REVIEW

Enantioselective Phytoeffects of Chiral Pesticides

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Chirality exists extensively in nature. Synthetic chiral plant growth regulators and other pesticides usually behave enantioselectively in phyto-biochemical processes. Chiral plant growth regulators regulate the physiological processes of plants enantioselectively, and chiral pesticides cause enantioselective toxicities or ecotoxicities to plants. On the other hand, these chiral agrochemicals can be absorbed and enantioselectively metabolized by plants. This review summarizes the enantioselective effects of chiral plant growth regulators on plants and the phytotoxic and biotransformation effects of chiral herbicides and several persistent organic pollutants (POPs) on plants. Together, this information on the interactions between chiral agrochemicals and plants might shed light on studies on the chemical and biological behaviors of chiral chemicals, and direct research into the selection of plants, which can potentially decontaminate the environment.

KEYWORDS: Nontarget plants; phytotoxicity; chiral pesticides; plant growth regulators; herbicides; POPs

INTRODUCTION

Chirality exists extensively in nature. Chemically, the principle of chirality was first discovered by Louis Pasteur, who separated two types of sodium ammonium tartrate crystals and tested their enantioselective degradation in mold (*1*). In addition, many biologically active molecules, such as amino acids, DNA, RNA, polynucleotides, and proteins, are chiral from a biological point of view (*2*). In plants, the most common known chirality is by configuration, seen through climbing and twining plants. For example, the plant morning glory (*Convulvulus sabatius* L.) always twists in a right-handed helix, whereas honeysuckle (*Linnea borealis* L.) twines in a left-handed helix (*1*).

Chiral enantiomers have identical physical and chemical properties in achiral environments (e.g., air−water exchange, sorption, abiotic transformation), but they show different activities in biological systems (*3, 4*), because the individual enantiomers can interact enantioselectively with enzymes and biological receptors in organisms. The thalidomide tragedy was the first to highlight the markedly different pharmacological effects of two enantiomers of a drug. Thereafter, the recognition of the potential health risks involving the usage of racemic mixtures of drugs has mandated the manufacturing of single-enantiomer chiral drugs in drug design and development for

the pharmaceutical industry. Recently, increasing research on the toxicity and environmental fate of chiral pollutants has revealed the enantioselectivity in the interactions between chiral substances and protein or enzymes, hormones, and DNA in animals and bacteria (*5−8*). The reviews by Ali et al. (*9*) and Garrison et al. (*10*) are excellent summaries in this field. In our group, we also have investigated the enantioselective ecotoxicities of several chiral pesticides to nontarget animals and human cancer cell lines (*11−13*).

However, although of equal or even greater importance, the enantioselective eco-effects and toxicities of chiral chemicals in plants have not received as much attention as those in animals (*14*). There are few summaries of the enantioselective phytotoxicities and biotransformations of chiral chemicals in plants. The only review was published by Su (*15*), who summarized the enantioselective physiological responses of plants caused by chiral herbicides and discussed the environmental fate of several herbicides. However, information on the phytotoxic effects of several new chiral herbicides and some chiral insecticides, such as *o,p*′-dichloro-diphenyltrichloroethane (*o,p*′-DDT) and chlordane, was deficient. Being producers in an ecosystem, plants are responsible for producing all of the energy in the ecosystem. The physiological changes due to chiral chemicals may affect the food chain and further ecosystems. Therefore, the phytotoxicity caused by chiral chemicals merits much research. Plants could be more complex than animals in terms of biochemistry, because they are immobile and cannot avoid harmful effects caused by animals, pathogens, viruses,

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or bacteria. Instead, they have to protect themselves via physical and chemical means, which can be quite complex. Generally, chiral plant growth regulators and herbicides behave enantioselectively in the physiological processes of plants, but the particular processes in which chiral chemicals act are unclear. The wide exploitation of new agrochemicals containing chiral centers has brought new challenges in the study of enantioselective effects between plants and chiral chemicals.

