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Chemical Treatment of Seeds and Its Application to Plant Growing

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Considerable attention is paid to the action on seeds of various plant-growth regulators and vitamins. A special place is occupied by the possibility of using chemicals to change the genetic peculiarities of plants, and also by the use of special polymer films as seed coatings. Great value attaches to the local introduction with the seeds of substances that protect both seeds and shoots from various pests and diseases. A list of 575 references is included.

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I. INTRODUCTION

As early as 1800 the founder of plant physiology, Jean Sénébier, remarked in his many-volume treatise that the attention of chemists must be drawn to processes of plant growth[1]. Only a hundred years later, in an address given at Moscow University in 1901 on "A Century of Progress in Plant Physiology", Timiryazev was able to state that "chemistry and physics, having come to the assistance of plant physiology, have given to man, over the course of a century, the possibility of extending his right to life and curtailing the power of death: no knowledge could have a more valuable application"[2].

The application of chemicals to the growing of plants has now acquired immense significance. This has been especially clearly shown in the treatment of problems connected with the root nutrition of plants and the production and application of fertilisers. During the past decade the attention of research workers has been attracted to the preparation and investigation of chemicals capable of controlling the growth and development of plants. The organisation of a laboratory for the preparation of physiologically active substances in 1946, by S.S.Nametkin at the Institute of Plant Physiology of the USSR Academy of Sciences, played an important part in the development of these investigations in the Soviet Union. High yields are at the present time unthinkable without the widespread application of various methods of plant protection.

One of the most convenient modes of application of the chemicals (pesticides) used in agriculture—in several cases the only method—is to treat the seeds. This plays an important part in the struggle against micro-organisms and pests, diminishing seed losses both during storage and during germination. The field germinating power of seeds is enhanced by enriching them before sowing with the vitally necessary compounds and substances controlling their germination and growth. The use of polymers to coat seeds is of considerable practical interest, and provides a solution to several important problems.

Although the production, properties, and application of pesticides are covered in a large number of reviews and monographs[3-8], insufficiently detailed consideration has been given during recent years to the whole complex of problems associated with the chemical treatment of seeds[9,10]†.

In the present Review, without claiming complete coverage of the literature and while disregarding problems connected with the biology of the germinating seed, we would like to examine the main classes of chemical substances employed for the treatment of seeds, together with certain aspects of their action. We have used information published mainly during the past 15–20 years both in original papers and in abstracts and books.

II. STIMULANTS AND INHIBITORS OF GERMINATION

Methods of treating seeds with growth regulators have been developed during the past forty years, and several groups of regulators, now being widely studied, were discovered only during the last two decades. The quantity of publications concerned with the action of regulators on germination is continually increasing. This information is being systematised to some extent in several monographs, reviews, and symposia[9,10,13-22].

Plant-growth regulators usually include stimulants and inhibitors, herbicides (substances causing destruction), desiccants (which dry up plants), and defoliants (causing leaves to fall). The last two groups are not used for treating seeds, and will not be discussed below.

Growth regulators are widely represented in plants, being products of normal metabolism. Such substances are often termed *plant hormones*. Synthetic products, by means of which it is also possible to control the vital activity of plants, are widely studied together with natural growth regulators. In this case stimulation is a consequence of the disturbance (usually only slight) of the normal functioning of the living system caused by the

† The first summaries of work on the treatment of seeds with various substances appeared in 1763 and 1876[11,12].

chemicals: the accompanying intensification of metabolism is a kind of protective reaction of the organism aimed at restoring its normal functioning as rapidly as possible[5].

The action of a regulator may vary with its concentration. Thus at low concentrations it has a stimulating effect, it retards metabolism with increase in concentration, and at doses exceeding the inhibiting dose it leads to destruction of the plant.

Various organic substances are mostly used as artificial regulators. The main groups of these compounds used for treating seeds before sowing are discussed below.

1. Auxins

An auxin was first isolated in 1931 by Kögl and Haagen-Smit[23]. They gave to the product the name *auxin*—a substance causing the growth and elongation of cells—and thereby introduced a new general term into scientific use. Some time later they isolated a second auxin, and then a third, termed a "heteroauxin", which on investigation proved to be indol-3'-ylacetic acid. This compound has since been detected in many plants. The ease with which indolylacetic acid can be synthesised explains its wide study as a stimulating regulator of plant growth.

It has since been found that auxin activity is possessed by other acids, e.g. those containing an aromatic carbocyclic or heterocyclic ring in the aliphatic radical[24]. The group of auxins most widely used for treating seeds are carboxylic acids derived from indole—indol-3'-yl-acetic, -propionic, and -butyric acids, as well as their esters, salts and amides.

Kholodnyi was the first Soviet worker to investigate[25] the effect of heteroauxin on the germination of seeds and the productivity of plants. Response to such treatment has since been confirmed by many investigators. Thus dipping rice seeds in auxin solutions before sowing was shown[26] to improve their germination in an unflooded soil, but this effect disappears on flooding. Indolylacetic acid increases the energy of germination of carrot and onion seeds by 9.0% and 9.4% respectively, and the germinating capacity by 5.6% and 13.7%.[27] It stimulates the germination of beans[28] and several other plants[29-31]. Keeping apple pips in a 0.01–0.001% solution for 30 min increases their germinating capacity by 10.6–18.1%.[32]

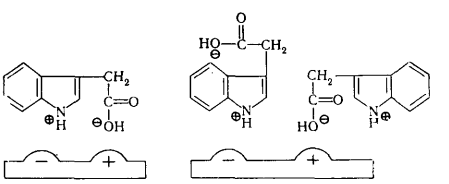
The intense physiological activity of auxins indicates that they are involved in the fundamental processes of metabolism. Thus indolylacetic acid plays a part in the phosphorus metabolism of plants[33], enhances the activity of 3'-nucleotidase[34], enhances oxidative phosphorylation, and activates the absorption of water[35]. It improves the binding of calcium by ribonucleic acid[36]. Activation of shoots of the cotton plant grown from seeds treated with the optimum concentration of auxin is accompanied by increased synthesis of nucleic acid and especially of ribonucleic acid[37].

The interconnection between the action of auxins and that of other growth stimulants is very interesting. Thus McLeod and Palmer have shown[38] that indolylacetic acid improves the conditions for the formation of α-amidase, which is dependent on the presence of gibberellins. The dependence of the action of gibberellic acid on the presence of auxins in plants has been confirmed[39]. The action of auxins on plants has been reviewed[40].

Many investigators were attracted by the discovery of auxins and by their great effectiveness in growth processes. The range of research on auxins has since been considerably extended: study of the responses of plants to treatment with auxins has been accompanied by attempts to synthesise new chemical compounds possessing auxin activity. In particular, the effect of introducing substituents into the heteroauxin molecule has been established. For example, auxin activity is suppressed by most substituents in the pyrrole ring[41]. Introduction of a 2-halogen, however, enhances it[42]. 2'-Substituted indolylacetic acids are considerably less active than their 3'-analogues[43]. Acids derived from naphthalene—naphth-1'-yl-acetic, -propionic, and -butyric acids—also exhibit auxin properties. On the other hand, 2-substituted naphthalenes are considerably less active[44]. Esters of the acids are used when a solution of the stimulant in a non-polar solvent is to be obtained. Naphth-1'-ylacetic acid is often used to treat seeds of various plants to stimulate germination and the development of shoots. It has been employed in particular to treat the seeds of wheat[45], tomato[44], red-currant[46], carrot[47], sunflower[29], and maize[48].

Acids containing a phenyl group, e.g. phenylacetic and phenoxyacetic, also exert a stimulating action. The nuclear-substituted acids often possess herbicidal properties, but at low concentrations even they have a stimulating effect. Thus 4'-chloro-2'-methyl-, 4'-chloro-2'-hydroxymethyl-, and 4'-chloro-2'-formyl-phenoxyacetic acids stimulate germination of seeds and development of the shoots of barley[49], tomato, and kidney-bean[50,51]. In low concentrations 2,4-dichlorophenoxyacetic acid (2,4-D) and its esters act as stimulants, e.g. on the seeds of pine, spruce, acacia, ash, and oak[52], annual weeds[53], and wheat[45]. Similar activity is developed also by substituted phenylbutyric acids[54] and indol-2'-ylglyoxylic esters[55].

