LIPIDS AND SECONDARY METABOLITES OF FUNGI IMPERFECTI CAUSING PLANT DISEASES

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The review generalizes information on the composition of the lipids and the structure of the secondary metabolites of phytopathogenic Fungi Imperfecti. The chemical properties of the main classes of lipids, their biosynthesis, their interconversions, and their possible role in the mutual relationships with the plant host are discussed. Methods for the diagnosis and practical ways of finding chemical agents for the fight against infectious diseases of plants are substantiated theoretically.

Of the one hundred thousand species of fungi existing in nature, 30% belong to the class of Fungi Imperfecti (Deuteromycetes). Many of them are the causative agents of various diseases of plants. Thus, for example fungi of the genus *Verticillium* of the order Hyphomycetes (Hyphales), family Moniliaceae alone attack more than 650 species of plants, including the cotton plant [1, 2].

Fungi of the class Deuteromycetes differ from other microorganisms by their capacity for synthesizing a large amount of lipids [3], the role of which in many infectious diseases is extremely important, since lipids, being components of biological membranes, may actively participate in interactions of micro- and macroorganisms [4-8]. It is assumed that the functional value of the membrane lipids of microorganisms is determined by the site of their localization, the complexity of their structure, and the rapidity of the change in their composition during the adaptation of the cell to a change in the conditions of the external environment [9-12]. At the present time, even more facts are being accumulated which indicate that the composition of the lipids and their metabolism represent precisely those features which determine the taxonomic individuality of fungi, the differentiation of species, their sensitivity to fungicides, and the type of pathogenesis [13].

Fungi Imperfecti are characterized by anatomical features and a metabolism that is characteristic of both plant and animal organisms. On the evolutionary plant, they are some of the most ancient microorganisms and possess the characteristic capacity for producing toxins for animals and plants [14].

It is known that the biosynthesis of lipids and that of biologically active secondary metabolites of the oligoketide type that participate in some way in the fungus–parasite and plant-host interrelationships are closely connected and are catalyzed by the same enzymes, as the result of which a common set of biosynthetic intermediate compounds is formed.

The widest investigations have been devoted to establishing the chemical nature and biosynthetic pathways of the lipids of fungi (mainly yeasts and filamentous fungi) [9, 10, 13, 15-19] and also to the investigation of the secondary metabolites produced by them [9]. The capacity of the majority of phytopathogenic fungi for producing lipids has been studied fairl well, but differences in the conditions of their cultivation and isolation do not permit the results of different authors to be compared.

With respect to their total lipid content, fungi can be divided into three main groups with a low (less than 4%), a medium (between 4 and 8%) and a high (more than 10%) lipid content [18].

The Fungi Imperfecti *V. dahliae* Kleb. and *Fusarium sporotrichiella* Bilai, like others, belong to the fat-producing fungi [20, 21]. In the general case, the amounts of lipids in

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the Fungi Imperfecti range from 1 to 50% of the total dry mycelium and depend on the type of fungus, the stage of growth, and the conditions of cultivation [18]. The most profound influence on the synthesis of lipids is exerted by such factors as the source of carbohydrate and inorganic nutrition, the temperature, the pH of the medium, aeration, and vitamins [18, 19, 22].

The best substrate for the growth of fungi consists of carbohydrates. Thus, in a study of the capacity of a number of fungi (*Aspergillus, Fusarium, Verticillium, Pencillium,* and others) for utilizing various mono- and disaccharides, it has been established [23-26] that the largest amount of lipids is synthesized in fungi when they are cultivated on media containing sucrose, glycerol, glucose, fructose, galactose, raffinose, starch, and inulin.

Increased aeration of the culture medium of *V. dahliae* as of other members of the Fungi Imperfecti leads to an increase of fat-formation [11]. A high level of lipids in the cells of pathogenic and nonpathogenic strains of fungus *V. dahliae* grown under conditions of increased aeration is one of the most important factors providing the energy of growth of the Oidial structures [11].

Lipids are subdivided into polar and neutral. Of these two large groups, the polar lipids have been less studied. The available information relates mainly to the phospholipids of yeasts [27]. Relatively recently, information has appeared also on the phospholipids of phytopathogenic fungi [28]. The interest in the study of phospholipids is due to their importance in connection with the activity of the enzymes of the cell membranes [29-31].

The neutral lipids of the Fungi Imperfecti have been found to contain hydrocarbons, methyl esters of fatty acids, mono-, di-, and triacylglycerols, free fatty acids, sterols, carotenoids, naphthoquinones, and other classes of compounds [18, 20].

The hydrocarbon chains of the alkanes of the spores of phytopathogenic fungi are mainly from 18 to 35 carbon atoms long with a predominance of the C_{27}, C_{29}, and C_{31} alkanes. The distribution of the alkanes in the spores, together with other indices, can serve as a taxonomic characteristic of the phytopathogenic fungi [18]. It has been suggested that the role of the alkanes in the spores consists in protecting them from drying out and from other extreme effects [18].

Methyl esters of fatty acids have been detected in the lipids of the Fungi Imperfecti (*V. dahliae*) only recently [20, 32, 33]. They have previously been found in maize pollen [32, 33], the surface waxes of higher plants [37] and of fresh-water algae [35], and in the seed oils of higher plants [32-34]. It is assumed that these compounds participate in the detoxification of the cell and affect the auxin and gibberellin activity of the plant [36].

The main components of the lipid fraction of the cytoplasm of the mycelium and the spores are triacylglycerols. Their amount depends on the conditions of cultivation and the stage of growth of the fungi. An increased amount of fungal lipids is formed in the juvenile (yeast) stage of development [3]. In different strains of *V. dahliae* the triacylglycerols amount to 60 to 80% of the total amount of neutral lipids [11, 20]. The high level of these substances is one of the main conditions of the maintenance and propagation of a fungus in a natural population [11].

Chemical investigations of the triacylglycerols of the Fungi Imperfecti are sparse. The type and species compositions of the triacylglycerols of the pathogenic fungus Beaveriatnella, family Moniliaceae, have been studied [37].

The main type of triacylglycerols of this fungus is the SU_2 type (where S is the sum of the saturated fatty acids and U is the sum of the unsaturated fatty acids) with the unsaturated acids being present predominantly in position 2 of the glycerol, which is characteristic of the majority of plant oils. The main types of triacylglycerols of *V. dahliae* are U_3 and SU_2 [20]. The role of the triacylglycerols in fungi and microorganisms, particularly in bacteria, differ substantially from their role in higher plants and animals.