Single-enantiomer drugs are now synthesized or separated from their racemic mixtures. In contrast, most chiral agrochemicals are still used as racemates in agriculture. When applied, chiral compounds are involved in biochemical interactions, and receptors generally distinguish between chiral pairs. Thus, the manufacture of enantiopure chemicals should be designed and developed in agrochemistry. Up to one-fourth of currently sold pesticides are chiral, and this proportion is expected to increase as increasingly complex compounds are being registered for use (*16*). It was estimated that chiral pesticides would account for >40% of currently used pesticides in China because of the popular use of chiral pesticides, such as synthetic pyrethroids, organophosphorus insecticides, metolachlor, and diphenyl (*17*). Authorities in The Netherlands and Switzerland have revoked registrations for racemic mixtures of chiral phenoxy herbicides while approving the registration of single-isomer products. Sweden has implemented a tax on agrochemicals based on the weight of the active ingredient. Williams (*16*) reported that only 28 chiral compounds of the total number are marketed as single-isomer products or as mixtures mainly containing the most active enantiomer. The chiral agrochemical compounds sold in single-isomer form contribute only 7% to the market value.

In this review, we do not discuss the naturally occurring chiral chemicals that exist as pure enantiomers or enantiomers found in excess in plants, such as terpenes (*18*), organic acids (*19*), plant hormones (*20*), and aromatic compounds (*21*). Instead, we focus on the exogenous chiral chemicals, in particular, chiral plant growth regulators and chiral herbicides, as well as some chiral persistent organic pollutants (POPs). The effects, toxicities, and biotransformations of these chiral chemicals in plants are all thought to be enantioselective. Chiral plant growth regulators consist of chiral plant stimulators and growth retardants. Chiral pesticides include the banned substances *o,p′*-DDT and chlordane and the currently used substances phenoxyalkanoic acids, aryloxy phenoxypropanoic acid, acetamide, nitrodiphenyl ethers, organophosphates, triazines, and heterocyclic herbicides. The enantioselective effects and biotransformations of chiral plant growth regulators and pesticides are summarized in this paper. In addition, the use of appropriate plants in the decontamination of the environment is discussed.

ENANTIOSELECTIVE EFFECTS OF PLANT GROWTH REGULATORS ON PLANTS

Plant growth regulators are generally small organic molecules that act as chemical signals to control plant physiological processes, such as accelerating abscission, inducing cell division and dormancy, elongating stems of seedlings, inhibiting root growth, stimulating stomata closure, and defending against environmental stresses such as excess heat, cold, and salinity (*22*). Chiral plant growth regulators have been in use for many years, but information on the enantioselective physiological effects of their enantiomers has been available only recently and is relatively insufficient.

Synthetic Auxins. Known as plant growth or development hormones, auxins are involved in a variety of plant activities. They are extensively used as growth promoters to produce

earlier and more prolific growth. Rooting hormone is a widely used auxin for plant propagation, because it can hasten root initiation, improve rooting percentages, produce more uniform rooting, and increase the number and quality of roots (*23*). Studies on chiral synthetic rooting hormone began in the 1990s. A commonly used auxin, 4,4,4-trifluoro-3-(indol-3-yl)butyric acid (TFIBA), is mainly used to promote the growth of roots in rice, legumes, and potato. In terms of root growth promotion, the activities of the enantiomers are different. The activity of the *S*-(+)-enantiomer of TFIBA was about 10-fold greater than that of the *R*-(−)-TFIBA in black matpe, Chinese cabbage, and lettuce and 5-fold greater in rice (*24, 25*).

Indole-3-succinic acid (ISA) is another synthetic chiral auxin. Both enantiomers of ISA and the racemic mixture have significantly greater "root growth promoting activity" compared with the commonly used indole-3-butyric acid (IBA) and naphthleneacetic acid (NAA) and natural indole-3-acetic acid (IAA) on tested plants, namely Variegated fuchsia (VF) and Swingtime fuchsia (SF) (*23*). Armstrong et al. (*23*) concluded that the ISA activity is concentration-dependent, and the maximum effect for both ISA enantiomers is observed within the concentration range of $10^{-7}–10^{-9}$ mol L^{-1}. The (*R*)- and (*S*)-enantiomers of ISA show different activities: (*R*)-ISA is more potent for SF and (*S*)-ISA is more potent for VF at 10^{-8} mol L^{-1}. Consequently, the differences in activities between the two enantiomers depend on the species of plant studied. Armstrong and co-workers noted that it may be beneficial to use *rac*-ISA in many cases, because a mixture of these two enantiomers could elicit a broader range of responses than the single enantiomer.