Seeds and shoots are extremely sensitive to excess of auxins. This is apparent both in a diminution of germinating power and in the retardation of growth processes. A schematic model has been suggested to explain this phenomenon on the assumption of a two-point interaction between the auxin molecule and the enxymic centres with formation of a growth-stimulating auxin–receptor complex[56]:



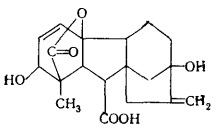
At high concentrations of indolylacetic acid two auxin molecules are adsorbed on the active site of the enzyme, and the required chemical conversion does not take place.

Study of the response of seeds to enrichment of their auxins has enabled the physiological role of auxins in the vital activity of seeds to be elucidated, and has also promoted the search for new plant-growth stimulants.

2. Gibberellins

The first gibberellin (subsequently termed gibberellin A_1) was obtained in 1937.[57] Several gibberellins were isolated, including gibberellin A_3—gibberellic acid—the most frequently used in practice and the most active of the 37 gibberellins known at the present time. Lona and Fioretti[58] have compared the activities of several gibberellins towards the germination of lettuce seeds.

Several new gibberellins have been described quite recently [16,59]. Gibberellic acid



like other gibberellins, is a fluorene derivative [320].

In industry, gibberellins are most often isolated from the fungus *Fusarium moniliforame* Sheld. A Soviet crystalline preparation of gibberellin A_3 contains gibberellic acid contaminated with certain other gibberellins, which widens the spectrum of its action and enhances its effectiveness. An inexpensive preparation—"gibberelate", containing ~10% of the active principle—has been manufactured in the Soviet Union since 1968. Its effectiveness has been demonstrated by trials [60]. Attempts are now being made to synthesise gibberellins [61].

Several surveys have appeared on the action of gibberellins [62-64]. The chemical structure of the compounds has been discussed in a review [65].

Although gibberellins are present in plants and seeds, the latter are extremely responsive to treatment with this plant hormone. Thus positive results have been obtained on treatment of the seeds of cotton [66,67], wheat [68,69], pea [69-71], barley [68,72], cucumber [73], maize [70,74], kidney-bean, parsley [70], lettuce [75,76], cabbage [77], radish [78], bean [71], belladonna [79-81], ginseng [82,83], and several other plants [84-90]. A large number of papers have dealt with the action of gibberellins on the germination of seeds of certain kinds of wood having seeds which germinate with difficulty (lime, ash, hornbeam) [91-99]. Such treatment with gibberellins increases the capacity for and vigour of germination of the seeds [68,71,78,91], and intensifies respiration [100]. Wheat and barley have shown rapid and harmonious growth with good development of the root system [68] (which is not usually characteristic of gibberellins). Beans and peaks have given good results with an increased moisture content in the soil [71].

The action of gibberellins can be promoted by preliminary chilling [84] and illumination [101] of the seeds. These and other facts suggest that a positive effect of gibberellins depends on the state of the seeds, the species of plant, and also the ambient conditions. Thus under identical conditions of treatment of the seeds, gibberellic acid stimulates the germination of cabbage but may depress that of carrots and tomatoes [77]. However, certain plants remained insensitive to such treatment [92]. Among 304 varieties of rice studied, seeds of southern origin were distinguished by a longer period of dormancy. These seeds proved especially sensitive to treatment with a gibberellin [102]. Early treatment of wheat grains undergoing prolonged storage was inadvisable, since it lowered the sowing qualities of the seeds [103]. The total quantity of gibberellins is determined photometrically [104] in practice, and the physiological activity of the preparations by means of a biological trial, e.g. on a dwarf pea [60].

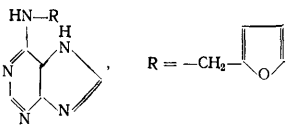
The mechanism of the action of gibberellins is illustrated by data published by Paleg [105] and Iomo [106] on the role of gibberellic acid in the formation of the hydrolytic enzymes of the endosperm of germinating barley. Work in this field has been continued very vigorously, and the main details of the mechanism have now been elucidated by researches on barley grains [38,107-113]. Zabolotskii has made a detailed survey of the regulatory mechanisms of the germination of seeds [114]. Formation of gibberellic acid during germination is assumed to be preceded by the synthesis of ribonucleic acid and of a protein in the embryo, which in turn are due to the activity of certain genes [21]. The synthesised gibberellin enters the endosperm, where it activates several enzymes—α-amidase, protease, ribonuclease, etc.—which reach the storage tissue, where they split up starch, proteins, and other materials. The cleavage products ensure normal growth of the shoot. Gibberellic acid also intensifies glycolysis and the activity of the ring in polycarboxylic acids [79]. Gibberellins promote plant growth by cell elongation, but do not stimulate cell division [86,115,116]. Such elongation assists better germination of the seeds.

Establishment of the presence in seeds of antagonists to gibberellins suggests that their favourable effect is due to the neutralisation of inhibitors [570]. A synthetic antagonist to gibberellins is chlorocholine chloride [117], which is used to oppose the flattening of wheat and other cultivated crops.

The treatment of seeds with gibberellins has provided a deeper insight into the favourable effects of light and low temperatures. The enrichment of seeds with this hormone replaces the stimulant action of light and temperature on germination [86,118]. These factors in the environment have been shown to stimulate the biosynthesis of gibberellins in seeds.

3. Kinins

During recent years the attention of research workers has been attracted by kinins, which are involved in the biosynthesis of proteins, chlorophyll, and other vitally necessary compounds [22,119]. Kinins are widely distributed in seeds, and have been detected in those of maize, sunflower, plum, peach, and other plants [120,121]. They are aminopurine derivatives, of which the best known is 6-fur-2′-ylmethylaminopurine or "kinetin"



Only eighteen years have elapsed since kinetin was obtained and its great physiological activity established [122], but many of its analogues have already been studied. Thus 6-benzylaminopurine surpasses kinetin in activity [123]. Another natural kinin—zeatin [$R = CH_2.CH:C(CH_3).CH_2OH$], isolated in 1967 from maize seeds [124]—also possesses very high activity. Many other purine derivatives have a stimulant effect, in particular those containing NRR′ and SR″ groups at position 6 (where R, R′, and R″ represent hydrogen or organic radicals). For example, 6-aminopurine and nitrogen-substituted aminopurines have proved active in experiments on the germination of horseradish and potato seeds [125]. 6-Benzylaminopurine raises the germinating capacity of lettuce seeds [126], as well as the long-keeping seeds of lupin, pea, maize, and barley [127,128]. Several other aminopurines have also been used to treat seeds [129]. Kinetin itself disrupts the dormancy of the seeds of beech, hazel, and mountain ash [130]; it stimulates germination of lettuce seeds [133] that have been treated with an inhibitor [131,132].

The initial effect of kinetin resembles that of gibberellins in enhancing the synthesis of nucleic acids. However, the second stage involves stimulating cell division, not elongation [134-138]. Kinetin and its analogues influence

mainly processes associated with the replication of deoxyribonucleic acid in cells. It intensifies the synthesis of ribonucleic acid and protein in cells, and stimulates the formation of ribosomes [139].

Kinins may delay the aging of plants. Thus treatment with kinetin has restored the colour of isolated yellowed leaves [140]. Finally, kinins restore the vital activity of irradiated plants. For example, viable ears could be obtained after the action of 6-benzylaminopurine on irradiated wheat grains [141].

Further study of the chemistry and biological action of kinins will be of great interest.

4. Vitamins

Seeds of all plants contain definite quantities of vitamins, which play an important part in germination and the development of shoots. The content of vitamins in seeds depends on many factors, in particular the ambient conditions. Therefore the quantity of vitamins necessary for germination sometimes accumulates in a seed; but sometimes the quantity present is insufficient. Although the vitamin content increases during germination, under unfavourable Spring conditions the accumulation of certain vitamins is insufficient for the normal course of the physiological processes. The presence in seeds of antivitamins and of enzymes which break down vitamins increases still further the deficiency of vitamins in germinating seeds. This makes it clear why supplying certain vitamins to such seeds will normalise metabolism and stimulate their germination.

