PLANT-PROTECTION AGENTS BASED ON COMPOUNDS OF THE PYRIDINE SERIES (REVIEW)

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The principal derivatives of pyridine bases that display pesticide activity are examined. It is shown that the accessible oxygen-containing functional derivatives of pyridine are intermediates for the synthesis of a large number of promising plant-protection agents.

The intensification of agriculture requires, in addition to modernization of agricultural technology, the use of highly effective chemical agents for the protection of plants; this has been reflected in the rich arsenal of pesticides that is now available in the world market [1-4]. The worldwide consumption of pesticides is constantly increasing. In the USA the output of plant-protection agents from 1967 to 1984 grew by a factor of 1.5 [5], whereas it increased by a factor of more than 10 from 1960 to 1985 [4]. At the present time the worldwide production of pesticides is 2 million tons per year [4].

According to the published data [3, 4, 6-18], compounds of virtually all classes of organic substances display pesticide activity. Heterocyclic preparations, including pyridine derivatives, have diverse types of pesticide activity.

Pesticides that are obtained or can be obtained from pyridinecarbaldehydes and pyridinecarbinols or their transformation products such as pyridinecarboxylic acids, aminomethylpyridines, dipyridyls, etc. are primarily examined in the present review. This is due to the fact that the catalytic methods that have been developed for obtaining pyridinecarbaldehydes (incorporated into industry) [19-27] and pyridinecarbinols [28-30] make it possible to create the industrial production of pesticides based on them [31].

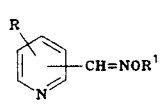
According to the data in [3], three groups of pesticides, viz., herbicides and plant-growth regulators (38.3%), insecticides (33.9%), and fungicides (27%), have found greatest application in the various spheres of the national economy.

Compounds with Herbicidal and Growth-Regulating Activity

Of the 244 herbicides included in a handbook in 1985 [3], the structures of 14 contain a pyridine ring. These are primarily derivatives of 2-hydroxypyridine, pyridinecarboxylic acids, pyridine N-oxides, and quaternary pyridinium and piperidinium salts.

The creation of new preparations is, for the most part, based on the principle of fusion of a pyridine fragment with derivatives of compounds that are known to have growth-regulating and herbicidal properties. Among the compounds for which herbicidal activity has been observed one encounters derivatives of pyridine-carbaldehydes [32-44], pyridinecarbinols [45-50], pyridinecarboxylic acids [3, 10, 51-73], aminomethylpyridines [60, 69], and other substituted alkyl- and alkenylpyridines [47, 74-81].

Oxmines of pyridinecarbaldehydes and their esters (I), [32, 33] as well as semi- and thiosemicarbazones, are effective in eliminating weeds in fields with grain crops and buckwheat.



I

R=H, CH_3; R^1=$C_2H_4C_6H_5$, $C_2H_4OC_6H_5$, C_3H_7, C_5H_{11}

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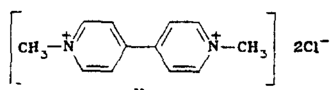
Pozdeeva and coworkers [34] have proposed that the higher herbicidal activity of pyridine-2-carbaldehyde thiosemicarbazone as compared with the semicarbazone is due to the ability to form slightly soluble complexes with metal ions.

A derivative of pyridine-2-carbaldehyde — (2-pyridyl)-hydroxymethanesulfonic acid, which acts on the biochemical photosynthesis and respiration processes — has been used to accelerate the buildup of biomass in plants for which high intensity of photorespiration is characteristic, primarily tobacco, sunflowers, and soybeans. It has been recently shown, however, that the action of (2-pyridyl)hydroxymethanesulfonic acid on a plant such as soya has low specificity, since it affects not only the processes involved in the oxidation of the glycolate but also the photosynthetic assimilation of carbon dioxide and the catabolism of pyruvic acid [82-96]. In addition, it was established that (2-pyridyl)hydroxymethanesulfonic acid has an inhibiting effect on the accumulation of ammonia in the synthesis of amino acids and peptides [95-98]. Its use in higher concentrations as a herbicide presents fewer problems [94-95].

Information on the high herbicidal activity of dipyridyl salts [99] was published in the 1950's; a number of preparations created on the basis of these salts were subsequently recommended for practical application not only as agents for battling weeds but also as dessiccants for some forms of crops [6, 9, 100, 101].

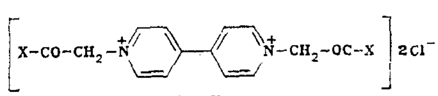
At the present time dipyridyls are most often obtained by dehydrogenation of pyridine in the presence of metals (sodium, magnesium) at 200-350°C [7]. A difficult-to-separate mixture of isomeric dipyridyls is formed as a result of the reaction. A selective method for the synthesis of dipyridyls from pyridine-carbaldehyde, acetaldehyde, and ammonia is more promising [102-107]. Thus, 4,4'-dipyridyl is obtained by condensation of pyridine-4-carbaldehyde with acetaldehyde and ammonia in the presence of an aluminum–cobalt–phosphate catalyst at 300-350°C. Preparations of this series include 1,1'-dimethyl-4,4'-dipyridylium dichloride (II) (paraquat), which is readily soluble in water [4, 11, 15].