Abscisic Acid. Abscisic acid (ABA) is a plant hormone that causes the formation of aerial-type characteristics, including elongation of petioles and roots, changes in leaf morphology, expansion of leaf surface area, and shortening of the internodes. Although ABA naturally exists as the *S*-(+)-enantiomer, the *R*-(−)-enantiomer can be obtained by synthetic means. Lin (*26*) reported that *S*-(+)-ABA and *R*-(−)-ABA can both induce a heterophyllous switch and regulate ABA-responsive heterophylly gene (*ABRH*) expression. However, *R*-(−)-ABA is associated with a greater morphogenic effect than *S*-(−)-ABA (at the same concentration) in the aquatic fern *Marsilea quadrifolia* L. The transformation of applied ABA enantiomers has been traced, and the metabolites from the endogenous counterparts were distinguished by labeling the ABA enantiomers with deuterium. In tissues, *S*-(+)-ABA was metabolized mainly to dihydrophaseic acid, whereas *R*-(−)-ABA was converted at a slower rate to 7′-hydroxyabscisic acid. Treatment with both enantiomers resulted in the increased biosynthesis of ABA, and *R*-(−)-ABA has two distinct mechanisms: intrinsically active or active owing to stimulation of ABA biosynthesis. However, Lin and co-workers noted that the possibility that *R*-(−)-ABA itself is intrinsically active cannot be excluded. It remains to be investigated whether some of the metabolites also have a role in induction, but these studies are now in progress.

Plant Growth Retardants. Plant growth retardants are used to control specific plant responses, such as height, lateral branching, and flower removal. Typical growth retardants are B-Nine, Cycocel, A-Rest, Bomzo, and Sumagic. These plant growth retardants reduce plant height by inhibiting the production of gibberellins, the primary plant hormones responsible for cell elongation. Their effects are mainly on stem, petiole, and flower stalk tissues. Use of these plant growth retardants can improve plant appearance by maintaining the plant size and

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shape proportional to the pot in which they are growing and also increase the stress tolerance of plants during shipping, handling, and retail marketing, thereby improving shelf life and increasing plant marketability.

The four enantiomers of the triazole plant growth retardant, paclobutrazol [(2RS,3RS)-1-(4-chlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)pentan-3-ol], were investigated as inhibitors of cell growth and sterol composition using a celery (*Apium graveolens*) suspension culture (*27*). This study found that the compound with the (2R)-configuration had the highest potency for retarding cell proliferation and inhibiting the cytochrome P-450-dependent sterol 14α-demethylation reaction in celery cells. The (2R)-enantiomers were potent inhibitors of cell growth and caused significant accumulation of the 14α-methylsterols obtusifoliol, cycloeucalenol, 14α,24-dimethylcholest-8-en-3β-ol, and 14α,24-dimethylcholesta-8,24(28)-dien-3β-ol. In contrast, the (2S)-enantiomers were inhibitory to growth and sterol 14α-demethylation only at higher concentrations.

Further studies have determined the primary mode of action of paclobutrazol in *rht3* (tall) wheat seedlings (*28*). They observed that (2S,3S)-paclobutrazol reduced shoot growth more effectively than root growth, whereas the opposite was seen with the (2R,3R)-enantiomer. Low concentrations (0.03−1.0 μmol L^{-1}) of (2S,3S)-paclobutrazol specifically inhibited gibberellin A_1 (GA$_1$) production in *Rht3* (dwarf) seedlings without affecting shoot growth. This result confirmed that the inhibition of GA biosynthesis is the main mode of action of this enantiomer. Reductions in shoot growth of *rht3* (tall) wheat treated with (2S,3S)-paclobutrazol were associated with reductions in GA$_1$ content, an effect that could be reversed by GA$_3$ application, showing that GAs are important regulators of light-grown shoot growth in wheat. Inhibition of root growth of wheat seedlings following treatment with (2R,3R)-paclobutrazol is associated with a reduction in de novo synthesis of major sterols, a reduction in the stigmasterol/sitosterol ratio, and accumulation of the 14α-methyl sterol, obtusifoliol. High concentrations of (2S,3S)-paclobutrazol (>3 μmol L^{-1}) also affected de novo sterol production in wheat roots, indicating that root growth is more responsive to interference with sterols than GA biosynthesis. There was a reduction in the ABA content in *Rht3* (dwarf) shoots treated with relatively high concentrations of (2S,3S)-paclobutrazol, but no effect was observed with its optical isomer.