Nicotinamide (vitamin PP) has been shown to act in this way towards the seeds of cotton [142,143], citrus [144], and vine [145]; pea, sorghum, cucumber, wheat, and beet seeds are also sensitive. Treatment raises the germinating power of the seeds, enhances development of the plant, and increases their yield [146-148]. This vitamin also improves the genetic properties of wheat, which is evident in a great development of vegetative parts, a higher grain content in the ear, increased weight of the seeds, and a higher protein content [149,150]. Treatment of the seeds of lemon, orange, and grapefruit considerably increases the number of seeds capable of giving several shoots [144].

Skrabka found [152] that wheat seeds of diminished germinating power and seeds germinating under anaerobic conditions contain lower contents of ascorbic acid and glutathione. The germinating capacity is raised appreciably by enriching the seeds with these two substances. Ascorbic acid has a favourable effect also on the germination of other seeds [88,153,155].

Seeds respond also to treatment with biotin, the sensitivity increasing during ripening. Seeds differing in quality react differently: seeds from the middle of the maize cob are usually more sensitive to enrichment with biotin, which is less active towards those from the upper part of the cob [156].

Treatment of the seeds of flax, pea, radish, buckwheat, and carrot with thiamine before sowing improves their germination and increases the yield [146]. This vitamin has a favourable effect on cotton seeds [143,158,159], whose growth processes are intensified by vitamin B_6. [142]

The observed biological action of vitamins involves not only normalisation of the metabolism in which a particular vitamin takes part but also an ensuing change in composition of the soil microflora [9]. For example, enrichment with thiamine, riboflavin, and nicotinamide of beans before sowing stimulates more intense formation of root nodules and nitrogen-fixing bacteria, which improves the supply of nitrogen to the plants and enhances growth processes and development of cultivated crops [146,161].

The above results indicate that seeds of several plants are deficient in certain vitamins. Timely treatment of such seeds with vitamins will therefore intensify metabolism, increase germinating capacity, and strengthen the growth and development of the plants.

5. Other Organic Compounds

Organic acids are widely represented in seeds, and are actively formed during germination [162]. The resulting organic acids are utilised in respiration, as well as for the synthesis of amino-acids and other vitally necessary compounds. In several cases, however, the quantities of such compounds remain insufficient for normal metabolism, and treating seeds with them has a favourable effect on growth processes.

Thus treatment of the seeds with succinic acid improves the germination of maize [163], cotton [164], pea [165], wheat [153,165,166], barley, and rye [166,167]. Improvement of germination and intensification of further growth are observed also with other plants [167-173]. The best results are obtained by treating seeds which are germinating in the presence of deficiencies of noisture and oxygen [166]. Not only succinic but also citric, malic, and fumaric acids increase the yield of wheat [153]. Succinic acid has a greater effect on radish and cucumber seeds than has fumaric acid [174]. Certain analogues of succinic acid, e.g. dodecylsuccinic acid, also have a stimulant effect [175]. The action of polycarboxylic acids on seeds has also been discussed in several papers [121,176-178].

Intensified germination of seeds is observed also on treatment with several other acids, e.g. amino-acids [179, 180,568], keto-acids [181], phenylboric acid [182], naphthenic acids [183-187], quinonecarboxylic acids [188,189], cinnamic acid [171,190], 1,2-benzocyclo-hept(and oct)ene-3-carboxylic acids [191], cedrenecarboxylic acid [192], and several others [193-195]. The seeds of wheat, barley, and several other plants are sensitive to formic and acetic acids (Ref. 10, p. 200). In some cases inorganic acids also accelerate germination [196,197].

Many substances belonging to other groups of organic compounds also affect the germination of seeds. Phenols (guaiacol, phloroglucinol, catechol) stimulate growth of the seeds of rye, beet, celery, carrot, and alder [198]; and quinol has a similar effect on wheat and pea [199]. In other cases phenols (tannin, guaicol, gallic acid, etc.) delay or completely suppress growth [200]. Vanillin and ferulic acid in small concentrations stimulate germination, increase the germinating capacity of seeds, and promote the development of shoots [171].

A method has been worked out for obtaining active furan derivatives, whose use for the treatment of wheat seeds produces better development of the root system together with an increased yield [201-204]. Derivatives of several other heterocycles also have a stimulant effect. Thus growth is stimulated, the yield of plants is raised, and resistance to wilting is improved by addition to seed disinfectants or use as a component part of steeping solutions. The greatest activity is exhibited by 1-cyano-2-methyl-5(6)-nitrobenzimidazole, 1-cyanoethyl-5(6)-nitrobenz-

imidazole, 5(6)-nitrobenzimidazole [205,206], 2-methyl-5(6)-nitrobenzimidazole, 5(6)-amino-2-methylbenzimidazole, 2-diethylaminobenzimidazole [171], and several other imidazoles [208]. Good results have been obtained by treating seeds with amino-, hydroxy-, and mercapto-derivatives of pyrimidine [209,210].

Development of the root system of maize, with simultaneous diminution of the height of the plants, is produced by the use of alkyl carbamates [211].

Halogenated alcohols—2-chloroethanol [67,212], 1,2-dibromo-3-chloropropanol [213], *N*-substituted chloroacetamides [214], dibromoethane [213], and *gem*-diarylcyclohexanol derivatives [215]—accelerate germination. In several cases preliminary treatment of the seeds with alcohols facilitates the penetration of moisture [216].

6-Aminopurine and several of its derivatives have a favourable effect on tomato and mustard seeds [217]. Salicylohydroxamic acid has proved useful for the germination of pea and tomato [218]. Wheat and pea germinate better after treatment of the seeds with derivatives of cyclohexane and cyclohexene containing hydroxy- and keto-groups [219], and seeds of grain crops with solutions of melamine and aminoethanol [220]. Seed germination has been enhanced by streptomycin [221], acetone [222], sucrose and hexoses [223], and chlorides of certain cyanine dyes [224].

Thiourea has a positive effect on the seeds of the Russian dandelion and of lettuce [225-228]. *N*-Alkyl-*N'*-arylthioureas, which have been tested on wheat grains, are more active [229]. The combined action of thiourea and indol-3'ylacetic acid on oats exhibits synergism [230]. The dry weight of the roots is increased by soaking peas, barley, and flax in glycothiourea solution [231], and cultivated lettuce seeds in methylurea solution [132].

Germination is stimulated also by certain nitrosulphonamides [232], mixtures of manganese salts of lower carboxylic acids [233], amines [101,234], and other synthetic compounds [235].

The supply of oxygen to seeds is of considerable importance. This is obviously responsible for the favourable effect of hydrogen peroxide on rice [236], sugar-beet [237], tobacco [238], and wheat [9]. Germination is accelerated and the percentage germination of seeds increased by the action of benzoyl peroxide, its halogenated derivatives, methyl hydroperoxide, and t-butyl perbenzoate [239].

Various products which protect plants from diseases and pests may also influence germination. Thus treatment of the seeds of certain crops with disinfectants has in several cases increased their germinating capacity [240-248]. Certain systemic pesticides have proved toxic to seeds [249]. Biologically active compounds containing sulpho-groups may also depress seeds [250].

It is interesting that ethylene is used to bring seeds out of their dormant state [126,251].

There are indications that certain inorganic substances—calcium cyanamide [9,252] and dilute alkalis [197]—may stimulate germination. Keeping seeds in solutions of salts of metals (potassium, calcium) and hydrohalic acids increases the accumulation of amino-acids [161,253].

The list of chemical compounds which have been tested for controlling the rate of germination of seeds could be considerably extended. However, most of the publications involve no knowledge of the mechanism of the action, but pursue the aim of determining whether a given compound stimulates germination and plant growth. Such work, of course, despite its usefulness, conveys little information on the germination of seeds and the mechanism of the action of particular compounds. Yet a solution of this problem would be invaluable for practical agriculture.