There is information on the phytotoxic action of triacylglycerols. For example, the fungus *Cercospora beticola* produces phytotoxic triacylglycerols containing octadecenoic (18:1), octadecanoic (18:0), octadecadienoic (18:2), octadecatrienoic (18:3), and hexadecanoic (16:0) acids [38]. It has been established that the phytotoxic triacylglycerols of *V. dahliae* possess a monuron-like action on the cotton plant [39]. The mechanism of the phytotoxic action of triacylglycerols has been little studied, but it is known [40], that they lower the rate of photosynthesis in the leaves, which is apparently connected with a disturbance of gas-ex-

change and also of water supply [41]. Since the phytotoxic triacylglycerols contain fatty acids, it is assumed that the acids decrease the rate of respiration in plants, but it is doubtful whether this physiological effect can be an important factor in the toxic action of the triacylglycerols. A more likely hypothesis is [41] that the phytotoxic oils have a tendency to accumulate in the plasmatic membrane and thereby to increase its permeability and, in extreme cases, to destroy the protoplast completely.

The opinion has been expressed that in the future, natural phytotoxic agents, including phytotoxic triacylgycerols will undoubtedly be widely used as general herbicides [41].

Triacylglycerols are also present in the extracellular lipids of yeasts and the Fungi Imperfecti [3, 42, 43]. The extracellular lipids cannot be considered as a reserve source of carbon nutrient and energy, since the living medium of yeasts and other agents producing exolipids usually contain a considerable amount of carbon [3].

The presence of extracellular lipids in the products of the vital activity of *V. dahliae* and other microorganisms gives grounds for assuming that a not unimportant role in pathogenesis (as virulence factors) can be played by "hypothetical toxins'" which are the products of the peroxide oxidation of lipids and other extracellular organic substances and which have not yet been identified because of their extreme lability. The possibility of the existence of the "hypothetical toxins" in other microorganisms as well has been widely discussed in the literature [44].

The composiition of the bound and free fatty acids of the lipids of fungi is wider and the structure of the acids is more complex and more diverse than in plants and animals. The amount of free fatty acids is determined by the virulence and mechanism of the pathogenesis of the microorganism.

It has been established that a high content of free fatty acids (about 20%) is characteristic for strongly virulent strains of the fungus *Verticillium dahliae* [45], while their amount in the nonvirulent strains is considerably smaller [11]. For this reason, the microorganisms are more resistant to a change in the external conditions [22].

The Fungi Imperfecti produce mainly 17 different acids with medium and long chains, the chief representatives of which are the 18:1, 18:2, 16:0, and 18:0 acids. In all the species of Fungi Imperfecti studied, the sum of the unsaturated fatty acids always exceeds the sum of the saturated fatty acids.

The composition of the fatty acids changes not only according to their localization in the cell and the period of development of the microorganisms but also under the influence of various factors of the environment.

As has already been mentioned [46], a lowering of the temperature of growth of the fungi increases the degree of unsaturation of the total acids. A similar correlation between the temperature conditions and the degree of unsaturation of the fatty acids is known for higher plants [47]. The qualitative and quantitative composition of the free acids is also affected by the source of carbon nutrition. Thus, for the fungus *V. dahliae* as an example it has been shown that when using sucrose as a nutrient in place of glucose none of the 18:2 acid is formed either during growth in a fermenter or under steady-state conditions. Other media favor the formation of the 18:3 acid [26]. When *V. dahliae* is grown on a medium containing hulled millet grain the formation of pentadecanoic (15:0) and of saturated iso-acids is observed [26]. The composition of the lipids and fatty acids of *V. dahliae* is affected not only by the source of carbon nutrition but also by the inorganic nutrients [18, 48].

Thus, on the addition of ions of iron, zinc, vanadium, copper, and cobalt to the nutrient medium, the variety of fatty acids increases greatly, particularly in the free-fatty-acid fraction (from $C_{9:0}$ to $C_{20:0}$) [48].

Among the minor fatty acids of the Fungi Imperfecti have been found acids with odd numbers of carbon atoms (13:0, 15:0, and 17:0) with carbon chains having 20 and more atoms (C_{20}-C_{24}), and acids with a high degree of unsaturation (18:3, 20:4) [18]. In addition, it has been shown that certain species of fungi have a tendency to accumulate some "unusual" fatty acids, i.e., those the structure of which differs from the structure of the widely distributed acids [46, 49, 50].

Of the unusual acids in higher fungi, acetylenic, branched, hydroxy- and epoxy-substituted, and other acids have been found [18, 19].

From the neutral lipids of *V. dahliae* grown on Czapek-Dox medium has been isolated 9,10-dichlorostearic acid [51a], which possesses a powerful toxicity for animal organisms [52] and a phytotoxic action on the cotton plant.

There is information in the literature on the existence and biosynthesis of halogen-containing compounds in microorganisms [53, 54]. The majority of them have a terpenoid nature. The structure of one of the halogen-containing compounds isolated from a *Fusarium sp.* fungus has been established [54]. The composition and amount of chlorohydrins of unsaturated fatty acids in the lipids of jellyfish have been determined [55]; the following were isolated by gas–liquid chromatography and identified by mass spectrometry: 9-chloro-10-hydroxy- and 10-chloro-9-hydroxypalmitic acids, 9-chloro-10-hydroxy- and 10-chloro-9-hydroxystearic acids, and 11-chloro-12-hydroxy- and 12-chloro-11-hydroxystearic acids.

In some species of fungi, the unusual fatty acids are localized in the lipids of the spores. The compositions of the fatty acids of the spores of fungi are, in the majority of cases, quantitatively similar to the composition of the parent mycelium [18]. In extracts of the spore walls of *Verticillium albo-atrum* and some other fungi [49] from 10 to 18 fatty acids have been detected, and from the surface layer of the spores from 21 to 31 fatty acids, among which saturated acids predominated. Investigations of the lipids of the spores of parasitic fungi have shown that they contain the unusual cis-9,10-epoxyoctadecanoic acid [19], and threo-9,10-dihydroxystearic acid is present in the lipids of some species of rust fungi [46, 56]. The hydroxy acids found in other fungi are mainly of the C_{16} and C_{18} series with a hydroxy group on carbon 3, 8, 12, or 18 [18].