With the development of agrochemicals, an increasing number of chiral plant growth regulators, such as triazole and imidazole compounds, have been developed and introduced into the market. Using racemates or single enantiomers according to their regulating activities will be more efficient and less harmful to the environment. Therefore, further research on the enantioselective biological activities of these chiral agrochemicals is needed to clarify the properties of the enantiomers and provide information on safety to the environment.

ENANTIOSELECTIVE EFFECTS OF CHIRAL HERBICIDES AND THEIR BIOTRANSFORMATION IN PLANTS

Enantiomers of chiral exogenous chemicals are of increasing interest in the field of environmental chemistry (*29*). Most pesticides, along with their degradation products, become widely dispersed in ecosystems and can be found in various food chains. Chiral pesticides may have enantioselective ecotoxic effects on nontarget plants and can also be enantioselectively metabolized by plants. Understanding the different plant biochemical processes in which exogenous chiral chemicals are involved can greatly help the development of appropriate synthetic chemicals and could reduce the environmental risks. Here, we focus on
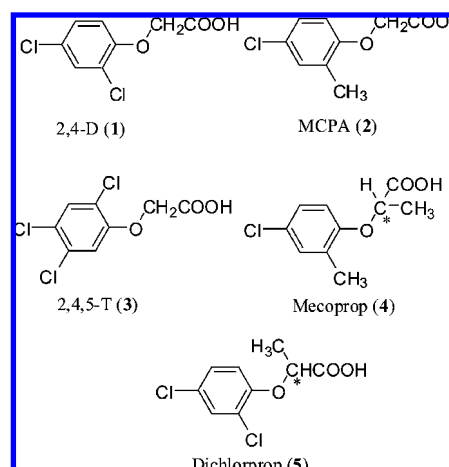

Figure 1. Chemical structures of phenoxyalkanoic acids. *, asymmetric carbon.

the major types of emerging and modern chiral pesticides, particularly chiral herbicides. In addition, some chiral insecticides and germicides, as well as several chiral POPs, have enantioselective toxic effects on plants.

Phenoxyalkanoic Acids. Phenoxyalkanoic acid herbicides were introduced in the 1940s and 1950s and are widely used against broad-leaved weeds in agriculture, gardening, and industry (*30*). Examples of this type of herbicide are 2,4-dichlorophenoxyacetic (2,4-D) (**1**), 2-methyl-4-chlorophenoxyacetic (MCPA) (**2**), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (**3**), and the chiral compounds 2-(R,S)-2-methyl-4-chlorophenoxypropanoic acid (mecoprop) (**4**) and 2-(R,S)-2,4-dichlorophenoxypropanoic acid (dichlorprop) (**5**) (**Figure 1**). Mecoprop and dichlorprop each have one stereogenic center and therefore two enantiomers, and the (R)-enantiomers have herbicidal activity (*31*). (R)-Dichlorprop development was protected by a patent (EP0009285) in 1980, and (R)-mecoprop development is protected by several patents (US4310689, EP9285, DE2949728, 3024265, 2734667) (*32*). Authorities in The Netherlands and Switzerland have revoked registrations for racemic mixtures of chiral phenoxy herbicides while approving registrations of single-isomer products (named mecoprop-P and dichlorprop-P). Nevertheless, the racemates are still used, thereby introducing large amounts of undesired isomers into the environment.