6. Inhibitors and Herbicides

A seed is a complicated biological system whose life is controlled by stimulants and inhibitors. The presence of the latter has long been known [254,255], and they have since been detected in many seeds [256-258]. Their quantity and nature depend both on genetic features of the plants and on the physiological state of the seeds. Thus extracts from 60-day green peas retarded the development of bean shoots more strongly than did extracts from ripe seeds [259]. Germination of seeds inside over-ripe fruits of the tomato, pumpkin, and water-melon is associated with a diminution in the content of inhibitors.

The retarding action of plant inhibitors is suggested by other facts. Germination of lime is delayed by extracts of the pericarp [260]. Flavonoid pigments, which inhibit the germination of cereals, have been found in the seed coat of barley [261]. Aqueous extracts of rice bran retard the germination and growth of rice and cultivated lettuce [262]. An extract of sugar-beet nodules greatly diminishes the germinating capacity of wheat [263].

Water-soluble substances from the leaves of steppe plants, which form a rosette at the roots, inhibited the germinating capacity of radish and poppy [211]; an onion paste delayed the germination of maize [224]. Extracts of several other plants exert an inhibiting effect on seeds [264-267].

Not only have several inhibitors occurring in plants now been identified, but in some cases the mechanism of their action has been established. Examples are coumarins in the seeds of sweet clover [268], cyanides in beans [269], parasorbic acid in the fruit of mountain ash [270], ferulic, vanillic, *p*-hydroxybenzoic, and *p*-hydroxycinnamic acids in sugar-beet seeds [271], and abscisic and paracoumaric acids in cotton seeds [173]. Abscisic acid has been detected in many seeds and plants [272-277]. It acts by inhibiting gibberellins and retarding the synthesis of nucleic acids. Several other inhibitors have been isolated from seeds [10,278].

A retarding and herbicidal effect on seeds and seedlings is exerted not only by natural inhibitors but also by many synthetic compounds. The considerable interest in this question led to study of the theoretical principles of the action of inhibitors and herbicides, which are antimetabolites of growth stimulants. Antimetabolites take the place of the most important metabolites in biological transformations during enzymic reactions and inhibit them. The antimetabolite, which is assumed to combine with the active centre of such a protein, forms a system which does not undergo the usual reactions, and the required products are not formed [279].

The structure of an inhibitor is often closely similar to that of the corresponding metabolite. The most active antimetabolites are those which show only slight structural differences from the corresponding metabolites. The main interrelationships in chemical structure between metabolites and antimetabolites have been established [279]. In particular, an inhibiting effect is produced by the replacement of e.g. carboxyl by sulpho, hydroxyl by alkoxyl, etc.

Antimetabolites can be divided into several groups according to the mechanism of their action [279]. Thus some inhibitors and herbicides—e.g. derivatives of phenoxy-, *p*-chlorophenoxy-, 2,4-dichlorophenoxy-, and *p*-methylphenoxy-propionic acids—suppress the activity of auxins and other growth stimulants [422]. A group of synthetic compounds which cause shortening of the stem, thickening of the cell walls, and intensification of leaf colour ("retardants") are antagonists of gibberellins [280,281].

The most widely known of such compounds is chlorocholine chloride ("CCC") $[ClCH_2.CH_2.N(CH_3)_3]^+Cl^-$, whose physiological action was first observed by Tolbert in 1960.[282] It was shown later that CCC is an antagonist of gibberellins[117,283,284]. A Soviet product TUR based on chlorocholine chloride is now available[285]. Plants are usually sprayed with chlorocholine chloride. Recently, however, seeds have also been treated with solutions or powders of retardants[286,287]. Thus the action of retardants on seeds of spring wheat, barley, oat[288-290], pea[291], and cotton[292] has been investigated. Treatment of seeds with CCC may determine the sex of plants[293].

Maleic hydrazide (brand MG-T) and its derivatives act as antagonists to plant-growth stimulants. The hydrazide inhibits cell division[294]. Gibberellins and maleic hydrazide have opposite effects when applied together[295]. These compounds are often used to treat seeds to prevent germination during storage. Maleic hydrazide inhibits the germination of cotton[296], beet[297], soya[298], peas, beans, cucumber, wheat, barley, maize, turnip, radish, tomato, and rye[300]. Analogous effects on metabolism are produced by hydrazides of several other acids—chloromaleic, methylmaleic, phthalic, and succinic[299]—*NN*-dimethylsuccinamic acid[296], 6-azauracil[300], and certain other uracil derivatives[301].

Halogenated aliphatic acids, which retard the biosynthesis of individual groups of enzymes, inhibit germination[279]. Thus investigations have been made on the action of sodium trichloroacetate on wheat and millet grains[302], of trichloroacetamidine on mono- and di-cotyledonous crops[303], of propionic acid, which protects grain forage of high moisture content from germination[304], and of chloral hydrate, which has a herbicidal action on the seeds of barley, millet, oats, mustard, and wheat[302].

Several other substances have an inhibiting action on seeds. Thus 3-acylated aminotriazines delay the germination of radish[305], sulphanilamide[306] and aminopteridine[307] that of maize and peas, diepoxides the germination of wheat, millet, and radish[308], and 1,3-diphenylprop-2-ylamine that of wheat and kidney-beans[309]. Vital activity is completely suppressed by isocyanates[310] and several other substances[311-316].

Study of the effect of physiologically active substances on the germination of various plants has shown that, whereas some seeds are destroyed by a particular compound, others are resistant. This has been used to develop ways of destroying the seeds of weeds in the soil. Thus many weeds are killed by introducing industrial herbicides into the soil before sowing.

Further study of the dependence of the inhibiting effect of synthetic antimetabolites on their chemical structure and examination of the mechanism of their action will permit the development of new types of selective weed-killers.

III. CHEMICAL MUTAGENS

Chemical compounds are able not only to stimulate or inhibit germination and plant growth but also to influence heredity[317]. The ability of chemical compounds to change genetic features was first observed as early as 1916.[318] A few new mutagens were discovered in the 1930s, when aziridine, diethyl sulphate, and several other substances were found to be highly active[318]. A broad investigation of this phenomenon was begun after valuable results had been obtained on barley and peas[3]. Whereas radiation methods became widely used in the 1930s to change heredity, nowadays chemical mutagens occupy the primary place[319].

The seeds are usually soaked in a solution of the mutagen of definite concentration[321]. *N*-Nitrosoethylurea, 1,8-bisdiazo-octane-2,7-dione, aziridinopiperidine[322-327], diazoacetic ester, bis-2,2-dichloroethyl hydrogen phosphate, *N*-nitrosomethylurea[328], ethyl methanesulphonate[329-334], *NN'N"*-triethyl-thiophosphoramide[335], diethyl dimethyl pyrophosphate, and tetraethyl dithiopyrophosphate[336] have found use for these purposes. Colchicine[337,338] and other substances[24] are employed as mutagens.

The largest number of publications have been concerned with obtaining valuable mutations in wheat and rice, as well as in maize[329], barley[330,333,339], sugar-beet[337], cotton[332], and peas[340].

Since traces of mutagens (or their decomposition products, e.g. ethyl hydrogen sulphate[341]) may have a deleterious effect, they are removed by washing with water, sometimes with the addition of chemicals, e.g. sodium thiosulphate[319]. Treatment and washing with water are followed by sowing.

The possibility of obtaining agriculturally valuable mutations of cultivated crops by treating the seeds with active compounds opens up new prospects for changing the genetic character of plants and will provide a deeper insight into the chemical nature of heredity[154].

IV. TREATMENT OF SEEDS WITH PLANT-PROTECTION AGENTS

Plants synthesise not only compounds that are directly involved in metabolic processes but also those which have a toxic effect on bacteria and fungi. The latter compounds were termed "phytoncides" by Tokin[342]. Investigation of the composition of gaseous and liquid examples showed that such products comprise various aldehydes, phenols, essential oils, and other compounds[343]. Available results indicate that treating seeds protects them from diseases caused by micro-organisms.