II

Compound II enters into the composition of the contact herbicide Gramoxone, which is used to battle weeds. Paraquat is also used to treat steam prior to the sowing of various crops (plowless agriculture). With respect to its properties, diquat — 1,1'-ethylene-2,2'-dipyridylium dibromide — is similar to paraquat [100, p. 158]. Diquat and paraquat are used to prevent the blossoming of beets and sugar cane and for the desiccation of clover seedings, rice, and vegetable crops [101].

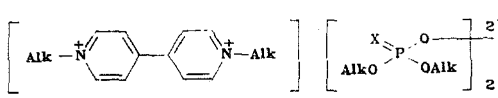
According to the data in [7], 1,1'-bis(piperidino-carbonylmethyl)-4,4'-dipyridylium chloride (III) (preparation PP-407), 1,1'-bis(diethylcarbamoylmethyl)-4,4'-dipyridylium chloride (IV) (preparation PP-831), and 1,1'-bis(3,5-dimethylmorpholinocarbonylmethyl)-4,4'-dipyridylium chloride (V) (preparation PP-745, morphamquat) are promising for use in agriculture.



III - V

III X= piperidino IV X=$N(C_2H_5)$, V X=3,5-dimethylmorpholino

Dipyridylium salts of esters of phosphoric and thiophosphoric acid VI are characterized by low toxicity for warm-blooded animals and selective herbicidal activity at an input norm of 0.6-1 kg/ha [108-112].



VI

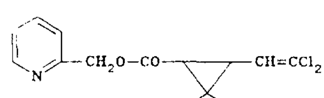
X=O, S

1,1'-Dimethyl-4,4'-dipyridylium dimethoxyphosphate has been studied under conditions of extensive field tests. Dipyridylium compounds, both those that are unsubstituted at the nitrogen atoms of the pyridine rings and those that contain methyl, propyl, butyl, phenyl, and diethylcarbamoylmethyl groups, have been synthesized and investigated [113-119]. Reports regarding the practical application of compounds with alkyl substituents in the pyridine ring [116, 117] have not yet been published. Research to find ways to improve the methods for obtaining active compounds of this type is continuing [120, 121].

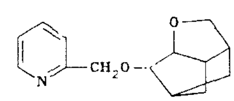
The physicochemical properties and reactivities of dipyridylium derivatives were investigated in order to establish the mechanism of their action and to study their herbicidal activity [122-125]. It was established [126, 127] that the phytotoxic effect of dipyridylium herbicides is due to their ability to undergo reduction to free radicals, the oxidation of which is accompanied by the liberation of hydrogen peroxide. A comparison of the results of spectroscopic and electrochemical investigations of various derivatives of dipyridyls showed that the high herbicidal activity is associated with the reversibility of one-electron transfer in the oxidation of the pesticide by air [128, 129]. Although they do not markedly change the reduction potential, the introduction of substituents and the incorporation of a carbimino group or heterocycle residues (triazine, 1,3,4-thiadiazole, 1,3,4-oxadiazole) between the pyridinium rings do disrupt the reversibility of electron transfer and substantially decrease the herbicidal activity [130, 131]. A number of complexes of paraquat and diquat with metals have been synthesized, and their reducibilities and biocidal activity have been examined [123, 132].

A number of formulations for the combined use of dipyridylium herbicides in a mixture with substances that act on plants via a different mechanism have been developed; this makes it possible to significantly decrease the consumption of the herbicidal components and increase the effectiveness of the activity. Thus compositions that consist of sulfates of alkali or alkaline-earth metals, N,N'-dimethyl-4,4'-dipyridylium or N,N'-ethylene-2,2'-dipyridylium ions, and herbicidal preparations of derivatives of urea or triazine have been described [133, 134]. In a number of cases emetics are added to the herbicidal preparations based on dipyridylium salts in order to prevent the poisoning of animals by them [135] or dyes are added to increase the safety of agricultural workers [136]. Multicomponent and, more often, two-component compositions that contain dipyridylium salts are being developed in order to achieve a synergistic effect and to extend the range of activity [137, 138] or to create not only safe but also convenient-to-use commercial forms in the form of a stable emulsions [139].

Herbicidal activity with respect to herbaceous and broad-leaved weeds has been noted for esters of 2- and 3-pyridylcarbinols [45, 46, 48, 49], for which pre- and postgermination application is recommended. Ester VII also displays fungicidal activity relative to the most widely abundant phytopathological fungi, while 6-oxatricyclo[3.2.1.1^{3,8}]nonan-4-ol ester VIII has growth-regulating properties.