The biodegradation of dichlorprop and mecoprop was investigated by Schneiderheinze et al. (*30*). According to their study, the degradation of the racemic mixtures of dichlorprop and mecoprop by three species of turf grass, four species of broadleaf weeds, and soil was enantioselective. Preferential degradation of the S-(−)-enantiomer of each herbicide was observed in most species of broadleaf weeds and soil, whereas the degradation in all species of grass occurred without enantioselectivity. In addition, the R-(+)-enantiomer of both herbicides was more resistant to degradation in plants. Schneiderheinze and co-workers suggested that degradation patterns differ greatly in different environmental media and among different species of plants.

Aryloxy Phenoxypropanoic Acids. Aryloxy phenoxypropanoic acid herbicides (AOPP) are systemic and postemergence herbicides introduced in the 1960s by Farbwerke Hoechst AG. These control the growth of grasses by inhibiting the plastid acetyl-CoA carboxylase (ACCase), a key enzyme in long-chain fatty acid biosynthesis. Similar to phenoxyalkanoic acid herbicides, the (R)-enantiomers have strong herbicidal activities, but the (S)-enantiomers are less active (*31*). Representatives of this
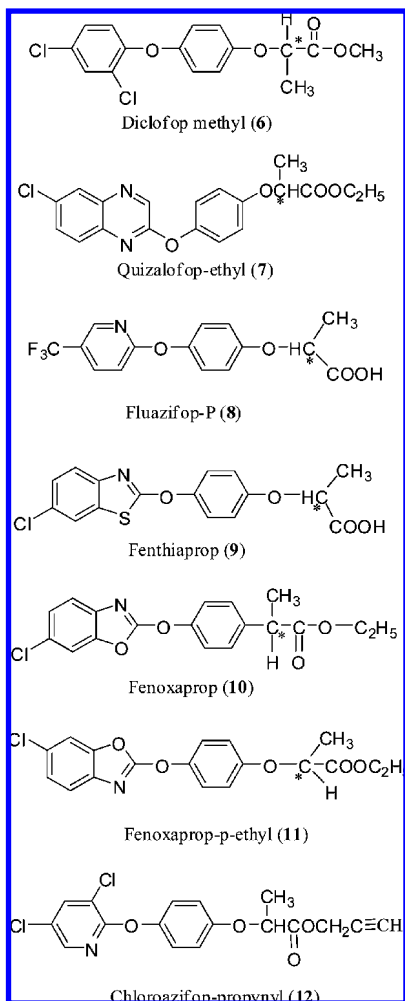
Figure 2. Chemical structures of aryloxy phenoxypropanoic acid herbicides.*, asymmetric carbon.

Figure 3. Chemical structures of acetamide pesticides.

type of herbicide include diclofop methyl (methyl-(*R*,*S*)-2-[4-(2,4-dichlorophenoxy) phenoxy]propanoate) (**6**), quizalofop-ethyl (**7**), fluazifop-P (**8**), fenthiaprop (**9**), fenoxaprop (**10**), fenoxaprop-P-ethyl (**11**), and chloroazifop-propynyl (**12**) (**Figure 2**). Among them, fluazifopp-P and fenoxaprop-P-ethyl are produced and used as (*R*)-enantiomers.