The biological role of fatty acids consists, on the one hand, of their influence on various biochemical processes taking place in the cells of the Fungi Imperfecti. For example, oleic acid is a growth factor of many microorganisms [22] and can inhibit the ATPase of plasmatic membranes [57]. A number of fatty acids possess phytotoxic properties of antibiotic activity [59-62].

On the other hand, fatty acids affect the intensity of respiration and the synthesis of protective substances (phytoalexins and progibbitins) in plant cells. In addition, it is known that biological activity is possessed mainly by free fatty acids, and in many cases the esters of the acids lose their activity. The authors of the present paper have established that the lipid fraction and secondary metabolites of *V. dahliae* cause the browning of the conductive vessels of cotton-plant shoots and the induction and accumulation of phytoalexins in the cotton plant. Since the virulence of strains of the fungus *V. dahliae* correlates with their free fatty acid content, it is not excluded that the inducing activity of the lipid fraction of *V. dahliae* is due to an increased amount of fatty acids in it. This hypothesis is in harmony with the results of Avazkhodzhaev et al. [83a] on the isolated lipid fraction of the protein-lipid-polysaccharide complex (PLPC) of *V. dahliae*, and also with the results of Ersek [83b] on the inducing action of the lipids of the mycelium of *Phytophthora infestans* on the accumulation of phytoalexins in potato tubers. The information available at the present time shows the necessity for studying the lipids of the Fungi Imperfecti in vivo, and also of the lipids of various plant organs in the norm and under disease conditions. Particular interst in the study of the acid-containing fractions of the lipids is presented by the unusual fatty acids, since it is known that the presence of such acids may be the result of the action of various stress factors on the cell [79].

Unfortunately, the information on the usual fatty acids of the cotton plant and other plants attacked by wilt is extremely sparse. In the literature, the composition of the lipids and fatty acids and also the composition of the phospholipids of the various organs of the cotton plant in the norm have been analyzed, in the main [63-73]. Of the unusual fatty acids of the lipids of higher plants, interest is presented by di- and tetrabromostearic acids, which have recently been found in the seed oil of one of the wild species of plants of the family Labiatae [74]. There is information that plants of this family are considerably affected by wilt [75].

Hydroxy acids have been found in the seed oil of the wilt-resistant variety of the cotton plant Tashkent-1 [76].

It is known [77, 78] that the function of hydroxylation and halogenation in microorganisms and plants is fulfilled by a hydroxylating or halogenating (chlorinating, brominating) peroxidase. The presence of hydroxyl- and halogen-containing unusual fatty acids in plant seeds shows a control of enzyme-substrate compartmentalization and specificity in the biosyn-

thesis of the substances [79]. When plant tissues are damaged by infection, apparently, the control of the biosynthesis of fatty acids at the cell level is lost and unusual fatty acids are formed as a consequence of enzymatic reactions which, in healthy tissues, must be inactivated [79]. Consequently, from the amount of unusual fatty acids present it is possible to judge the activity of the enzymatic reactions and thereby the resistance of the plants to attack by infection. On the other hand, the presence of unusual fatty acids in microorganisms makes it possible to judge indirectly the degree of their virulence.

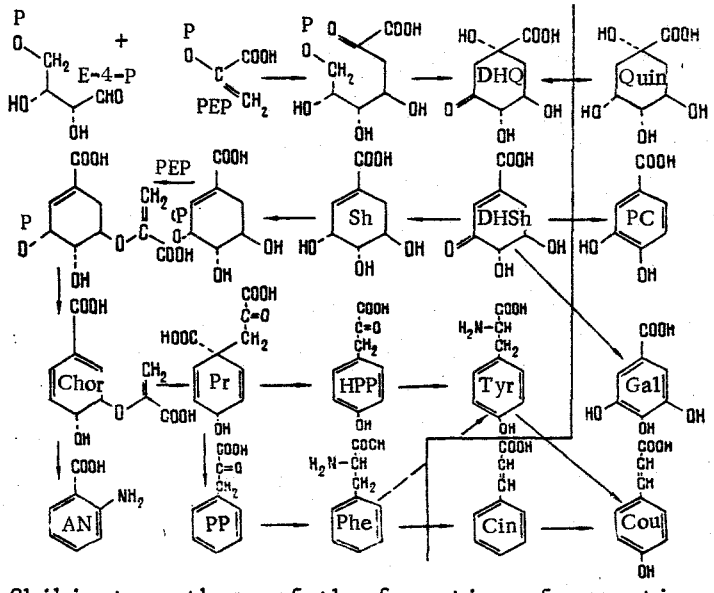
An interesting class of lipids — cyclic depsipeptides — has been found in fungi, actinomycetes, and bacteria.

The structure of these compounds usually consists of regularly alternating α-hydroxy acids and α-amino acids. A publication has recently appeared on the establishment of the structure of an insecticidal cyclodepsipeptide isolated from the mycelium of *Verticillium lecanii* [80]. It is assumed [19] that in the spore-forming stage these compounds are included in the coat of the fungal spores and are therefore connected with processes of cell differentiation.

Cyclic depsipeptides possess an antimicrobial activity, which shows their special biological importance [19]. A large set of fatty acids has been found in the composition of the PLPC isolated from *V. dahliae* and *V. albo-astrum* and consisting of 70% of polysaccharides, 15% of protein, and 15% of lipids. Its lipid fraction includes 11 fatty acids, the main ones being the 16:0, 18:1, and 18:2 acids [81, 82]. It has been established that the PLPC possesses a phytotoxic action. The physiological activity of the PLPC is apparently connected with the lipid component, since after hydrolysis of the PLPC and separation of the lipids, the protein and polysaccharide components are inactive [83].

At the present time, considerable advances have been achieved in the study of the secondary metabolites of microorganisms [84, 85]. Many of these substances possess a high biological activity, some being phytotoxins and others phytoalexins (Tables 1 and 2).

Two pathways of the biosynthesis of secondary metabolites that are the most characteristic for fungi are known [86, 87]. The first pathway is through shikimic acid, which is formed in the pentose phosphate cycle with the subsequent synthesis of aromatic amino acids and their derivatives (Scheme 1) [68]. The second pathway for the biosynthesis of secondary metabolites



Scheme 1. Shikimate pathway of the formation of aromatic compounds [68]: E-4-P) erythrose 4-phosphate; PEP) phosphoenolpyruvic acid; DHQ) dehydroquinic acid; DHSh) dehydroshikimic acid; Chor) chorismic acid; Pr) prephenic acid; HPP) hydroxyphenylpyruvic acid; Phe) phenylalanine; Cin) cinnamic acid; Cou) p-coumaric acid; An) anthranilic acid; Quin) quinic acid; PC) protocatechuic acid; Gal) gallic acid. The lines in the scheme separate the primary and secondary products.

