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Shree Nath Singh *Editor*

Microbe-Induced Degradation of Pesticides

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To parents in heavenly abode

Preface

Pesticides are usually referred as a broad range of insecticides, fungicides and herbicides. Presently, there are 900 pesticide products and 600 active pesticide ingredients available in the market. Although millions of tonnes of pesticides are applied in the agriculture and horticulture, less than 5 % of pesticides only reach to the targeted organisms and rest gets deposited on the soil and non-targeted organisms and also moves to water bodies and the atmosphere. The fate of these pesticides is governed by the abiotic factors (temperature, moisture, soil, pH, etc.) as well as biological and chemical reactors. Abiotic degradation of pesticides is mediated by oxidation, reduction, hydrolysis and photolysis and rearrangement, while biotic degradation is caused by both microbial communities (bacteria, fungi, etc.) and plant species.

In view of the above facts, the editor has compiled the latest developments on biodegradation of chemical pesticides used in agriculture in this edited volume contributed by Indian and foreign scientists which will serve as a ready reckoner not only to scientists, but also to policymakers, teachers, students and the farmers.

In this endeavour, I would like to thank all the contributors for their positive response and active participation by contributing the latest updates on the degradation of different chemical pesticides. I would like to thank my research scholars Ms. Nitanshi Jauhari and Mrs. Shweta Mishra for their academic and technical support. Besides, untiring support by Mr. Dilip Kumar Chakraborty in preparing the book manuscript is heartily acknowledged.

Lastly, I would like to thank my family members: Mrs. Manorama Singh (wife), Ragini (daughter) and her kids Antra and Avantika and Pritish (son) and Vishali (daughter-in-law) for their inspiration, endurance and moral support in this endeavour.

Lucknow, India — Shree Nath Singh

Contents

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Microbe-Assisted Degradation of Aldrin and Dieldrin

Adi Setyo Purnomo

1 Introduction

Environmental pollution is an inseparable evil associated with anthropogenic activities. Increasing human needs resulted in the growth of the industries which produce new products through modern technologies. Among the various kinds of environmental issues, synthetic pesticides, produced in the agricultural industry have become a serious environmental problem. Among the chemical pesticides, aldrin and dieldrin are chlorinated cyclodiene pesticides which are classified as persistent organic pollutants (POPs) that cause serious environmental problems. They are highly ecotoxic to higher organisms, because of their low solubility, their tendency to partition into the lipophilic phase, and also contain chlorine atoms (Foght et al. 2001). They cause numerous negative effects, including disruption of the endocrine system in birds and mammals, impairment of male reproductive ability, interference with sex hormones, eggshell thinning, and a carcinogen for humanbeings (WHO 1989). As a result of their chemical stability and lipophilicity, aldrin and dieldrin are extremely persistent in the soil and sediment environments, with a half-life of 1 year or more. Although these compounds have been prohibited over the past decades in most countries around the world, they are still found in the environment, especially in the soil in agricultural fields. In 2001, more than 100 countries signed the Stockholm Convention on Persistent Organic Pollutants (POPs), committing to eliminate the use of the 12 POPs of greatest concern, including aldrin and dieldrin (Xiao et al. 2011).

The removal of pollutions from contaminated waters and soils has become an environmental priority, and both physicochemical and biological remediation pro-

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cesses have been studied. Although chemical and physical treatments are more rapid than biological treatments, they are generally destructive and intrusive to affected soils, energy intensive and also more expensive than bioremediation (Foght et al. 2001). Biodegradation using microorganisms, including bacteria and fungi, has been found to be a cost-effective method of treating various pollutants including aldrin and dieldrin, which has been existing in the environment since late 1960s.