Diclofop methyl is a typical AOPP herbicide used on wheat, barley, and golf courses (turf). Currently, two mechanisms have been proposed to account for the primary activity of diclofop methyl and other aryloxy phenoxypropionic acid herbicides. One model is based on the specific binding of these herbicides to acetyl-CoA carboxylase, a plastid-localized enzyme involved in the synthesis of fatty acids. Hoppe and Zacher (*33*) studied the effects of nine phenoxyphenoxypropionic acid derivatives and structurally related compounds on the incorporation of [14C]acetate into free fatty acids in isolated bean and maize chloroplasts. They demonstrated that the de novo fatty acid biosynthesis in isolated maize chloroplasts was >40 times more sensitive to the *R*-(+)- than to the *S*-(−)-stereoisomer of diclofop acid. This agrees with the low herbicidal activity of the *S*-(−)-enantiomer in vivo. The results suggested that the mode of action for this type of herbicide may be closely linked to the inhibition of fatty acid biosynthesis. Later, Rendina et al. (*34*) confirmed this suggestion by demonstrating that acetyl-CoA carboxylase is the site of action for the aryloxy phenoxypropionic acid herbicides; this may explain their selectivity for monocotyledonous species.
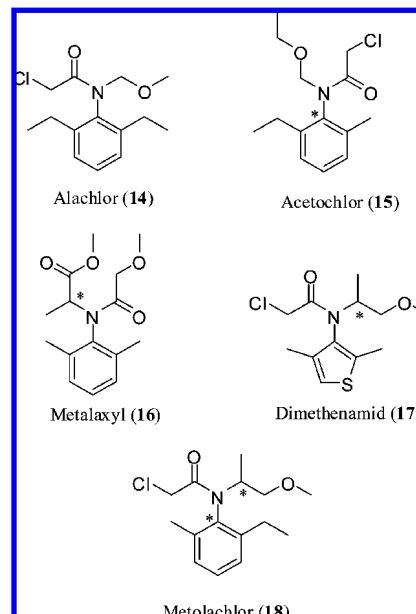
A second model suggests that the effect of diclofop can be explained by its action as a specific ionophore that shuttles protons across the plasmalemma. Shimabukuro and Hoffer (*35*) indicated that oat root growth was inhibited significantly by (*R*)-diclofop but only slightly by (*S*)-diclofop, owing to the role of oxidative membrane catabolism by free radical lipid peroxidation and its coupling to the effect of diclofop on the transmembrane proton gradient.

In our recent study (*14*), we found that the aquatic ecotoxicities of *rac*-, (*R*)-, (*S*)-diclofop (**13**), and OH-diclofop on three freshwater algae, *Chlorella pyrenoidosa*, *Chlorella vulgaris*, and *Scenedesmus obliquus*, are different. The degradation of three diclofop acids by three algae was also different. Cai and co-workers suggested that the organic compounds destroy the cell membrane of algae, increase the permeability of algae cells, and thus facilitate the penetration of toxic substances into the cell, where they react with bioactive compounds and disturb normal biological processes. From a study of the permeability of algae and degradation by heat treatment, Cai and co-workers (*14*) found that the toxicities of these compounds and their different degradation rates were related to the category of compound, species of treated organisms, and some environmental factors. However, the evidence presented for both models to date has been incomplete and often contradictory. The specific mechanism of chiral diclofop and other related herbicides needs more in-depth study in the future.

Acetamide Pesticides. Acetamide pesticides are widely used to control annual and broadleaf weeds in maize, soybean, and peanut. Acetamide pesticides act as protein synthesis inhibitors (*36*) and RNA-polymerase I inhibitors. This group of pesticides includes alachlor (**14**), acetochlor (**15**), metalaxyl (**16**), dimethenamid (**17**), and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] (**18**) (**Figure 3**). Alachlor is achiral, acetochlor is axial-chiral, and metalaxyl is C-chiral, giving two enantiomers. Dimethenamid and metolachlor are axial and C-chiral, so there are four stereoisomers. For metolachlor, the herbicidal activity is associated with only the 1′*S*-isomers. In the case of metalaxyl, the (*R*)-enantiomer has about 3−10 times greater fungicidal activity than the (*S*)-enantiomer (*37*). (*S*)-Metolachlor products were registered in New York State as general use products in 2007 (*38*). The production of (*R*)-metalaxyl has already been protected by
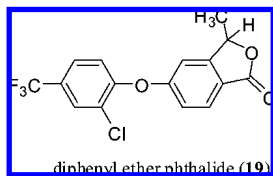
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Figure 4. Chemical structure of diphenyl ether phthalide.

several patents: EP1104990B1 (*39*), US7150877 (*40*), and WO/2000/013505A2 (*41*).