Thus during 1953–1954 it was found that treatment of clover and lucerne with the "phytoncides" of garlic had a protective effect on the seeds for a year[344]. Treatment of seeds of perennial grasses with onion "phytoncides" proved to be more effective. The morbidity of perennial grasses[345], barley, kidney-beans, peas, wheat, cucumbers, flax, and other plants[346] was lowered by applying analogues of pseudoallicin to their seeds. "Phytoncides" of onion, garlic, and horseradish lowered the incidence of vascular bacteriosis in cabbage, and of bacterial cancer in tomatos (seeds were treated before plants)[347,348]. Antimicrobial substances of mustard, horseradish, and eucalyptus protected cotton seeds from gummosis[346].

Treatment of tomato seeds with "phytoncides" from the fruit of nightshade completely eliminated morbidity due to bacterial disease[349], and of clover, lucerne, and tomato seeds with arenarin (a "phytoncide" of everlasting sandwort) tended to lower the susceptibility of the plants to bacteria, in some cases to fungi as well, and to a greater extent than treatment with Gramosan [an ethylmercuric chloride seed fungicide equivalent to Ceresan][346]. Fusariosis in melons is prevented by treating the seeds with anabasine (an alkaloid isolated from a leafless blackberry)[350]. Extracts of the seeds of certain kinds of wood (ash, acacia, wild rose) have a bactericidal effect on wheat grains[351].

Antibiotics have a special place in the fight against plant diseases. Streptomycin is the most widely used for disinfecting seeds. Thus tests on beet seeds in England gave such promising results that in 1960 almost all beet growers in that country had changed to treating seeds with a solution of streptomycin. It gave good results with oats, wheat, and barley [352]. However, products of the vital activity of organisms and plants have not found wide application for protecting seeds from fungal and bacterial diseases. This is due not only to the complexity of their isolation in considerable quantities but also to the inhibiting effect of some of them on germination.

Nevertheless, agriculture demanded readily available and effective agents to reduce the immense losses of production due to micro-organisms and pests. According to the most recent data, for example, the world losses merely of wheat are 85.6 Mt or 23.9% of the total production of this most important crop [353]. Comparable losses occur in stored grains and rice: in 1947 the United Nations estimated them to be 33 Mt, a quantity which would have fed a human population of 150 millions for a year [354].

A considerable proportion of plant disease is transmitted through the seed stock from generation to generation. Furthermore, the eggs of many insects are distributed with the seeds on sowing, so that the great attention paid to the chemical disinfection (decontamination) of seeds becomes understandable. This plays an important part also in the struggle against pests and micro-organisms inhabiting the soil, as well as against granary pests [3,355-359,160].

The local treatment of seeds with protective agents has considerable advantages over the continuous application of chemicals. Contamination of the soil with poisons is avoided. The introduction of protective agents is combined with sowing, which eliminates additional types of field operations, and considerably diminishes the quantities of pesticides required [360-363].

Although the disinfection of seeds with various chemical reagents has been employed for a long time, widespread use has occurred only during the past 30–40 years. At the present time hardly any seeds of agricultural crops are sown in developed countries without chemical treatment [364-366]. When especially injurious substances are applied, the seeds are dyed bright colours or are treated with compounds having a characteristic odour [367].

Substances used for plant protection can be divided according to their type of action into insecticides, fungicides, bactericides, zoocides (against rodents), nematocides (against roundworms—nematodes), repellents, and several others. The same substance can offer different types of protective action, but such pesticides are usually classified according to their most characteristic range of activity.

Below we shall survey the main classes of synthetic chemical compounds used for the protective treatment of seeds, primarily on the basis of their chemical structure, and secondarily their type of action.

1. Phosphorus Compounds

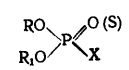
Phosphorus compounds form one of the chief classes of pesticides used for plant protection [368]. Several thousands of active phosphorus compounds are already known, among which about 80 are employed in agriculture. In the present Review, of course, it is impossible to consider all these products. We shall mention only the main phosphorus compounds used for the disinfection of seeds.

Although these are usually organophosphorus compounds, there are several active inorganic compounds, primarily zinc phosphide Zn_3P_2, which is used as a zoocide [4]. In several cases it also possesses insecticidal properties. Zinc phosphide has a strong disinfectant effect, but the substantial disadvantage of high toxicity towards farm animals: thus wheat, barley, and sunflower seeds remained toxic towards cows, calves, and pigs for 35, 43, and 96 days respectively after disinfection with zinc phosphide [369].

Organophosphorus compounds occupy a most important position among pesticides. Their total production now approaches that of chlorinated pesticides. Their useful properties include high activity, wide spectrum and rapidity of action, low consumption of products, and decomposition to give non-toxic or only slightly toxic products. An important aspect is that several of the organic compounds of phosphorus have a systematic effect [4].

The basis of the action of organophosphorus compounds is supposed to be inhibition of the enzyme choline esterase [4]. An impetus to a broad study of active organophosphorus compounds was given by the publication of Schrader's papers [370]. Soviet scientists have made a great contribution to developing the chemistry of organophosphorus compounds. Several reviews and monographs have appeared on the chemistry and application of organophosphorus pesticides [4,370,372,374].

Mel'nikov [4] made a detailed examination of the dependence of the pesticidal activity of organophosphorus compounds on their chemical structure. Compounds of general formula



are most often used, in which R and R_1 are organic radicals, usually lower alkyls (methyl, ethyl, isopropyl), while X is a group which can be replaced by a nucleophilic agent [371]. Increase in chain length leads to loss of activity. New active derivatives are therefore obtained by varying X. Replacement of oxygen by sulphur lowers the toxicity towards mammals without significant loss of pesticidal activity. The toxicity is still further reduced in derivatives of phosphorodithioic acids, which are more resistant to hydrolysis, so that the duration of their action is lengthened [4].

Among the large number of organophosphorus compounds for treating seeds use is made in particular of the products—2,2-dichlorovinyl dimethyl phosphate, 1,2-dibromo-2,2-dichloroethyl phosphate (Dibrom), dimethyl *N*-isopropoxycarbamoylphosphonate (Avenin, K-69-79), dimethyl 2,4,5-trichlorophenyl phosphorothioante (Ronnel, Trolene, trichlormetaphos, Etrolene, Dow ET-14, Korlan, Nankov), diethyl 2-isopropyl-4-methylpyrimidin-6-yl phosphorothionate (Dianisone), and 2-ethylthioethyl *OO*-dimethyl phosphorothioate (a mixture of isomers) (Meta-Systox, methyl demeton) for the treatment of grain [4,375]; *S*-1,2-diethoxycarbonylethyl *OO*-dimethyl phosphorothiolothionate (Carbophos, Malathion) for treating the seeds of kidney-bean, maize [4,376], barley, oats, rye, rice, sorghum, and wheat [4,377]; and *OO*-dimethyl *S*-*N*-methylcarbamoylmethyl phosphorothiolothionate (Phosphamide, Rogor, Dimethoate, BI-58) and pyrophosphoric octamethyltetra-amide (Octamethyl, OMPA, Tradane, Systam, Pestox-111) for the seeds of wheat, sugar-beet, and savoy [4,378]. Several other organophosphorus compounds are also used for disinfecting seeds [4,377-384].

Organophosphorus insecticides can be arranged in the sequence—Diazinon, Guthion, Ronnel, DDVP, Dibrom—according to the maintenance of the protective effect on the grain. Protection becomes weaker with increase in the moisture content and rise in the temperature of the grain.

Certain organophosphorus insecticides exert a stimulant effect on the germination of sugar-beet [378].

2. Mercury Compounds

Organic compounds of mercury occupy a leading position among means of protecting plants from fungal and viral diseases and from bacterioses. They possess the advantage of high toxicity towards micro-organisms and lack of toxicity towards seeds. In several cases, moreover, a stimulating effect on the growth processes of plants is observed [4]. Organic mercury compounds have already been widely used for several years in the disinfection of seeds. The history of and the prospects for their application have been discussed in several reviews [385,386]. Mercury preparations are considered to act by inhibiting the functioning of respiratory enzymes [387,388].