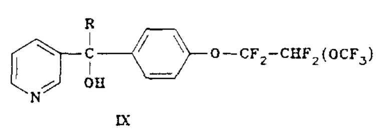


VII



VIII

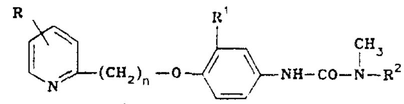
Some esters of 3-pyridylcarbinol have been proposed for battling the plant growth (Hydrilla verticulata) in reservoirs [98]. α,α-Disubstituted 3-pyridylcarbinols [50, 79] with the following general formula are growth regulators that display herbicidal and fungicidal activity:



IX

R = C_1—C_{12} -alkyl, C_5—C_6 —cycloalkyl, phenyl, pyridyl

Alkyl and alkoxy derivatives (X) of urea display high herbicidal selectivity [76].



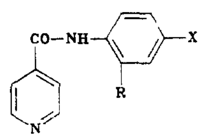
Xa-c

X a $R=2\text{-}CH_3$, $R^1=H$, $R^2=Alk$, OAlk; $n=2$; b $R=3\text{-}C_2H_5$, $R^1=CF_3$, $R^2=Alk$; $n=3$; c $R=R^1=H$, $R^2=Alk$, $n=2$

For example, Xb, which has been proposed for battling weeds in wheat seedings [78], and derivatives of the Xc type, which effectively eliminate weeds in fields of maize, for which they are nontoxic, are used in the form of 10-90% emulsions, moistened powders, 0.1-10% dusts, or 1-20% granulated preparations.

Phenoxy derivatives of pyridine, which, in a number of cases, can be obtained from pyridylcarbinols, constitute a relatively new group of herbicides. Compounds of this group eliminate chiefly monocotyledonous weed plants at relatively low output norms (0.25-0.5 kg/ha) [8].

A large number of active pesticides have been obtained on the basis of pyridinecarboxylic acids and their derivatives. Nicotinic acid and anilides of nicotinic and isonicotinic acid such as XI are regulators of the growth of herbaceous plants [8, 54, 57, 58, 64, 65].



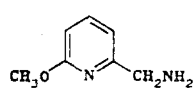
XI

$R=COCH_3$, CH_2OH, C_6H_5O; $X=Cl$, Br

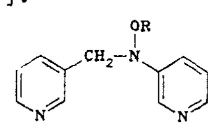
A broad spectrum of herbicidal activity is characteristic for 3,6-dichloropicolinic acid (Lontrel), which is used individually or in a mixture with other preparations to battle weeds in seedlings of most agricultural crops (herbaceous, maize, and beets) [72, 140].

One of the most active herbicides of the pyridine series is 4-amino-3,5,6-trichlorpicolinic acid [141], which enters into the composition of the retardant pikloram as such or in the form of salts (Tordon) and is used to accelerate the blossoming and ripening of tobacco leaves. Pikloram is a herbicide with prolonged activity that eliminates both annual and perennial weed plants [142-144].

Aminomethylpyridines XII and XIII have been proposed for the elimination of herbaceous weeds in seedlings of broad-leaved crops [60, 74].



XII



XIII

R = phenyl, p-chloro, and p-nitrophenyl, butyl, tert-butyl, tert-amyl, methoxymethyl, phenoxymethyl

Amine XII can be obtained from 6-methoxypyridine-2-carbaldehyde by known methods.

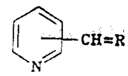
Pyridine Derivatives with Fungicidal Activity

According to recent data, fungicides constitute ~1/5 of the total world arsenal of pesticides. The consumption of fungicides in individual countries depends on climatic conditions and the agricultural crops; for example, in the USA in 1981 the consumption of fungicides was 1/5 of the amount of herbicides, and in Japan the consumption of these chemicals was approximately the same, whereas in Italy and India fungicides were used even more extensively (by a factor of almost two) than herbicides [2, 3].

Pyridine bases display fungicidal activity relatively rarely; of the 172 preparations presented in a handbook [3], only three are pyridine compounds. These are derivatives of aminopyridine and hydroxypyridine and a quaternary piperidinium salt. 4,4'-Dichlorodiphenyl-3-pyridylcarbinol (parinol or parnon) has found application in the USA [6].

Bis(4-chlorophenyl)(3-pyridyl)- and alkyl-4-halobenzyl(3-pyridyl)carbinols have systemic fungicidal activity [4]. Derivatives of 2- and 4-pyridylcarbinols [145-149] and pyridylethanols [149, 150] have been synthesized and studied as fungicides.

Fungicides have been sought among pyridinecarbaldehyde derivatives XIV [151-157]:



XIV

R = NOCOAlk; $CHCHO-C_6H_4-F$; $N-C_6H_4-OCH_3$; 5-nitrofurfurylideneazo

There are reports regarding the fungicidal action on phytopathogenic fungi (powdery mildew, wheat mildew, etc.) of substituted anilides of isonicotinic acid such as 2-(p-fluorophenacyl)anilide of isonicotinic acid and its analogs with various substituents in the aniline and phenacyl fragments [158].

Pyridine Derivatives with Insecticidal Activity

Of the 216 insecticidal preparations presented in [3], seven are pyridine derivatives. They include 3-(1-methyl-2-pyrrolidyl)pyridinium sulfate, which is an effective and highly toxic preparation that is used to combat aphids, thrips, and other sucking pests. The preparation Dow-417, which includes 6-phenoxy-2-pyridyl(α-cyano)methyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, has been proposed to combat sucking insects and house flies [159-161].