Metalaxyl is widely used in the control of plant diseases caused by pathogens of the *Oomycota* division. The (*S*)-enantiomer is inactive in herbicide tests, so the racemate is not phytotoxic to nontarget plants. The effects of stereoisomerism on the biological activity of fungicides must be characterized by considering both the pathogens and the host plant. Marucchini and Zadra (*42*) reported that (*R*)-metalaxyl was degraded more rapidly in soil, whereas (*S*)-metalaxyl was metabolized more rapidly in sunflower plants. Zadra and co-workers (*43*) studied the behavior of (*R,S*)-metalaxyl and its pure (*R*)-metalaxyl in sunflower plants (*Helianthus annuus*) and determined the stereospecific and/or stereoselective mechanism of the two compounds. They found that the behaviors of (*R,S*)-metalaxyl and (*R*)-metalaxyl were similar in terms of protection against plant infections. However, this biotransformation process in sunflower plants was enantioselective. Both (*R,S*)-metalaxyl and (*R*)-metalaxyl were readily biodegraded via ester hydrolysis, which generated carboxylic acid metabolites. The degradation rates of (*R,S*)-metalaxyl and (*R*)-metalaxyl are different: the (*R,S*)-metalaxyl acid metabolite is produced more rapidly than the (*R*)-metalaxyl acid metabolite. The hydrolysis process of the (*S*)-enantiomer was faster than that of the (*R*)-enantiomer in sunflower plants. Furthermore, conversion of metalaxyl to its metabolite retained its chiral configuration. (*R,S*)-Metalaxyl was converted to the (*R,S*)-metalaxyl acid metabolite and (*R*)-metalaxyl was converted only to the (*R*)-metalaxyl acid metabolite, and there was no inversion of configuration. Zadra and co-workers highlighted the importance of examining the fate of both stereoisomers of a chiral agrochemical in an environmental system for the correct use of enantiopure agrochemical compounds.

Diphenyl Ethers. Nitrodiphenyl ethers are highly effective and fast-acting herbicides that are used mainly in the selective control of broadleaf weeds in a variety of crops such as soybean, barley, wheat, and rice. They cause light-dependent membrane lipid peroxidation in the plants *Vicia faba* and *Hordeum vulgare*, as reported by Camilleri et al. (*44*). The biochemical processes of diphenyl ether phthalide 5-[2-chloro-4-(trifluoromethyl)phenoxy]-3-methylphthalide (**19**) (**Figure 4**) were enantioselective: the *S*-(−)-isomer was found to be substantially more active than the *R*-(+)-isomer. This result arises from the different bindings of isomers with the enzyme that plays a key role in the biosynthetic path between protoporphyrin IX and protochlorophyllide. It has been shown that the *S*-(−)-enantiomer had a stronger combination ability with the enzyme compared with the *R*-(+)-enantiomer. This was the first evidence for the likely involvement of an enzymatic binding process in the mode of action of peroxidizing diphenyl ether herbicides. However, the specificity of this enzyme has not yet been determined.

Phenylureas. The first examples of these were marketed in the 1950s. They are absorbed by roots and leaves and act as photosynthetic electron transport inhibitors on photosystem II (*45*). Most phenylureas are achiral owing to the N center. However, α-methylbenzyl *p*-tolylureas (**20**) and α-methylbenzyl phenylureas (**21**) (**Figure 5**) are chiral because of their chiral C
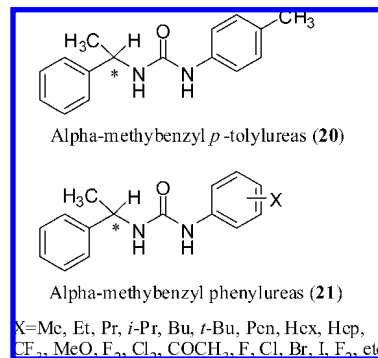

Figure 5. Chemical structures of optically active α-methylbenzyl-*p*-tolylureas and α-methylbenzyl phenylureas.