The compounds used as fungicides and bacteriacides usually have the formula R–Hg–X, where R is an unsubstituted or substituted aliphatic, aromatic, or heterocyclic radical, and X is an organic or inorganic acid radical [4,387]. The relation between the activity of these compounds and their chemical structure has been revealed by Mel'nikov [4]. Mercury compounds are often applied as components of combined disinfectants, but they also find independent usage. Many mercury compounds are used as seed disinfectants, of which only a few will be discussed here.

Ethylmercuric phosphate (NIUIF-1) is mostly used for the moist disinfection of seeds of various crops. However, other modes of disinfection are also applied. Thus a semi-dry treatment with ethylmercuric phosphate of the seeds of rye, winter wheat, and maize increases the yield, the energy of germination, and the germinating capacity [389]. Good results are obtained by immersing the seeds in a solution of the fungicide [390].

Methylmercury cyanodiamide (as the preparations Panogen, Aldrogen, Radogen [392]) is used in the form of solutions, often with mechanised treatment of the seeds [4]. This product gives favourable results for seed disinfection on flax [391], cereals, maize, tobacco, and vegetables [392].

Methoxymethylmercuric chloride (Ceresan Universal, Arethan) is a disinfectant for the seeds of grain, sugar-beet, and other crops [4].

Phenylmercuric acetate (Ceresan, PMATs, FMA, Tag, Quixane [4], Ruberone [393]) is sometimes supplied mixed with ethylmercuric chloride. Phenylmercuric acetate is used against kernel smut on seeds [393]. It can be mixed with a synergistic additive—dehydroabietylamine [394].

Phenylmercuric propionate is a bactericidal and fungicidal product [395].

Ethylmercuric chloride is the active principle of the disinfectant Granosan (NIUIF-2 [396]). It ensures decontamination of the seeds of almost all agricultural crops—cereals [397,398], fodder [400], industrial [399], horticultural, and ornamental [401]—from bacteria and fungi. Granosan increases the germinating capacity of the seeds of various crops [240].

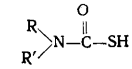
Among other mercury compounds used to disinfect seeds mention must be made of methylmercuric oxide [394], methylmercuric pentachlorophenoxide [402], and compounds of formula R'HgSR (where R' is a lower alkyl and R the residue of a polyhydric alcohol) [403]. The advantages of this group include the possibility of the advance treatment of wheat seeds with mercury-containing products [404], their comparatively high efficiency [405], and the possibility of application as oil emulsions [406].

Liquid disinfectants based on organomercury preparations have found wide application [357]: they are active not only on direct contact but also by the action of the gas phase. The best known are the above products Panogen and Aldrogen, as well as liquid preparations based on phenylmercuric acetate, mercury toluene-*p*-sulphonamide [407], and other products [408].

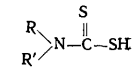
Czech workers have proposed an interesting method for obtaining small-volume arylmercury disinfectants by a series of ion-exchange reactions [409-412].

3. Thiocarbamates and Dithiocarbamates

A large group of seed disinfectants are derivatives of thiocarbamic acid



and dithiocarbamic acid

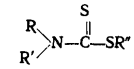


These compounds exhibit herbicidal activity, but they can also be used as fungicides or nematocides. Dithiocarbamates are the most widely used to disinfect seeds, although isolated publications have appeared on the use of derivatives of thiocarbamic acid to disinfect seeds of e.g. wheat and cotton [413].

Many papers have been published on the mechanism of the action of dithiocarbamates. It is assumed that their conversion products, isothiocyanates, possess toxic properties [387]. It is noteworthy that various isothiocyanates are used independently to treat seeds [414,415]. Discussions of the relation between the chemical structure of these compounds and their activity [4,387] reveal that the most active are those in which R and R' are methyl groups: lengthening the radical diminishes the activity.

The fungicidal properties of dithiocarbamic acids were discovered in 1934. [416] Many derivatives, primarily salts, are now used to treat seeds. Thus fungicidal activity is exhibited by the chelated dimethyldithiocarbamates of zinc [4,387,417] (marketed as Zineb), iron (Ferbam) [4,387], and manganese (Maneb) [4].

Another large group of derivatives of dithiocarbamic acid used for disinfecting seeds are compounds of general formula



where R'' may be various organic radicals, while R and R' both represent methyl. For example, compounds in which R'' = $SArX_nY_k$ (where X = NO_2; Y = H, Cl, cyclo-C_6H_{11}; and $n + k = 3$) are harmless to heat-resistant seeds and do not affect the properties of the grain [418]; compounds with R'' = $-\overline{N.CO.[CH_2]_n.CO}-$ are used to decontaminate rye seeds and possess slight phytotoxicity [419]; a preparation containing $(CH_3)_2N.NH.CO.S.S.CO.NH.N(CH_3)_2$ is used as a fungicidal disinfectant for the seeds of wheat and

oats[420]; and preparations containing a furan ring in the group R″ are applied to wheat and cotton seeds. Fungal diseases of wheat and cotton are resisted by treating the seeds with several heterocyclic derivatives of dimethyldithiocarbamic acid[413].

Derivatives of polymethylenethiocarbamic acids (usually ethylenethiocarbamic) form a separate group. The best known are manganese and zinc ethylenedithiocarbamates and bisdimethylthiocarbamoyl ethylenebisdithiocarbamate (Tekoram)[4]. Compounds of these salts with ethylenebis(thiuram disulphide) possess stronger fungicidal properties[4,421]. Tetramethylthiuram disulphide finds very wide application as a seed disinfectant, both alone and in various mixtures (Thiuram D, Thiuram, TMTD)[4]. It not only decontaminates the seeds of cereals, beans, and several other crops[397,423-425] but also raises the field germinating capacity of wheat, maize, and cotton[240,241]. The fungicidal and bactericidal properties of TMTD are strengthened by the addition of dehydroabietylamine[394].

4. Chlorinated Hydrocarbons

Chlorinated hydrocarbons (and more rarely other halogenated derivatives) form the main group of plant-protection agents, widely used both in the Soviet Union and abroad. They are employed mainly as effective insecticides and nematocides, although several also possess fungicidal properties. This class of compound is usually divided into three groups according to their chemical nature and mode of synthesis. The first group comprises halogen derivatives of aliphatic hydrocarbons, among which those which produce a sufficient concentration in the gas phase (fumigants) are usually applied to seeds.

The simplest member of the second group—halogenated aromatic hydrocarbons—is hexachlorobenzene, employed as a seed disinfectant in various mixtures against smut fungi of cereals, often together with the toxic ethylmercuric chloride[4]. Halogenated derivatives of diphenylmethane—primarily bis-*p*-chlorophenyl-2,2,2-trichloroethane (DDT)—have found considerably greater use. Several monographs have been published on the production, properties, and application of DDT.[426-428] In the treatment of seeds DDT is used mainly as a component of composite disinfectants, but references have been made to its independent application, e.g. for dusting the seeds of maize, kidney-bean, and ground-nut to protect them from pests. The germinating capacity of the treated seed was undiminished by storage in sealed vessels for up to 18 months[429]. In spite of the thorough study and adequate manufacturing capacity, the question of reducing the scale of production of DDT [4] arises from its considerable toxicity towards human beings and animals.

The third of these groups of seed disinfectants comprises halogenated alicyclic hydrocarbons. One of the most widely used insecticides of this group is hexachlorocyclohexane. Among its eight stereoisomers only the γ-isomer exhibits toxicity. A preparation containing 99–100% of the γ-isomer appears on the market as Lindane[4,430]. Hexachlorocyclohexane may also be a component of composite disinfectants. It can find independent application, e.g. to protect a seed stock from harmful insects[429]. The δ-isomer is used in disinfectant mixtures as a synergistic additive to certain fungicides[4].