The search for new insecticides with less pronounced overall toxicity is being carried out for the most part among derivatives of 6-phenoxy-2-pyridylcarbinol [159-166].

According to preliminary data a number of esters of 2-pyridylcarbinol display insecticidal activity that is comparable to that for Allethrin and high acaricidal activity [164]. Compounds of this series are obtained by acylation of pyridylcarbinol derivatives [158-166].

2-Dialkylaminoethyl esters of nicotinic acid have insecticidal and nematocidal activity [4].

Insecticidal activity has been established for derivatives of pyridinecarbaldehyde phenylhydrazones [167]. It has been proposed that 6-fluorophenoxypyridine-2-carbaldehyde be used as an intermediate for the synthesis of pyrethroids – synthetic analogs of the natural compounds pyrethrins, which have insecticidal activity [4].

It follows from the literature data presented that oxygen-containing derivatives of pyridine such as carbinols, carbaldehydes, and carboxylic acids are promising for the creation of pesticides with herbicidal, growth-regulating, fungicidal, and insecticidal activity.

The industrial production of pyridinecarbaldehydes based on the oxidation of methylpyridines with air oxygen in the presence of heterogeneous catalysts ensures an accessible raw-material base for the synthesis of the most diverse chemical agents for the protection of plants.

LITERATURE CITED

1. N. N. Mel'nikov, Zh. Vses. Khim. Obshchestva, 29, 3 (1984).
2. N. N. Mel'nikov, Yu. N. Fadeev, and K. V. Novozhilov, The Scientific Foundations of Plant Protection [in Russian], Kolos, Moscow (1984).
3. Handbook of Pesticides [in Russian], Khimiya, Moscow (1985).
4. N. N. Mel'nikov, Pesticides, Chemistry, Technology, and Application [in Russian], Khimiya, Moscow (1987).
5. V. K. Bel'skaya and Z. A. Belous, Khim. Prom. za Rubezhom, No. 8, 1 (1987).
6. N. N. Mel'nikov, The Chemistry and Technology of Pesticides [in Russian], Khimiya, Moscow (1974).
7. N. N. Mel'nikov, E. G. Novikov, and B. A. Khaskin, The Chemistry and Biological Activity of Dipyridyls and Their Derivatives [in Russian], Khimiya, Moscow (1975).
8. Yu. A. Baskakov, Zh. Vses. Khim. Obshch. 29, 22 (1984).
9. O. V. Titova, Exogenous Growth Regulators and Their Role in the Development and Productivity of Plants: Interuniversity Collection [in Russian], No. 187, Yaroslavl (1980), p. 5.
10. Handbook of the Chemization of Agriculture [in Russian], Kolos, Moscow (1969).
11. N. N. Mel'nikov (editor), New Pesticides. Collection of Translations and Review [in Russian], Mir, Moscow (1970).
12. Handbook of Herbicides [in Russian], Rossel'khozidat, Moscow (1977).
13. Plant-Growth Regulators [in Russian], Kolos, Moscow (1979).
14. V. P. Deeva, Retardants – Plant-Growth Regulators [in Russian], Nauka i Tekhnika, Minsk (1980).