TABLE 1. Phytotoxins and Secondary Factors of the Virulence of Fungi Imperfecti

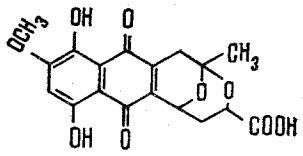
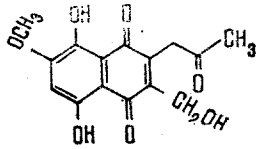
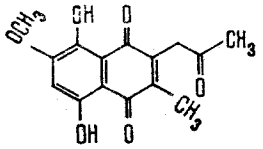
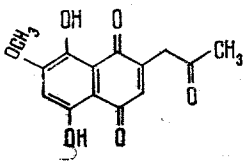
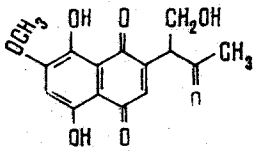
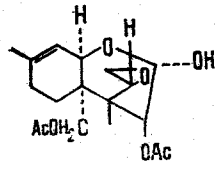
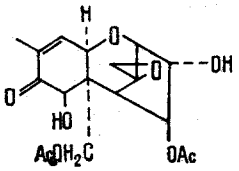
Substance	Structure	Source of isolation
1. Marticin		Fusarium solani [90]
2. Fusarubin		Fusarium solani [90]
3. Javanicin		Fusarium solani [90]
4. Norjavanicin		Fusarium solani [90]
5. Novarubin		Fusarium solani [90]
6. Diacetoxy-scirpenol		Fusarium roseum [91]
7. $C_{19}H_{24}O_9$-toxin		Fusarium roseum [91]

TABLE 1 (continued)

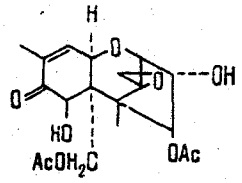
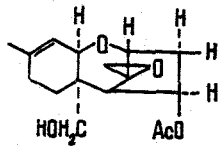
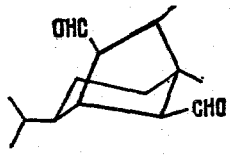
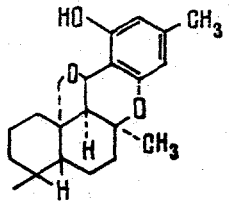
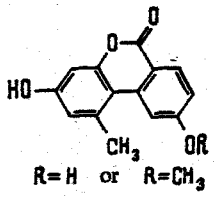
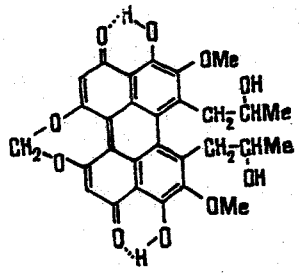
Substance	Structure	Source of isolation
8. $C_{21}H_{28}O_{10}$-toxin		Fusarium roseum [91]
9. Trichodermin		Trichoderma viride [91]
10. Helmintosporol		Helmintosporium sativum [91]
11. Siccanin		Helmintosporium siccans Drechsler [38]
12. Alternariol and its monomethyl ether		Alternaria zinniae [38]
13. Cercosporin		Cercospora beticola [38]

TABLE 1 (continued)

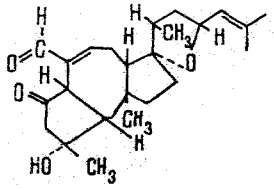
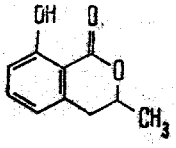
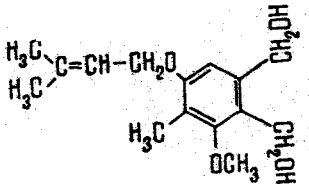
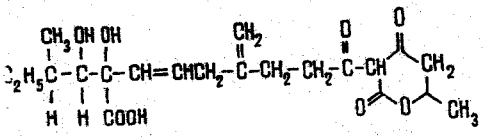
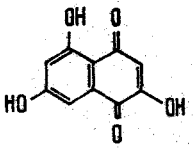
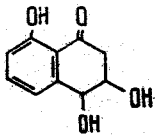
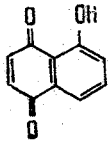
Substance	Structure	Source of isolation
14. Ophiobolin A		Helmintosporium oryzae [38]
15. Mellein		Aspergillus melleus [92]
16. Zinniol		Alternaria zinnie [38]
17. Alternaric acid		Alternaria kikuchiana [38]
18. Flaviolin		Verticillium dahliae [93, 94]
19. 3,4,8, Trihydroxy-1,2,3,4-tetrahydrons phthalen-1-one		Pyricularia oryzae [95]
20. Juglone		Verticillium dahliae [94]

TABLE 1 (continued)

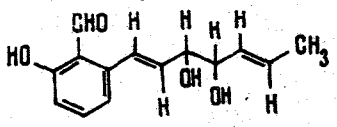
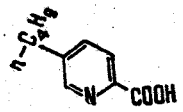
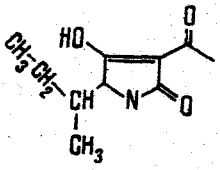
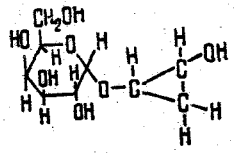
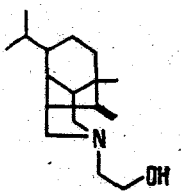
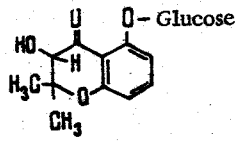
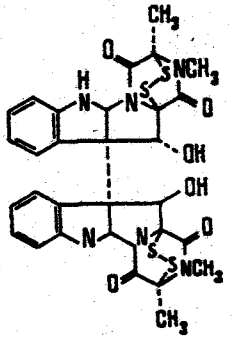
Substance	Structure	Source of isolation
21. Pyriculone		Pyricularia oryzae [95]
22. Fusaric acid		Fusarium oxysporum (Schl./Sny et Hans) [90]
23. Tenuazonic acid		Pyricularia oryzae [95]
24. Helmintosporoside		Helmintosporium sacchari [97]
25. Victoxinine		Helmintosporium victoriae [97]
26. Stemphylin		Stemphylium botryosum [97]
27. Verticillin A		Verticillium dahliae [98]