Chlorinated derivatives of polycyclic compounds are widely used. Several effective products, which have found application in composite and in individual disinfectants, are obtained by diene synthesis, in particular with hexachlorocyclopentadiene as one of the reactants. Several of these products are listed below.

Allodan is 1,2,3,4,7,7-hexachloro-5,6-bischloromethylbicyclo[2,2,1]hept-2-ene

Endrin is 1,2,3,4,10,10-hexachloro-1,4 : 5,8-di-*endo*-methylene-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydronaphthalene

Aldrin is 1,2,3,4,10,10-hexachloro-1,4-*endo* : 5,8-*exo*-dimethylene-1,4,4a,5,8,8a-hexahydronaphthalene

Heptachlor is 1,4,5,6,7,8-heptachloro-4,7-*endo*-methylene-3a,4,7,7a-tetrahydroindene

Dieldrin is 1,2,3,4,10,10-hexachloro-1,4 : 5,8-di-*endo*-methylene-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydronaphthalene.

These products proved effective against harmful insects on treatment of the seeds of maize, sorghum, kidney-bean[431], carrot, onion[432], and cotton[433]. Dieldrin gives better results than other insecticides in protecting seeds from the Swedish fly[434]. These products are used also for several other plants.

Among other halogenated derivatives we must note the chlorothiophens, which are no less active than mercury preparations[435,571].

5. Other Groups of Seed Disinfectants

The earliest seed disinfectants were copper compounds, mainly organic derivatives. Copper 2,4,5-trichlorophenoxide is used[4], also constituting 20% of the disinfectant of the same name. The major portion of the product, marketed as a dust, is talc[355]. Copper trichlorophenoxide is employed e.g. for treating cotton[436] and soya[437] seeds. Another copper compound is the quinolin-8-yl oxide, the active principle of the disinfectant Quinolate-15[438] (Quinolene-15[439]).

Derivatives of trichloromethanethiol possess good fungicidal properties[440]. Attention was first directed by Kitleson[441] to the fungicidal activity of compounds containing a trichloromethylthio-group. Compounds of this series at present in use for treating seeds are tetrahydro-*N*-trichloromethylthiophthalimide (Captan)[4] and bistrichloromethyl trisulphide (possesses also stimulant properties)[242].

Among other groups of disinfectants used for treating seeds we must mention inorganic and organic arsenic compounds (e.g. calcium arsenite in Protas Preparation PD[355] and methylarsine sulphide[442]), tin compounds[443,444], and nitro-compounds, e.g. dinitrobenzene[397] and dihalogenonitrobenzenes[445,446].

The search for seed disinfectants less toxic than organometallic compounds led to the discovery of a large group of biologically active *N*-substituted carbamic esters, which were mainly highly active insecticides and herbicides. Derivatives of carbamic acid possessing also fungicidal activity are known[4,396,447]. These compounds have not yet found wide application for the treatment of seeds, but show promise in this respect[447].

Substances used to overcome pests and diseases by seed disinfection include pentachlorophenylmethanethiol and its zinc salt[449], *p*-hydroxyphenylazoformamide[450], lower 2,4-dihalogenophenyl halogenoalkanesulphonates[451], ethylenedisulphonic acids[452], 2-methoxyethylamine[453], methanol[454-456], various heterocyclic derivatives—of isothiazole[457], benzimidazole[458], benzoxazolinone[459], and thiophen[460]—oxathi-in derivatives (in particular

3-carboxyanilido-5,6-dihydro-2-methyl-1,4-oxathi-in—Vitavax)[461,572-575], substituted maleimides[462], sorbic acid[463], and several other substances[454,464]. In particular sorbic acid diminishes considerably the disease of fusariosis in cotton seeds.

Great attention has recently been paid in seed treatment to disinfectants containing more than one active principle, e.g. one or two fungicides, an insecticide, sometimes with the addition of trace elements and other active substances[157]. Such preparations are highly efficient[207,373,379,448,508]. In individual cases mixtures of different insecticides are used[151].

A mixture of the disinfectants—tetramethylthiuram disulphide and γ-hexachlorocyclohexane—is most often employed, against pathogenic fungi and bacteria, by treating seeds of grain crops[241,439,465], peas[466], and maize[246,467]. The mixture is marketed as the composite disinfectants Thiuram-gamma (50% TMTD + 20% γ-isomer + filler)[465-467], Germal (50% TMTD + 40% γ-isomer + filler)[439], and Thiramin[468]. Other mixtures are also used[241]. Manganese sulphate may be introduced into such a composition[246].

Tetramethylthiuram disulphide (40%) and γ-hexachlorocyclohexane (20%) are widely used in combination with copper trichlorophenoxide (10%) as the disinfectant Phenthiuram (containing also 5% of sulphite–alcoholic residue + 3% of carboxymethylcellulose + 20% of kaolin), employed for treating seeds of cotton and cereal–legume crops[439,469-472]. Phenthiuram possesses a broader fungicidal and bactericidal action than tetramethylthiuram disulphide[4]. Phenthiuram mixed with 8% of ammonium molybdate is marketed as Phenthiuram Molybdate[4], which gives good results against pea ascorosis[473].

Mercurhexane (containing 1% of ethylmercuric chloride + 15–20% of hexachlorobenzene + 15–20% of γ-hexachlorocyclohexane + talc + kaolin) has found widespread application as a composite disinfectant. It possesses high fungicidal activity, together with insecticidal properties[471,474-476]. Other composite disinfectants containing mercury include a mixture of Granosan and Hexachloran used for treating sugar-beet seeds[477], the preparation VV (a mixture of Lindane and organomercury compounds) for the seed treatment of wheat[478], a fungicidal mixture of ethylmercuric chloride and tetramethylthiuram disulphide stabilised with thioglycerol for preventing the infestation of seeds with fungi[479], and a mixture of tetramethylthiuram disulphide and methylmercuric dicyanodiamide[480] for grain.

Other composite disinfectants—e.g. mixtures of copper trichlorophenoxide and γ-hexachlorocyclohexane[481], tetramethylthiuram disulphide and pentachloronitrobenzene[482], zinc chromate and Heptachlor[467], tributyltin and chlorinated aliphatic compounds[483], and of tetramethylthiuram disulphide, chlorinated hydrocarbons, glycols, and quinones[484]—are also used for treating seeds to protect them from various pathogens.

Seeds are treated also with active vapours to protect them from pests and diseases. Halogenated lower hydrocarbons are most widely used in this way (as fumigants). They are applied to the seeds of sunflower[485,486] wheat[487,488], pea[489,490], barley[491-493], maize[491,494], oats[491,492], flaz[494], sorghum[491], carrot, cabbage, radish, and turnip[495].

Methyl bromide, which destroys nematodes as well as certain injurious insects, is most often used[185,485,488,490-497]. However, several disadvantages are entailed: being an alkylating agent, methyl bromide may act as a mutagen, disturbing the growth processes of plants[4] and in several cases retarding the germination of seeds[242]. Furthermore, this compound may also impair the quality of the oil obtainable from treated seeds of oil-yielding crops[486]. In this connection, the brief application of high concentrations is more effective than prolonged exposure at lower concentrations[491].

Among other halogenated hydrocarbons used for fumigation we must mention chloroform[487,498], carbon tetrachloride[485,487,499], dichloromethane[498], dichloroethane[485,499], dibromoethane[485,497], and dichloropropene (the active principle of the fumigants DD and Telon[497]), as well as dichloroethylene, trichloroethylene, dibromoethylene[499], and 1,2-dibromo-3-chloropropene[497]. The application of mixtures of these halogenated hydrocarbons has been reported. In some cases better results are given by halogenated nitro-hydrocarbons, such as chloropicrin and dichloro-1-nitroethane[490,500].

Other groups of compounds are also used as disinfestants in fumigation. Thus aluminium phosphide pellets, which evolve phosphine on hydrolysis, lead to complete destruction of granary weevils[498,501]. Sulphur derivatives—carbon disulphide[499], sulphuryl fluoride[502], sulphur dioxide, and volatile sulphur-containing decomposition products of coal[503]—are used for fumigation. This has been effected also by means of hydrogen cyanide[504] and oxiran[490]. Application of morpholino-α-methylacetonitrile and 2,2-dichloro-1-hydroxyvinyl dimethyl phosphonate showed high activity[505].

