proces produkcji papieru i celulozy, prowadzący do wytworzenia silnie toksycznych chlorowanych pochodnych metoksyfenoli. Syringol i gwajakol stosowane są także w przemyśle jako składniki oraz związki prekursorowe w produkcji barwinków azowych, pestycydów oraz związków o działaniu przeciwbakteryjnym. Na skalę przemysłową metoksyfenole wykorzystywane są do produkcji waniliny oraz środków antyseptycznych, np.: eugenolu.

Metoksyfenole występują zarówno w glebie, wodach powierzchniowych oraz powietrzu atmosferycznym. Środowiskowe narażenie ludzi na omawiane związki związane jest z konsumpcją wody pitnej oraz żywności, a w szczególności wędzonych serów, wędlin oraz mięsa ryb. Narażenie zawodowe, dotyczy głównie osób zatrudnionych przy produkcji koksu oraz pracowników spalani odpadów przemysłowych i rolniczych.

Liczne drobnoustroje zarówno prokariotyczne i eukariotyczne zdolne są do transformacji metoksyfenoli, z wytworzeniem silnie toksycznych katecholi oraz weratroli.

Związki z omawianej grupy wykazują działanie toksyczne. Toksyczność gwajakolu porównywalna jest z toksycznością fenolu. Gwajakol, chlorogwajakole oraz chlorowane syringole hamują syntezę DNA oraz RNA, związki te wykazują ponadto działanie mutagenne.