TABLE 1 (continued)

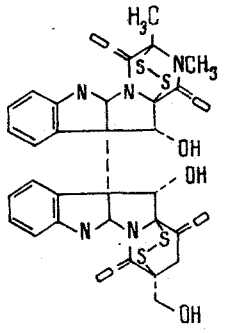
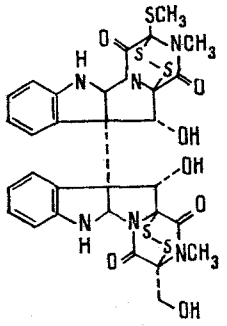
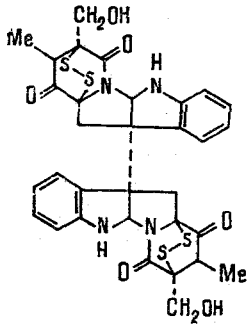
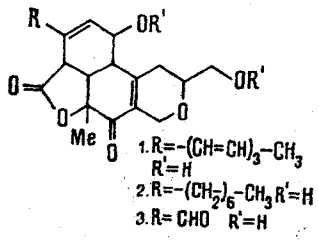
Substance	Structure	Source of isolation
28. Verticillin B		Verticillium dahliae [98]
29. Verticillin C		Verticillium dahliae [98]
30. 11α,11α'-Dihydroxychaetocin		Verticillium tenerum [99]
31.	 1. R=-(CH=CH)$_3$-CH$_3$ R'=H 2. R=-(CH$_2$)$_6$-CH$_3$ R'=H 3. R=CHO R'=H	Epicoccum purpurascens [856]

TABLE 1 (continued)

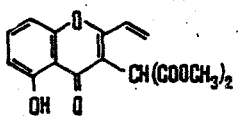
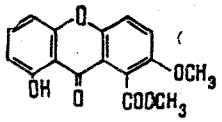
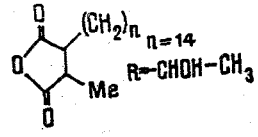
Substance	Structure	Source of isolation
32		Mycosphaerella rosigena [856]
33		
34.		Aspergillus wentii [856]

TABLE 2. Phytoalexins and Plant Progibbitins

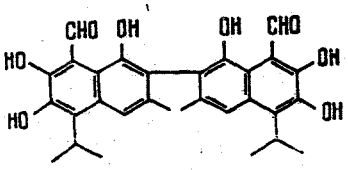
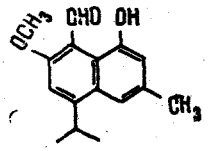
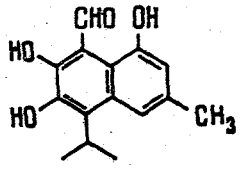
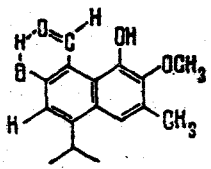
Substance	Structure	Sourceof isolation
1. Gossypol		Gossypium hirsutum L., Gossypium barbadense L. [100]
2. Vergosin		Gossypium hirsutum L., Gossypium barbadense L. [101]
3. Hemigossypol		Gossypium hirsutum L. [101]
4. Gossivertin		Gossypium hirsutum L., varieties 108-F, Tashkent-1, and Tashkent-3 [102]

TABLE 2 (continued)

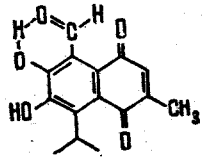
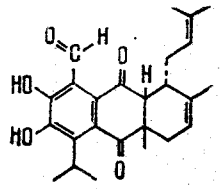
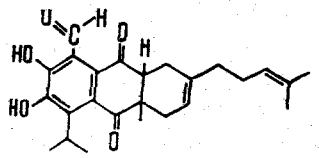
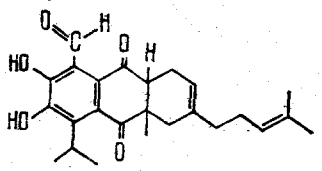
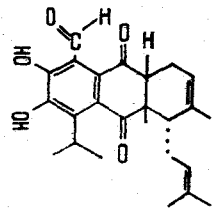
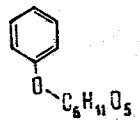
Substance	Structure	Source of isolation
5. Hemigossypolone		Gossypium hirsutum variety 108-F [103, 104]
6. Heliocide H[1]		Gossypium hirsutum L. [106]
7. Heliocide H[2]		Gossypium hirsutum L. [108]
8. Heliocide H[3]		Gossypium hirsutum L. [107]
9. Heliocide H[4]		Gossypium hirsutum L. [106]
10. Arbutin		Pyrus communis, P. molus [109]

TABLE 2 (continued)