15. N. N. Mel'nikov, K. V. Novozhilov, and T. N. Pavlova, Chemical Agents for the Protection of Plants. Handbook [in Russian], Khimiya, Moscow (1980).
16. A. A. Kravtsov and N. M. Gol'shin, Preparations for Plant Protection. Handbook [in Russian], Kolos, Moscow (1984).
17. L. G. Lagunov, Pesticides in Agriculture [in Russian], Agropromizdat, Moscow (1985).
18. A. V. Fisyunov, Handbook for Combating Weeds [in Russian], Kolos, Moscow (1984).
19. L. Ya. Leitis, Advances in Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds [in Russian], Zinatne, Riga (1984), p. 64.
20. M. V. Shimanskaya, L. Ya. Leitis, I. G. Iovel', Yu. Sh. Gol'dberg, R. A. Skolmeistere, and L. O. Golender, Problems in Kinetics and Catalysis. 19. Partial Oxidation of Organic Compounds [in Russian], Nauka, Moscow (1985).
21. L. Ya. Leitis, "Catalytic oxidation of nitrogen-containing methyl-substituted heterocycles to hetaryl aldehydes," Doctoral Dissertation, Riga (1986).
22. L. Ya. Leitis, R. A. Skolmeistere, L. O. Golender, D. P. Yansone, P. A. Meksh, and M. V. Shimanskaya, Khim. Geterotsikl. Soedin., No. 1, 75 (1986).
23. L. Ya. Leitis, R. A. Skolmeistere, and M. V. Shimanskaya, Khim. Geterotsikl. Soedin., No. 1, 64 (1987).
24. M. V. Shimanskaya and L. Ya. Leitis, Order of the Red Banner of Labor Institute of Organic Synthesis: Organic Synthesis: 1957-1987 [in Russian], Zinatne, Riga (1987), p. 205.
25. A. A. Avots, G. V. Glemite, I. Ya. Lazdyn'sh, L. Ya. Leitis, and M. V. Shimanskaya, USSR Author's Certificate No. 253065; Byull. Izobret., No. 30, 30 (1969).
26. A. V. Avots, V. A. Aizbalts, V. A. Belikov, V. A. Kuplenieks, I. V. Smorodina, and V. D. Shatts, USSR Author's Certificate No. 556139; Byull. Izobret., No. 16, 66 (1977).
27. A. A. Avots, G. V. Glemite, I. Ya. Lazdyn'sh, L. Ya. Leitis and M. V. Shimanskaya, Koks Khim., No. 8, 50 (1971).
28. L. Ya. Leitis and M. V. Shimanskaya, Zh. Prikl. Khim., 53, 917 (1980).
29. D. P. Yansone, L. Ya. Leitis, and M. V. Shimanskaya, Izv. Akad. Nauk Latv. SSR. Ser. Khim., No. 4, 470 (1983).
30. L. Ya. Leitis, D. P. Yansone, V. V. Stonkus, V. N. Sokolova, and S. K. Germane, USSR Author's Certificate No. 1167182; Byull. Izobret., No. 26, 108 (1985).
31. L. Ya. Leitis, R. A. Skolmeistere, D. P. Yansone, K. I. Rubina, and M. V. Shimanskaya, Izv. Akad. Nauk Latv. SSR. Ser. Khim., No. 7, 89 (1984).
32. A. Steinhards and W. Mathes, US Patent No. 3043675; Chem. Abstr., 57, 10282 (1962).
33. A. Steinhards and W. Mathes, US Patent No. 2924604; Chem. Abstr., 56, 736 (1962).
34. A. G. Pozdeeva, L. D. Stonov, and L. A. Bakumenko, Khim. Skh. Khozyaistve, 4, 435 (1966).
35. H. Hatt and J. Schmiedel, J. Comp. Physiol. A., 154, 855 (1984).
36. K. S. Moorthy, B. K. Reddy, K. S. Swami, and C. S. Chetty, Arch. Int. Physiol. Biochim., 92, 147 (1984).
37. R. A. Khavari-Nejad, Photosynthetica, 19, 155 (1985).
38. T. C. Ta, K. W. Jou, and R. J. Meland, Plant Physiol., 78, 334 (1985).
39. B. Bergman, G. A. Godd, and L. Z. Haellbon, Pflanzenphysiologie, 113, 451 (1984).
40. T. Takematsu, M. Konnai, K. Tachibana, K. Matsumoto, Y. Sekizawa, and T. Watanabe, French Patent No. 2518872; Chem. Abstr., 99, 153871 (1983).
41. V. B. Avdeev, I. S. Berdinskii, Z. D. Belykh, and G. F. Rozenblat, Zh. Org. Khim., 19, 1184 (1983).
42. J. E. Rockley and L. A. Summers, Aust. J. Chem., 33, 1397 (1980).
43. H. G. Kurt, US Patent No. 4108399; Ref. Zh. Khim., 100496P (1979).
44. Tsern-Shi Chang and M. G. Merkle, Weed Sci., 30, 70 (1982).
45. R. E. Cherpeck, U. S. Patent No. 4407806; Ref. Zh. Khim., 160370P (1984).
46. M. L. Ash and R. G. Pews, US Patent No. 4423222; Ref. Zh. Khim., 180307P (1984).
47. M. D. Barker, European Patent No. 13581; Chem. Abstr., 94, 46756 (1981).
48. G. B. Payne, US Patent No. 4486220; Ref. Zh. Khim., 180383P (1985).
49. C. A. Henrick, US Patent No. 4238614; Chem. Abstr., 94, 139309 (1981).
50. R. L. Benfiel, Romanian Patent No. 64649; Ref. Zh. Khim., 210440P (1979).
51. D. R. Ciarlante, R. R. Fine, and T. E. Peoples, Tenth International Congress on Plant Protection: Proceedings of the Conference, Vol. 1, Brighton (1983), p. 339.
52. H. A. Pass and B. J. Watt, Canadian Patent No. 1158453; Ref. Zh. Khim., 10443P (1985).
53. H. Tomioka, M. Shirakawa, M. Yoshimoto, I. Iwane, and Y. Murakami, Ref. Zh. Khim., 10438P (1985).
54. N. Shirakawa and H. Tomioka, Japanese Patent No. 59122402; Ref. Zh. Khim., 160358P (1985).
55. A. N. Mikhno, F. L. Kalilnin, and O. A. Kochina, USSR Author's Certificate No. 1132883; Byull. Izobret., No. 1, 19 (1985).