To prevent infestation with insects it is recommended that grain should be stored in an atmosphere of an inert gas, e.g. carbon dioxide or nitrogen[506], or else heptane[498].

Special attention is paid to the preservation of seeds of high moisture content[485,500,507] as well as seeds of oil-yielding crops[486,509-514], which are sensitive to several fumigants.

Repellents—in particular a mixture of 2-methylquinoline and naphthenic acids[515], cycloheximide[516]—are used against insects and rodents in the storage of grain reserves, as well as bird repellents[569].

Thus the combined efforts of plant growers and chemists have led to the manufacture of effective products that have greatly reduced crop losses. An intense search has recently been made for compounds possessing a wide spectrum of action and high activity but yet harmless to man, animals, and useful insects, as well as decomposing within required periods of time. For these reasons, in particular, interest has diminished in chlorinated, copper, and mercury products, and the use of derivatives of carbamic acid and certain other substances has increased[364,365,517].

V. APPLICATION OF CHEMICALS TO SEEDS

The seeds of certain plants are small (carrot, onion, tomato, parsley, etc.), and contain little of the reserve materials required for germination. Owing to the small size it is difficult to mechanise sowing: considerable quantities of these expensive seeds must be sown, and the shoots thinned after germination, which makes large demands on labour. As a consequence, the size of such seeds has been increased by covering their coats with bulky materials[518-524]. Such treatment (seed pelleting) was undertaken in the Soviet Union by Peterburgskii[525], who coated seeds with superphosphate mixed with starch paste. Peat, humus, feldspar, bentonite, and several other inert bulking materials are most often used for

pelleting[526,527]. The supply of mineral nutrients to the germinating seeds is improved by introducing major and minor fertilisers[528,529], as well as pesticides, into the pellet.

The experience which has accumulated shows that pelleting is a promising method, reducing the consumption of seeds, improving their germination and the development of shoots, and increasing the yield[519-521,526,530]. An important advantage over steeping seeds is that they can be prepared long before sowing, whereas soaked seeds must be sown immediately.

Protective substances are usually applied in three ways—dry, semi-dry, and moist disinfection—and usually in special equipment—disinfectors[4,356].

In dry disinfection the surface of the seeds is covered with a thin layer of the dry product. A dust is often used for this purpose, consisting of the active principle and an inert filler (kaolin, bentonite, gypsum, talc, etc.); the active part is applied from solution with subsequent evaporation of the solvent or with joint grinding[4]. In spite of the cheapness and convenience of application, dry treatment has several substantial disadvantages, primarily poor adhesion of chemicals, increased consumption thereof, and the dispersion of substances into the air, which impairs the hygienic conditions of the work[356]. Better results are obtained by applying substances in an electrostatic field, but this procedure has not been widely used[531].

"Semi-dry" disinfection improves adhesion to the seed surface and diminishes dispersion of the materials in the air[356]. This implies treatment of the seeds with moistened products and a liquid consumption usually not exceeding 30 litres per tonne of seeds. With a larger quantity of liquid such treatment is termed "moist disinfection". This is not usually applied to large batches of seeds, and requires preliminary slight drying before sowing or storage[356].

A great problem is retention of the chemical on the surface of the seeds. So called stickers are used to improve adhesion, among them a concentrate of sulphite–alcoholic residues[532], sulphite lye[533], silicate cement, flour paste, skimmed milk, molasses, liquid manure[534,535], oils[536], and alabaster[537].

The quality of the applied coating of pesticides is considerably improved by introducing a polymeric film-forming agent into the composition. This is most often a water-soluble polymer—polyacrylamide[538], methylcellulose[539], carboxymethylcellulose[540], a vinylpyrrolidone polymer or copolymer[540,541], partly hydrolysed poly(vinyl acetate)[542], polyvinyl alcohol[526], or a urea—formaldehyde resin[543]—usually amounting to a few percent. However, there are references to the use of compositions containing up to 15% of the polymer, e.g. polyvinylpyrrolidone, polyvinylimidazole, polyvinyloxazolidone, or their mixtures[544,545], epoxide resins, poly(vinyl chloride), polyethers, polyesters, polyurethanes, poly(vinyl acetate), and synthetic rubber[546]. These compositions can be applied from solution or from a dispersion in kerosene[544].

Polymeric materials are also applied that possess intrinsic fungicidal, bactericidal, and herbicidal properties without the addition of active agents of low molecular weight. Thus the polymeric complex of polyvinylpyrrolidone and iodine[547] and ligninacetic acid[548] have a bactericidal action, the product of the condensation of aminoethanol with formaldehyde is fungicidal[547], and poly(vinyl aryloxyacetates), obtained by polymerisation of the monomeric vinyl esters or by aryloxyacetylation of polyvinyl alcohol, are herbicidal[549].

Wetting powders—products giving stable suspensions when mixed with water—have recently occupied an important place among preparations applied to seeds. They are produced by introducing surface-active agents into the compositions[4,550-553].

It has long been established that seeds of many crops, after having been subjected to the action of low temperatures, will give more productive plants: they ripen sooner and give a higher yield. However, practical application of these results encountered considerable difficulties, since seeds sown early in Spring, on germinating, were destroyed by Spring frosts. In this case germination could be delayed by coating the seeds with water-repellent films. By restricting the entry of water into the seeds, such films thereby delay the metabolic processes governing germination. The application of hydrophobic films is especially important for Spring wheat, whose cultivation encounters certain difficulties in several regions. The use of water-repellent seed coatings enables Summer crops to be sown not in Spring but in Autumn, even before the soil is frozen.

Attempts were made to use paraffin wax and a liquid silicone to effect such water-repellency[554-557], but polymeric seed coatings were found to be more promising. Even previously pelleted seeds can be coated with such polymer films. In particular, the presowing treatment of pelleted vegetable seeds with copolymers of vinyl chloride and vinylidene chloride has been reported[558].

Polymer coatings comprising several layers are used for seed treatment[559,560]. The outer, poly(vinyl chloride) film, by disintegrating under the influence of variable temperatures, frees the inner, hydrophilic layers, thereby promoting penetration of moisture into the seeds. Cellulose derivatives have been used as the second layer. The application of such coatings enables the yield to be raised by 15–16% and more convenient sowing times to be used for Spring crops. Plants were found to bush more intensely, have a shorter and stronger culm, ripen two weeks sooner, and give a grain of enhanced protein content.

Union Carbide has proposed an interesting method for controlling germination, by the factory sealing of the seeds into a continuous polymer ribbon which, when placed in the soil, will dissolve within a short period (from 1 min to 1 h). Use of such a ribbon facilitates the sowing of vegetable crops, assists the production of harmonious seedlings and uniform plant growth, increases the yield, and improves the quality of production[561].

It is seen that polymers are finding increasing application for improving the sowing qualities of seeds. In the future the coating of seeds with special films may occur on a larger scale.

A solution in water or in an organic solvent is usually employed for the coating of seeds with polymers. Organic solvents are used also for the application of compounds of low molecular weight. The solvents employed have been acetone, methanol and ethanol[562], halogenated hydrocarbons[4], dimethyl sulphoxide, dimethylformamide, and dimethylacetamide[450]. The germinating power of the seeds may be affected by the organic solvent[563,564].

References have been made to the possibility of the direct polymerisation of monomers on the seed surface. Thus Kozlov and Tarusov polymerised vinylpyrrolidone on the surface of irradiated seeds in aqueous solution at 30–70°C for 2–24 h.[566,567]

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The facts reported here indicate the wide possibilities of the application of chemicals to the treatment of seeds. These include disruption of their dormancy, stimulation of germination, increase in field germinating capacity, and heightened resistance to pathogenic micro-organisms and unfavourable weather conditions. Further cooperation of chemists with physiologists and growers may not only promote a more fundamental study of the processes occurring during storage and germination but also yield new possibilities of controlling the vital activity of seeds.

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