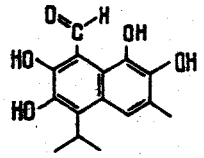
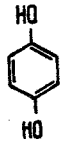
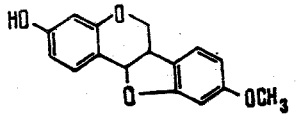
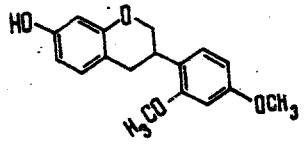
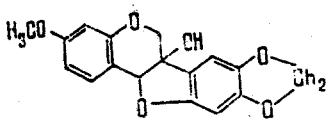
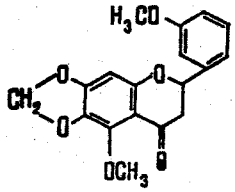
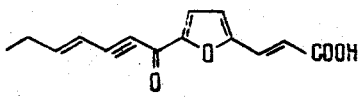
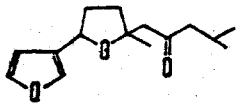
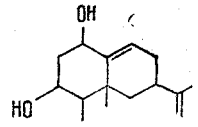
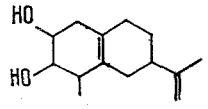
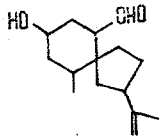
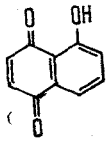
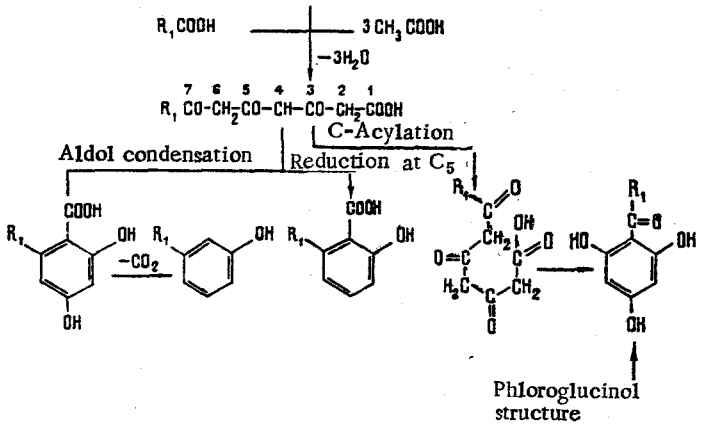
Substance	Structure	Source of isolation
11. Isohemigossypol		Gossypium hirsutum L. [105]
12. Hydroquinone		Pyrus communis, P. malus [109]
13. Medicarpin		Canavalia ensiformis [97]
14. Sativan		Lotus corniculatus [97]
15. Pisatin		Pisum sativum [97]
16. 6,7-Methylenedioxy-2',5-dimethoxy flavanone		Beta vulgaris [97]
17. Wyeronic acid		Vicia faba [97]
18. Ipomeamarone		Ipomoea batatus [97]

TABLE 2 (continued)

Substance	Structure	Source of isolation
19. Capsidiol		Capsicum frutescens [97]
20. Rishitin		Lycoperisicon esculentium, Solanum sp. [97]
21. Lubimin		Solanum sp. [110]
22. Juglone		Juglane regia [109]
23. Safynol	$CH_3CHCH(C\equiv C)_3$ $CHCHCH(OH)CH_2OH$	Carthamus tinctorius [97]

is the acetate pathway, leading to the formation of fatty acids and their derivatives, polyketides, steroids, terpenes, naphthoquinones, and other compounds classified [18, 88] as lipids (Scheme 2) [89].



Scheme 2. Acetate pathway of the biosynthesis of phenolic compounds [89].

Phytotoxins have been detected among the steroid secondary metabolites of the Fungi Imperfecti. For example, a steroid phytotoxin from *Fusarium oxysporum f. niveum* in biotests causes the symptoms of wilt in tomato plants [38].

Sterols are important components of cell membranes of lower fungi [18, 19], and their synthesis varies considerably as the result of the action of extremal factors on the cell [111, 112].

The amount of sterols in pathogenic strains of fungi is higher than in nonpathogenic strains [11, 113]. These facts have permitted the hypothesis [11] that the increased synthesis of sterols in pathogenic strains leads to the neutralization of the fungicidal metabolites of plants (various phenols and their derivatives).

The total composition of the sterols of representatives of the lower fungi, including phytopathogenic fungi, has been little studied, just like their role in pathogenesis.

At the present time, about 50 compounds of this class have been detected in fungi [19], the main ones being cholesterol and ergosterol [114, 115], and ergosterol peroxide and cerevisterol [116].

However, the available reviews on the sterols of fungi mainly consider the yeast sterols [18, 19, 117, 118], and it is reported [19] that ergosterol is the main representative of this class of sterols in yeasts. The presence in fractions of fungal sterols of 7,8-dihydroergosterol was unusual [19], but no information was given on the role of this substance in dermatophytoses.

Highly toxic sterol lactones have been found in the sterol fraction of *Fusarium sporotrichiella* Bilai [21].

In one of the papers of [119], features of the biosynthesis of sterols in plants and fungi, and also the role of plant steroids in their interrelationships with individual phytopathogenic fungi, are discussed. An antibiotic activity of certain steroids and their capacity for binding a number of toxins are mentioned. The opinion is expressed that it is desirable to use sterols as targets for the fight against phytopathogenic fungi. It is suggested that a genetic link exists between mycotoxins of steroid nature and mycotoxins belonging to the trichothecene group [21].

A fairly large series of phytotoxic compounds found in the lipids of the lower fungi have a terpenoid nature. As an example we can give the toxic diacetoxyscirpenol (Table 1) and some of its derivatives, which are produced by many microorganisms, including *Fusarium roseum* and *F. scirpi*. All these compounds are derivatives of 12,13-epoxytrichothecenes [91] and were first found in the screening of gibberellins. 12,13-Epoxytrichothecenes possess a high cytotoxicity which is due, in the opinion of Dawkins and Grove [120], to the presence of an epoxy group in their structure.

Of pigments in the lipids of the lower fungi, compounds of the carotene and quinone series and melanins have been detected. A detailed review of the present state of the chemistry of fungal carotenoids, including phytogenic compounds, has been given by Valadon [121]. Consequently, we shall not dwell on a discussion of this class of pigments. We may note only the fact that the chemical study of the carotenoid pigments of fungi of the genus *Verticillium* has begun quite recently and it is just among the pigments of the fungus *V. agaricinum* that methyl β-apo-4-carotenoate has been found [122]. The carotenoid pigments are localized mainly in the intracellular lipids of fungi. The role of the carotenoids in the Fungi Imperfecti is that they participate in the transport of oxygen and in cell differentiation processes [123] and protect enzymes localized in the cell membrane from photooxidation and the action of a number of chemical compounds.

In recent years, in connection with the discovery of the capacity of microorganisms for forming free radicals during spore-formation, the role of pigments in the processes of the multiplication of lower fungi has been investigated. The trisporic acids formed from a carotene molecule are regulators of one of the stages of the sexual processes of lower fungi and affect the amounts of the components in the electron-transfer chain, sterol-formation, and lipogenesis [123]. As investigations of the last few years have shown, regulators of the sexual reproduction of the lower fungi can also be used as plant growth regulators.

Quinones, including napththoquinones, make up the bulk of the other pigments of fungi that belong to the nonspecific phytotoxins. Phyllosinone, phyllostine, helicobaside, oosporein, and corcosporin have been detected in the Fungi Imperfecti and other microorganisms [38]. The main naphthoquinone pigments of phytopathogenic fungi are shown in Table 1. The biosynthesis of the quinone pigments takes place mainly by the acetate pathway. The most typical representatives of the naphthoquinones isolated from the products of the vital activity of the Fungi Imperfecti are the red pigments [123]: flavolin (*V. dahliae*, *Aspergillus sp.*), fusarubin (*Fusarium solani*), marticin (*Fusarium solani*), and others (Table 1). Marticin and isomarticin, which are produced by *Fusarium solani f. sp. pisi.*, possess a high phytotoxicity [90].