2 Microbial Degradation of Aldrin and Dieldrin

For several years, dieldrin residues were assumed to appear as a result of microbial epoxidation of aldrin in soil in areas, where dieldrin itself had never been used. The indirect evidence for the conversion of aldrin to dieldrin by epoxidation was provided by Lichtenstein and Schulz (1960). Aldrin was rapidly converted to dieldrin in non-sterile soil, while little conversion occurred in the sterile soil. Aldrin also disappeared more quickly in moist soil than in dry soil, as microbes are more active in moist soil. Subsequently, Lichtenstein et al. (1963, 1965) showed that the conversion of aldrin to dieldrin was inhibited by methylenedioxyphenyl synergists (sesamex, piperonyl cyelonene, piperonyl butoxide, sulfoxide and n-propyl isome). Sesamex was the best inhibitor for the conversion of aldrin to dieldrin compared to other methylenedioxyphenyl compounds. Sesamex was also found to reduce populations of microorganisms when added to pure cultures, soil suspension, or soils, which caused no dieldrin formation. A breakdown product of sesamex, i.e. sesamol, which is also known as antioxidant, caused no significant inhibition of dieldrin formation. It indicated that the conversion of aldrin to dieldrin in soil was inhibited by synergists at relatively high rates, due to their high toxicity to microorganism populations.

Many studies have shown the microbial transformation of aldrin and dieldrin to intermediate metabolites under aerobic conditions, but the metabolic pathways are still unclear. The investigation on biodegradation of aldrin by pure cultures of soil microorganisms had been reported by Tu et al. (1968). Ninety-two pure cultures of soil microorganism were screened for degrading aldrin of which a majority showed some ability for converting aldrin to dieldrin by epoxidation. Among the fungi, *Trichoderma, Fusarium,* and *Pinicillium* were the most active for aldrin transformation. Besides, *Actinomycetes* were also effective converters, with one exception, *Bacillus* sp. which was of less importance. *Fusarium* sp., the most active isolate, converted 9.2 % of the added aldrin to dieldrin during 6 weeks of incubation period.

In some instances, the production of dieldrin was linear in relation to time. Besides, some microorganisms transformed aldrin to products other than dieldrin. Moreover, dieldrin had been transformed into 6,7-trans-dihydroxydihydroaldrin (trans-aldrin diol), photodieldrin, and ketoaldrin (Matsumura and Boush 1967, 1968; Matsumura et al. 1970; Patil et al. 1970).

The ability to epoxidize aldrin to dieldrin is obviously a common trait widely distributed among soil bacteria. Ferguson and Korte (1977) have described a number of strains of gram-positive and gram-negative soil bacteria which produce

exclusively the exoisomer of dieldrin. Twenty-two strains of soil bacteria, including representatives of the genera *Bacillus, Micromonospora, Mycobacterium, Nocardia, Streptomyces, Thermoactinomyces* and *Pseudomonas* were found to degrade aldrin to its epoxide dieldrin. Previously, Tu et al. (1968) reported production of dieldrin in 30 g-positive isolates out of 45 tested, whereas Patil et al. (1970) found 11 g-negative and gram-positive soil bacteria with this trait.

Maule et al. (1987) reported that anaerobic microbial populations, developed from soil, freshwater mud, sheep rumen, and chicken litter, could transform dieldrin to monodechlorinated products. The freshwater mud microbial population was the most effective, and transformed 96 % dieldrin to the *syn-* and *anti-* monodechlorinated products in a culture, initially containing 10 μg ml^{-1} of dieldrin approximately for 7 days. Three isolates from this culture, classified as the genus *Clostridium*, were capable of dieldrin dehalogenation, although the dehalogenation rate by each isolate was much less than by the parent population. *Clostridium bifermentans*, *Clostridium glycolium*, and *Clostridium* sp. required 54, 87 and 95 days, respectively, to transform 80 % of the dieldrin in a culture.

On the other hand, degradation of aldrin and dieldrin was also achieved in free cell cultures of *Pseudomonas fluorescens* to the level of 94.8 % for initial concentration of 10 mg L^{-1} (Bandala et al. 2006). Sakakibara et al. (2011) also reported that strain KSF27 converted dieldrin to aldrin dicarboxyric acid via aldrin trans-diol (Fig. 1). Strain KSF27 exhibited a high sequence similarity to *Pseudonocardia* spp. Based upon the genetical and morphological characteristics, strain KSF27 was found to be a new species of the genus *Pseudonocardia*, designated as *Pseudonocardia* sp. strain KSF27. Although the endo-isomer of dieldrin is less stable than the exo-isomer, there is no reason to expect microbial epoxidation to lead to exo-dieldrin in every case. In fact, exo-isomer is only produced in dissimilar genera, such as *Pseudomonas*, *Bacillus*, and the members of *Actinomycetes*.