56. T. Numamata, T. Sumida, D. Watanabe, and T. Imai, Japanese Patent No. 59225180; Ref. Zh. Khim., 210515P (1985).
57. H. Sugiyama, M. Takguti, H. Tomioka, and N. Shirakawa, Japanese Patent No. 584767; Ref. Zh. Khim., 110409P (1984).
58. M. Koizumi, S. Shirokawa, and H. Tonioka, US Patent No. 4435202; Ref. Zh. Khim., 230447P (1984).
59. R. B. Rogers, J. S. Claus, and E. A. Egli, US Patent No. 4383851; Ref. Zh. Khim., 40361P (1984).
60. P. K. Ten Haken and S. B. Webb, British Patent No. 2124615; Ref. Zh. Khim., 10395P (1985).
61. P. J. Wepplo, US Patent No. 4460776; Ref. Zh. Khim., 80470P (1985).
62. De H. F. Reinach and D. Ambrosi, French Patent No. 2537580; Ref. Zh. Khim., 100434P (1985).
63. K. Rewald and U. Hain, East German Patent No. 210262; Ref. Zh. Khim., 12N202P (1985).
64. M. Takeuchi and H. Shiguyama, Japanese Patent No. 59122468; Ref. Zh. Khim., 160357P (1985).
65. N. Shirokawa, H. Tomioka, M. Koidzumi, and M. Takeuchi, Japanese Patent No. 5759867; Ref. Zh. Khim., 90390P (1983).
66. De H. F. Reinach and D. Ambrosi, European Patent No. 44262; Chem. Abstr., 97, 109876 (1982).
67. G. Sandmann, P. M. Bramley, and P. Böger, J. Pestic. Sci., 10, 19 (1985).
68. A. Diskus and E. Auer, Tenth International Congress on Plant Protection: Proceedings of the Conference, Vol. 2, Brighton (1983), p. 945.
69. G. V. Galaktionova, V. K. Promonenkov, and N. S. Kol'tsov, USSR Author's Certificate No. 1085581; Byull. Izobret., No. 14, 212 (1985).
70. De H. F. Reinbach and D. Ambrosi, French Patent No. 2508446; Ref. Zh. Khim., 10394P (1984).
71. M. S. Raskin, Yu. Ya. Spiridonov, and N. K. Bliznyuk, Khim. Skh. Khozyaistve, No. 6, 44 (1984).
72. A. Clayton, Hort. Ind. Nos. 14/15, 17 (1981); Ref. Zh. Khim., 140304 (1981).
73. T. Ikeda, Yu. Tanaka, and S. Otari, Japanese Patent No. 58206505; Ref. Zh. Khim., 200456P (1984).
74. K. Tsudzuki and H. Morinaka, Japanese Patent No. 58208272; Ref. Zh. Khim., 230445P (1984).
75. N. S. Prostakov, A. T. Soldatenkov, P. K. Radzhan, A. P. Krapivko, A. P. Shapovalov, and O. P. Kartomysheva, USSR Author's Certificate No. 1004384; Byull. Izobret., No. 10, 106 (1983).
76. Y. Kawamatsu, T. Saraie, and H. Yoshikawa, US Patent No. 4443246; Ref. Zh. Khim., 30455P (1985).
77. I. Iwataki, A. Nakayama, and M. Kaeriyama, Japanese Patent No. 5967265; Ref. Zh. Khim., 80469P (1985).
78. H. Miki, T. Kamikado, and H. Yosikawa, Japanese Patent No. 59110672; Ref. Zh. Khim., 130469P (1985).
79. E. Lilly and Co., Irish Patent No. 39242; Ref. Zh. Khim., 110478P (1979).
80. D. Jahn, R. Becker, M. Keil, W. Spiegler, and B. Würzer, West German Patent No. 3310418; Ref. Zh. Khim., 140463P (1985).
81. T. J. Walter, US Patent No. 449535; Ref. Zh. Khim., 160356P (1985).
82. J. Zelitch, Plant Physiol., 41, 1623 (1966).
83. J. L. Hess and N. E. Tolbert, J. Biol. Chem., 241, 5705 (1966).
84. J. Zelitch, Science, 188, 626 (1975).
85. M. L. Salni and P. H. Homan, Can. J. Bot., 51, 1857 (1973).
86. S. G. Vaklinova, Yu. Khobanova, and D. D. Moskova, Dokl. Bolg. Akad. Nauk, 26, 1533 (1973).
87. G. Codd and W. D. Stewart, P. Arch. Microbiol., 94, 11 (1973).
88. B. S. Bhuller, J. M. Daly, and D. W. Rehfeld, Plant Physiol., 56, 1 (1975).
89. Z. Kaminska, R. Gutkowski, and S. Z. Maleszewski, Pflanzenphysiologie, 91, 17 (1979).
90. N. Yasunori and M. Shigetah, Plant Cell. Physiol., 21, 1541 (1980).
91. C. Passera, Agric. Ital., Nos. 1-2, 323 (1979).
92. Z. Kaminska and S. Maleszewski, Photosynth. Rev., 1, 45 (1980).
93. A. M. Amory and C. F. Creswell, Fifth Photosynth. Proc. Int. Congr., 6, 39 (1980).
94. J. C. Latche, G. Bailly, and F. G. Cavalie, Comp. Rend., Ser. 3, 293, 765 (1981).
95. G. Bauman, J. Balfanz, and G. Guenther, Biochem. Physicol. Pflanz., 176, 423 (1981).
96. J. Klos, G. Guenther, and Z. Wiss, Paedagog. Hochsch. "Karl Liebknecht" Potsdam, 23, 57 (1981).