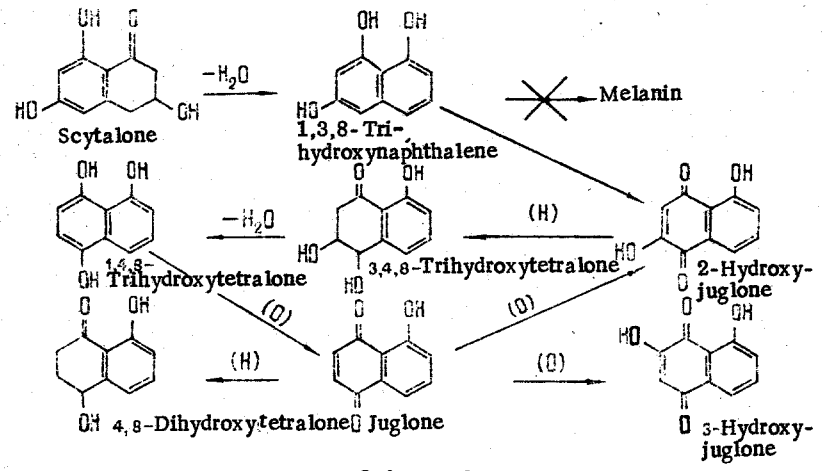
Depending on their pathogenicity, various species of fungi of the genus *Fusarium* produce different amounts of naphthoquinone pigments [90]. Strongly pathogenic fungi such as *Fusarium solani* form more than 150 mg of marticin per liter of medium, while the weakly pathogenic

species *Fusarium solani f. sp. pisi* form considerable amounts of fusarubin and only traces of marticin.

A phytotoxic metabolite of which the chromophoric group is flaviolin has been isolated from the culture liquid of *Verticillium dahliae* [94, 124-127]. The amount of this metabolite in *V. dahliae* also correlates with the pathogenicity of the strain [45]. Another five naphthoquinone pigments of the juglone series having an orange coloration have been found in the culture liquid of the mutant strain brm-2 of *Verticillium dahliae*, and straw-yellow compounds of the indole series — verticillins A, B, and C (Table 1) — have been isolated from the mycelium of *Verticillium spp.* [96, 98].

The role of hydroxyphthalic acid and of phathalic anhydridein the biosynthesis of naphthoquinones is a matter of discussion [128]. Phthalates possessing a toxic action on higher organisms [131], especially di-2-ethylhexyl phthalate, have been identified in the phytotoxic fractions of the lower fungi [129-132]. Particular interest is presented by a large group of polymeric pigments varying in color from light brown to yellow but biologically and chemically related to the black or dark brown pigments that are known under the name of melanins [133]. Many workers have reported the production of melanins by fungi of the genera *Verticillium* and *Fusarium* [134-136]. The main precursor in the biosynthesis of the melanins is the pentaketide metabolite (+)-3,6,8-trihydroxy-1,2,3,4-tetrahydronaphthalen-1-one (scytalone) isolated from mutants of *V. Dahliae* in which the synthesis of melanin had been blocked [93]. It is assumed that intermediates other than scytalone in the biosynthesis of melanins in fungi may be pyrocatechol (*Ustilago maydis* and *Verticillium spp.*) and 3,4-dihydroxyphenylalanine (DOPA) and DOPA derivatives (*Aspergillus nidulans, Phomopsis spp.* and *V. Dahliae*), and 1,8-dihydroxynaphthalene (*Daldinia concentrica, T. basicola, V. dahliae*) [137]. As is assumed [137], the melanin of *Verticillium dahliae* consists of 1,8-dihydroxynaphthalene subunits. The same or similar allomelanins are apparently present in many other fungi, since pentaketides are widely distributed among the lower fungi and actinomycetes containing black and brown pigments [95].

Scheme 3 shows how the secondary metabolites of *V. dahliae* can participate in the biosynthesis of naphthoquinones and melanins [96].



Scheme 3

The search for the enzyme system responsible for pigmentogenesis has shown that in extracts of the microsclerotis of *V. albo-atrum* there is an active peroxidase which apparently also plays the main role in the synthesis of melanin [137].

It has been established that in *V. agaricinum* the synthesis of naphthoquinones takes place on growing in the dark only when hydrogen peroxide is present in the medium [123].

The main biological function of the melanins of the Fungi Imperfecti is the protection of the cells from lysis and from various types of radiation acting as a severe ecological selection factor [133]. It is also considered that these pigments take part in the mechanism of cell detoxication in the final stages of the growth of the fungus [123].

Recently, even more facts in favor of the hypothesis that the pathogenic properties of the Fungi Imperfecti are connected with the secondary metabolites have accumulated [138].

The secondary metabolites, including the napththoquinones and naphthazarin pigments of

the healthy and diseased cotton plant, and also of other plants, are being widely investigated in view of the fact that a large role is assigned to them in the resistance of the cotton plant to wilt.

In spite of the fact that the role of lipids and of the lipid metabolism in the interrelationships of plant and parasite have still been little studied, the significance of the lipid metabolism of the Fungi Imperfecti both in the result of the plant—parasite interactions and also in the determination of the routes and methods of the fight against plant diseases is obvious. Apparently, the adaptive regulation of the function of the molecules is of decisive importance in the outcome of the interrelationships of the micro- and macroorganisms.

The sparse information available in the literature indicates that in the plant and the fungus the adaptive biochemical reactions are similar in certain respects [97].

The action of extremal factors on the fungal parasite and plant host leads to a change in the mechanism of their biochemical adaptation which, at the level of the lipid metabolism, is shown in a change in the amount of lipids, changes in their composition and molecular structure in a particular system of the organism, particularly in the cells of the fruit-bearing organs, and in the adaptive regulation of the functions of the lipid components.

A single given compound participating in cell metabolism may fulfill various functions according to the action of the surrounding factors. It has been reported previously that the action of extremal factors lead to the synthesis in plants and fungi of secondary metabolites: alkaloids, anthraquinones, fatty acids, pigments, etc. Some of these compounds may fulfill the function of fungal phytotoxins and others of phytoalexins in plants.