Recently, white rot fungi (WRF) was found to degrade lignin, a complex high-molecular-mass aromatic polymer, as well as a wide spectrum of recalcitrant organopollutans, including biphenyls, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (Kamei et al. 2010). WRF are generally more tolerant to high concentrations than bacteria (Xiao et al. 2011). Xiao et al. (2011) reported that 20 white rot fungi belonging to genus *Phlebia* were investigated for their ability to degrade dieldrin. In that experiment, screening of fungi was done with 50 μL (5 mmol L^{-1}) of dieldrin. Based on the screening results, *Phlebia acanthocystis*, *Phlebia brevispora*, and *Phlebia aurea* was evaluated for their degradation capacity and metabolic products of dieldrin and aldrin degradation.

As evident from Table 1 the degradation ability of three *Phlebia* fungi was to remove over 50 % of dieldrin in a low nitrogen (LN) medium, after 42-d of incubation. Three hydroxylated products were detected as metabolites of dieldrin, including 9-hydroxyaldrin and two carboxylic acid products. It suggested that in *Phlebia* strains, hydroxylation reaction might play an important role in the metabolism of dieldrin, in which methylene moiety of dieldrin molecules might be prone to enzymatic attack by white rot fungi.

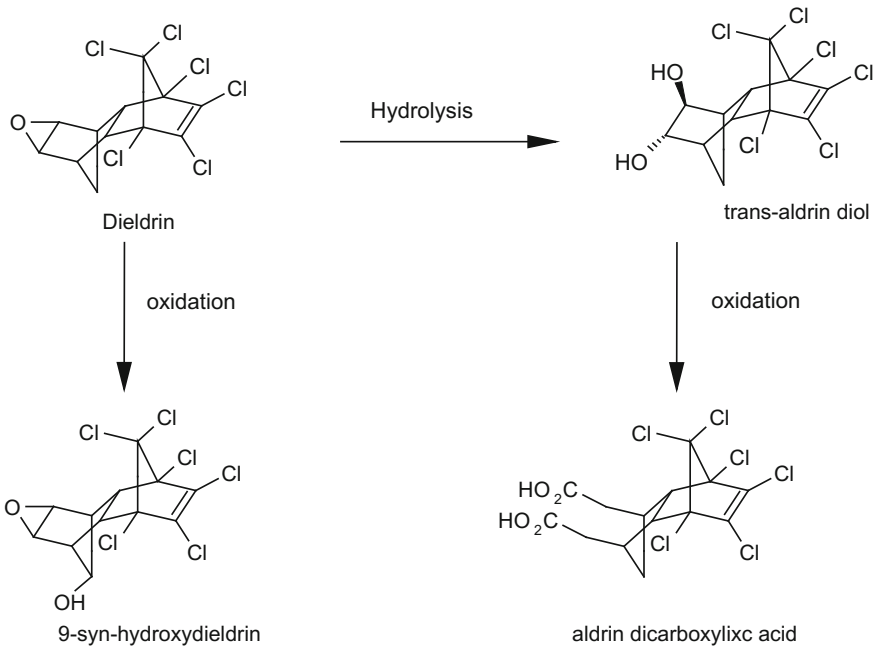

Fig. 1 Proposed metabolic pathway of dieldrin transformation by strain KSF27 (Sakakibara et al. 2011)

Kataoka et al. (2010) reported that an aerobic dieldrin-degrading fungus, *Mucor racemosus* strain DDF was isolated from a soil to which endosulfan had been annually applied for more than 10 years until 2008. Strain DDF degraded dieldrin to 1.01 mM from 14.3 mM during 10 days incubation at 25 °C. Approximately, 0.15 mM (9 %) of aldrin trans-diol was generated from the dieldrin degradation after a 1 day incubation. The degradation of dieldrin by strain DDF was detected over a broad range of pH and concentrations of glucose and nitrogen sources.