97. F. Martin, M. J. Winspear, and J. D. McFarlane, Oaks and Plant Physiol., 71, 177 (1983).
98. E. Lilly and Co., Netherlands Patent No. 7800052; Chem. Abstr., 92, 53384 (1980).
99. R. C. Brian, R. F. Homer, J. Stubbs, and R. L. Jones, Nature, 181, 446 (1958).
100. Handbook of the Application of Growth Regulators in Plant Growing [in Russian], Shtiintsa, Kishinev (1981).
101. A. A. Cherkasova, Khim. Prom. za Rubezhom, 11, 43 (1987).
102. O. S. Otroshchenko, A. A. Ziyaev, and A. S. Sadykov, USSR Author's Certificate No. 172803; Byull. Izobret., No. 14, 27 (1965).
103. I. Ya. Lazdyn'sh and A. A. Avots, Khim. Geterotsikl. Soedin., No. 8, 1011 (1979).
104. I. Ya. Lazdyn'sh and A. A. Avots, Izv. Akad. Nauk Latv. SSR. Ser. Khim., No. 4, 427 (1974).
105. I. Ya. Lazdyn'sh, "Catalytic synthesis of dipyridyls", Author's Master's Disseration Abstract, Riga (1974).
106. I. Ya. Lazdyn'sh and A. A. Avots, Catalytic Synthesis and Transformations of Heterocyclic Compounds (Heterogeneous Catalysis) [in Russian], Zinatne, Riga (1976), p. 99.
107. Imper. Chem. Ind. Ltd., Polish Patent No. 85308; Ref. Zh. Khim., 11N195P (1979).
108. A. H. Jubb, British Patent No. 926326; Ref. Zh. Khim., 12N140P (1964).
109. N. N. Mel'nikov, B. A. Khaskin, L. D. Stonov, L. A. Bakumenko, and N. M. Usacheva, USSR Author's Certificate No. 183206; Byull. Izobret., No. 13, 20 (1966).
110. N. N. Mel'nikov, B. A. Khaskin, and I. V. Sablina, USSR Author's Certificate No. 209458; Byull. Izobret., No. 5, 32 (1968).
111. B. A. Khaskin, N. N. Mel'nikov, and I. V. Sablina, USSR Author's Certificate No. 273198; Byull. Izobret., No. 20, 32 (1970).
112. N. N. Mel'nikov, L. D. Khaskin, I. V. Stonov, I. V. Sablina O. G. Gordon, and N. A. Gruzinskii, USSR Author's Certificate No. 249113; Byull. Izobret., No. 24, 125 (1969).
113. L. W. Hedrich, Ger. Offen. No. 2223716; Chem. Abstr., 78, 84262 (1973).
114. ICI, French Patent Application No. 84655; Chem. Abstr., 64, 712 (1966).
115. M. F. Chan, US Patent No. 4223150; Chem. Abstr., 94, 121333 (1981).
116. R. F. Homer and J. E. Downes, French Patent No. 85046; Chem. Abstr., 64, 14173 (1966).
117. D. Jerchel, E. Fischer, and K. Thomas, Chem. Ber., 89, 2921 (1956).
118. K. Tamashima and S. Watanabe, Japanese Patent No. 5920268; Ref. Zh. Khim., 60479P (1985).
119. K. Tamashima and S. Watanabe, Japanese Patent No. 595161; Ref. Zh. Khim., 12N203P (1985).
120. S. Gigi, V. Pancescu, D. M. Rizescu, and I. Neascu, Romanian Patent No. 58782; Ref. Zh. Khim., 17N198P (1977).
121. M. F. Chen, Brazilian Patent No. 7900527; Chem. Abstr., 94, 174897 (1981).
122. Ch. Sh. Kadyrov, Herbicides and Fungicides as Antimetabolites and Inhibitors of Enzyme Systems [in Russian], FAN, Tashkent (1970).
123. N. Burke, K. C. Milloy, T. G. Purcell, and M. R. Smyth, Inorg. Chim. Acta, 106, 129 (1985).
124. C. Felttke, Biochemical Responses Induced by Herbicides. Symposium of the 181st ASC National Meeting, Atlanta, 1981, Washington, D.C. (1982), p. 231.
125. C. A. Rebeiz, A. Montazer-Zouhoor, H. J. Hoper, and S. M. Wu, Enzym. Microbiol. Technol., 6, 390 (1984).
126. R. F. Homer, G. C. Mess, and T. E. Tomlinson, J. Sci. Food Agric., 11, 309 (1960).
127. J. E. Dickenson and L. A. Summer, J. Sci. Food Agric., 20, 74 (1969).
128. D. M. Conning, K. Fletcher, and A. A. B. Swan, Br. Med. Bull., 25, 245 (1969).
129. A. L. Black and L. A. Summers, J. Chem. Soc., C, No. 4, 610 (1969).
130. L. A. Summers, Nature, 215, 381 (1967).
131. D. A. Kennedy and L. A. Summers, J. Heterocycl. Chem., 18, 409 (1981).
132. J. Duggan and N. Gassman, Plant Physiol., 53, 206 (1974).
133. T. Midzuno and T. Sato, Japanese Patent No. 5347656; Ref. Zh. Khim., 210350P (1980).
134. T. Midzuno and T. Sato, Japanese Patent Application No. 54-140729; Ref. Zh. Khim., 210350P (1980).
135. J. P. Milionis and J. E. Fischer, US Patent No. 4432787; Ref. Zh. Khim., 240106P (1984).
136. Ya. Sumita and S. Furuhashi, Japanese Patent No. 5933202; Ref. Zh. Khim., 60499P (1985).
137. T. Takematsu, S. Shinnai, T. Hosogai, S. Tsudzii, and S. Omura, Japanese Patent No. 5955806; Ref. Zh. Khim., 110446P (1985).
138. Ya. Korobi and K. Yamada, Japanese Patent No. 59128308; Ref. Zh. Khim., 130479P (1985).
139. T. Wanatabe and T. Terado, Japanese Patent No. 5970602; Ref. Zh. Khim., 120495P (1985).
140. G. S. Gruzdev and S. I. Kovrigo, Khim. Skh. Khozyaistve, 18, 39 (1980).
141. V. G. Ovchinnikov, V. P. Danil'chenko, I. B. Grebenyuk, E. I. Tkachenko, and G. V. Esipov, USSR Author's Certificate No. 445662; Byull. Izobret., No. 37, 63 (1974).
142. A. A. Mordovets and V. V. Golovin, Khim. Skh. Khozyaistve, 18, 39 (1980).