At the same time, the secondary metabolites can also be bioantioxidants of lipids. A marked deviation from the normal oxidation of lipids in the organism leads to the development of "autoxidative disease" [7], by which is understood a disturbance of the mechanisms controlling this oxidation. The appearance of peroxides in plant tissues is one of the important factors of the action of attacking agents such as phytotoxins, etc. [139].

It is known that oxidative processes regulated by oxidases are activated in fungi in the juvenile phase and in plants in the flowering and fruit-bearing stage [3, 97, 109, 140].

In view of the fact that the synthesis of fatty acids and of secondary metabolites in fungi is a maximum in the juvenile phase [3] and in plants in the flowering and fruit-bearing stage [109, 141], it must be assumed that the most favorable moment for the beginning of the development of a disease is the time when these periods of development of the two organisms coincide. The capacity of the Fungi Imperfecti, as of some other microorganisms, of synthesizing an increased amount of intracellular lipids and readily oxidized exolipids in the juvenile phase gives grounds for assuming the presence in the phytopathogenic fungi of such an injurious factor as the products of the peroxide oxidation of lipids, which possess a toxic action ("spontaneous toxins") [139, 142-144].

It has been established that two types of oxidation — free-radical and enzymatic — exist in the cell in competing relationships [139]. The biological mechanism of the action of bioantioxidants consists in a displacement of the competitive relationship in favor of enzymatic oxidation. The accumulation of information on the antioxidant activity of the secondary metabolites and their synthetic analogs will permit us to find the most effective inhibitors of radical processes, which may prove to be effective agents in the fight against the development of various infectious diseases of plants. An example may be a study of the use of inhibitors of radical processes of the oxidation of lipids as a means of combating the development of a tumoral process in the organs and tissues of the potato [145].

One of the methods for the early diagnosis of plant diseases is the study of the peroxide oxidation of lipids in the biological membranes of the cells of the diseased plant and the investigation of the kinetic laws characteristic for chain reactions [139]. Reports have appeared confirming the promising nature of the above-mentioned approach in the development of the theoretical foundations and practical answers to questions of the pathogenesis of infectious diseases of plants [126, 139, 146-150].

Information on the connection of the secondary metabolism with the mechanism of the reproduction of the species shows that in some cases the substances obtained by modifying the intermediates in the biosynthesis of the secondary metabolites may be an effective means for fighting against a plant disease [151]. Thus, for example, 2,3-dichloro-1,4-naphthoquinone inhibits the growth of fungi of the genus *Fusarium* [152] and is effective as an antiwilt agen

Control of a plant disease may be based, on the one hand, on reinforcing fungitoxicity within the plant host or of the resistance mechanisms of the host [97] and, on the other hand, on a change in the pathogenic properties of the fungus parasite, which in the Fungi Imperfecti are connected with the secondary metabolism [138]. It has been reported that tricyclazole, which is an effective systemic fungicide, blocks the secondary metabolism of the fungus at the final state of the formation of the phytotoxin. However, the action of tricyclazole on the fungus in vivo is not connected with a suppression of the fungal phytotoxin [138]. The same authors showed that tricyclazole blocked the synthesis of melanin and induced the formation of a root pigment in *V. dahliae* in a similar manner to what has been observed in the natural growth of a mutant strain.

Another desirable direction in the search for agents of the fight against the development of infectious diseases of plants, including cotton-plant wilt, is, from our point of view, the use of phytotoxins in concentrations below the toxicity threshold [153] and of some other physiologically active fungal metabolites [154-156]. As mentioned above, these compounds can induce protective reactions of the plant organism, namely: the synthesis of phytoalexins, the mobilization in the plants of a system of bioantioxidants and the activation of their oxidase systems.

As an example we can give the results of experiments on the induction of the resistance of the potato to infectious diseases by treating the tubers with metabolites of fungal parasites [156]. In this case, the role of inductor of protective reactions was fulfilled by a lipoglycoprotein [LGP] the lipid component of which was responsible for the inducing activity. The authors of this investigation considered that such treatment of tubers increases the potential capacity of the plant for switching on a system of protective reactions, including the formation of phytoalexins at the moment of contact with the parasite.

Thus, it follows from the material presented that the lipids of the Fungi Imperfecti contain, in addition to the usual components, a number of biologically active compounds that are specific or "nonspecific" phytotoxins.

The biosynthesis of lipids and that of phytotoxic components in the Fungi Imperfecti are closely connected. The lipid metabolism apparently plays a key role in the formation of the pathogenic properties of the fungus, since the processes of lipid metabolism are also connected with processes of cell differentiation and cell division, the reproduction of the species, and the viability of the fungi.

The lipids and secondary metabolites also play an important role in the interrelationship of phytopathogenic Fungi Imperfecti with the plant host. Decisive importance in the outcome of these interrelationships is possessed by the adaptive regulation of the function of the molecules of the plant and fungus at the level of the lipid metabolism.

A study of the mechanism and products of lipid metabolism will permit the theoretical substantiation of methods for the diagnosis of diseases in plants and the planning of practical routes for finding chemical agents of the fight against infectious diseases of plants.

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SYNTHESIS OF LEAF ALDEHYDE

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The comparative oxidation of trans-hex-2-enol to leaf aldehyde has been effected with the aid of manganese dioxide, chromium oxide, and sodium dichromate in DMSO. It has been established that sodium dichromate in DMSO gives the best yield (not less than 80%) and a product of higher purity. It is a comparatively new reagent in organic synthesis. The use of sodium dichromate in DMSO is promising in the preparation of compounds requiring the use of mild conditions.

trans-Hex-2-enol and trans-hex-2-enal are extremely widespread in nature [1, 2]. Hex-2-enal is one of the components of the aroma of verdure, and therefore it has been called leaf aldehyde [3]. In addition to this, it is present in many other natural aromas, including the essential oil of tomatoes [4], olive oil [5], citrus leaves [9], and tea [7]. trans-Hex-2-enal is also present in the volatile components of many plants, such as oranges [8], hops [9], black currents [10], etc., usually together with trans-hex-2-enol. Leaf aldehyde has not been detected only in plants. It has been isolated from the scent glands of the nymph of *Ptermistria bispina* Stal. [11] and is one of the components of the pheromone of the silkworm [12]. It has also been isolated from the poisonous secretion of the insects *Eurycotis flori-*

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