Kamei et al. (2010) reported thirty-four isolates of wood-rotting fungi were investigated for their ability to degrade dieldrin. Among these fungal isolates, *Phlebia* sp. YK543 degraded 20 % of dieldrin during the initial 7 days and then

Table 1 Degradation rate of aldrin and dieldrin by *Phlebia* fungi in low-nitrogen (LN) medium during 42-d incubation period

Phlebia fungi	Substrate	Degradation (%)
P. acanthocystis	Aldrin	96.0
	Dieldrin	56.0
P. brevispora	Aldrin	97.6
	Dieldrin	51.6
P. aurea	Aldrin	96.4
	Dieldrin	54.0

39.1 % of dieldrin during 30 days of incubation period in LN medium. 9-Hydroxylation was detected as a metabolite in the cultures of *Phlebia* sp. YK543.

On the other hand, Birolli et al. (2015) isolated marine-derived fungi *Aspergillus sydowii* CBMAI 935, *A. sydowii* CBMAI 933, *Penicillium miczynskii* CBMAI 930 and *Trichoderma sp*. CBMAAI 932 from the marine sponges *Geodia corticostylifera* and *Chelonaplysylla erecta*. In degradation studies, *P. miczynskii* CBMAI 930 showed the highest tolerance to dieldrin and catalyzed the biotransformation of dieldrin (50 mg L^{-1}) with high conversion rates (90 %) after 14 days in liquid medium. The organochlorine compounds were identified in the biodegradation reaction as endrin, endrin ketone and cyclopentene.

Matsumura and Boush (1968) reported that *Trichodermaviride*, isolated from soil heavily contaminated with various insecticides, had the ability to degrade dieldrin in liquid medium after 30 days of incubation without shaking and identified aldrin, dieldrin aldehyde, ketoaldrin, and photoisomer of ketoaldrin as metabolic products of the degradation of dieldrin in soil by microorganisms. Yamazaki et al. (2014) observed that *Mucor racemosus* strain DDF could decrease dieldrin levels with simultaneous production of a small amount of aldrin-trans-diol. The degradation was performed by adding 50 μL of an aldrin-trans-diol stock solution (1000 mg L^{-1}) and incubated for 14 days at 25 °C in the absence of light.

3 Involvement of Enzymes in the Degradation Process

Organochlorine pesticides (OCPs) act as prooxidant stressors and increase the intracellular generation of reactive oxygen species (ROS) and oxidative conditions, which, in turn, modulate levels and function of antioxidants enzymes (Osburn and Kensler 2008). Superoxide dismutase (SOD), catalase (CAT) and glutathione peroxidase (GPx) are the first line of defence against ROS and other free radicals while glutathione S-transferases (GSTs) are phase II enzymes providing defence against the toxicity cause by ROS. The cytochrome P450 dependent monooxygenase (MO) and glutathione S-transferase (GST) are among the most widely studied enzymes involved in the metabolism of xenobiotics (Jensen et al. 1991). Glutamic oxaloacetic transaminase, glutamic pyruvic transaminase and lactic dehydrogenase in the form of serum are capable of degrading aldrin and dieldrin found in the animal body (Luckens and Phelps 1969).

In the rat, dieldrin is metabolized through the three different degradation routes. Judging from the *in vitro* studies alone, the major metabolite of dieldrin, produced in the liver, is conjugated with glucuronic acid. This metabolite is probably excreted through urine and feaces mediated by β-glucorinadase (Matthews and Matsumura 1969). Aldrin and dieldrin are substrates specific to purified armyworm midgut enzyme epoxide hydrolase. The purified armyworm enzyme is able to hydrate mono-substituted epoxides faster than 1,2-disubtituted epoxides and these, in turn,