143. A. A. Mordovets and V. V. Golovin, Khim. Skh. Khozyaistve, 20, 33 (1982).
144. Yu. A. Spiridonov, V. G. Shestakov, Yu. M. Matveev, and G. S. Spiridonova, Agrokhimiya, No. 3, 83 (1984).
145. G. Steensholt and O. G. Clausen, Acta Pathol. Microbiol. Scand., 56, 327 (1962); Chem. Abstr., 63, 15387 (1965).
146. F. Sauter, O. Eberle, B. Süss, and R. Weissgerber, West German Patent No. 2659117; Ref. Zh. Khim., 100468P (1979).
147. E. Lilly and Co., Netherlands Patent No. 141359; Ref. Zh. Khim., 60423P (1976).
148. N. N. Mel'nikova (editor), Systemic Fungicides [Russian translation], Mir, Moscow (1975).
149. T. Wekado, H. Miki, and H. Dantsudzi, Japanese Patent No. 59110673; Ref. Zh. Khim., 140430P (1985).
150. G. Holmwood and P. E. Frohberger, West German Patent No. 2909287; Chem. Abstr., 93, 239256 (1980).
151. S. P. Sacehar, S. C. Bahel, and A. K. Singh, Bokin Bobai, 11, 269 (1983); Chem. Abstr., 99, 139709 (1983).
152. P. N. Panditrao, S. D. Deval, S. M. Gupte, S. D. Samant, and K. D. Deodhar, Indian J. Chem., 20B, 292 (1981).
153. F. J. Freenor, US Patent No. 4244959; Chem. Abstr., 94, 156770 (1981).
154. M. T. Clark and P. Ten Haken, US Patent No. 4212868; Chem. Abstr., 94, 15577 (1981).
155. ABJC Chem. Lab. Ltd., British Patent No. 933682; Chem. Abstr., 60, 1703 (1964).
156. P. D. Naeff, Swiss Patent No. 315516; Chem. Abstr., 51, 14196 (1957).
157. CIBA Ltd., British Patent No. 842968; Chem. Abstr., 55, 8434 (1961).
158. K. Hosoda, N. Shirakawa, H. Shiguyama, I. Kumatani, M. Takeuti, and M. Okata, Japanese Patent No. 6023364; Ref. Zh. Khim., 230502P (1985).
159. S. K. Malhotra and J. C. Van Heertum, US Patent No. 4228172; Chem. Abstr., 94, 121340 (1981).
160. S. K. Malhotra and M. J. Ricks, West German Patent No. 2810881; Chem. Abstr., 90, 22824 (1979).
161. J. C. Van Heertum and S. K. Malhotra, US Patent No. 4221799; Chem. Abstr., 94, 192151 (1981).
162. A. F. Grapov and N. N. Mel'nikov, Zh. Vses. Khim., Obshchestva, 29, 40 (1984).
163. R. Fuhs, I. Hamman, B. Homeyer, and W. Stendel, West German Patent No. 3111644; Chem. Abstr., 98, 71936 (1983).
164. Nisson Chem. Ind. Ltd., Japanese Patent No. 80115869; Chem. Abstr., 94, 121338 (1981).
165. C. A. Henrick, US Patent No. 4248875; Chem. Abstr., 94, 191721 (1981).
166. C. A. Henrick, US Patent No. 4247701; Chem. Abstr., 94, 174909 (1981).
167. M. T. Clark and P. Ten Haken, West German Patent No. 2744385; Chem. Abstr., 89, 43103 (1978).