centers. The enantiomers of the herbicides show diverse plant physiological properties. Enantiomers of α-methylbenzyl phenylureas have different effects on the root growth of rice and barnyard millet (*46*). The configuration that preferentially inhibits the root growth and toxicity depends on the substituents in the phenyl ring. The (*R*)-enantiomers with smaller alkyl group have similar effects on both rice and barnyard millet. (*R*)-4-Pr and (*R*)-4-Bu derivatives have the greatest effects on rice, whereas the (*R*)-2-F-5-CF₃ derivative is the most potent inhibitor of barnyard millet. (*S*)-2-F, (*S*)-2, 3-F₂, (*S*)-2, 5-F₂, and (*S*)-4-COOEt inhibit the root growth of barnyard millet but have no effects on rice. Only the chiral pairs of the 3-Me and 4-Me derivatives have a cross intergenus response and affect both rice and barnyard millet. Rice is more sensitive to (*R*)-enantiomers, whereas barnyard millet is more sensitive to (*S*)-enantiomers. In subsequent studies, Omokawa et al. (*46, 47*) also determined the inhibitory effects of 1-α-methylbenzyl-3-tolylurea (MBTU) on the root growth of 24 species of *Oryzeae* plants and 8 species of *Echinochloa* plants. The root growth of all members of the genus *Oryzeae* was inhibited more by (*R*)-MBTU than by *Echinochloa* plants. This enantioselectivity provides information for the exploitation of new paddyfield herbicides.

Triazines. This group of herbicides includes a number of achiral members such as amitrole, atrazine, cyanazine, and simazine. Although they have a chiral N center, the molecules are achiral, because the enantiomers can easily be converted to the opposite enantiomer. Representative chiral members are dimethametryn (**22**), sebuthylazine (**23**), and secbumeton (**24**), which contain chiral C centers. They are used as selective weedkillers and act by inhibiting photosynthesis. The inhibition of the α-methylbenzyl moiety of 2,4-diamino-6-chloro-*s*-triazine (**25**) (**Figure 6**) on the root growth of rice and barnyard millet was similar (*48*). For the monoalkylamino series, the most suitable configuration was changed by the substituent on the other amino acid moiety. For the dialkylamino series, the (*S*)-enantiomer was the active inhibitor. The (*R*)-enantiomer exhibited clear species selectivity between rice and barnyard millet, showing a high herbicidal activity on *Echinochloa* plants but no effects on rice. Moreover, (*R*)-EtNH controlled the growth of barnyard grass by leaf burning, whereas (*S*)-EtNH and (*S*)-Et₂N controlled the growth by a different approach. Interestingly, it is beneficial to use a *rac*-EtNH derivative in controlling grass because the growth of barnyard grass at the just-germinated stage is controlled by the (*R*)-enantiomer and growth at the early middle stage is controlled by the (*S*)-enantiomer.

Organophosphorus Herbicides. Glufosinate is a foliar-applied and nonselective herbicide used as its ammonium salt. D-Glufosinate (**26**) shows no activity, but L-glufosinate (**27**) (**Figure 7**) is a natural phytotoxin that is a potent inhibitor of
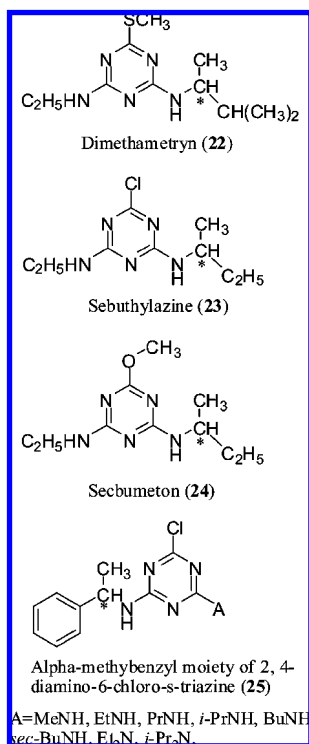
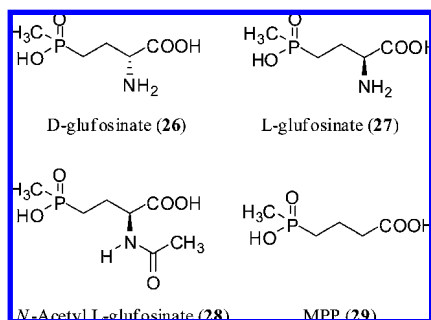**Figure 6.** Chemical structures of chiral triazines.

Figure 7. Chemical structures of glufosinate, *N*-acetyl L-glufosinate, and MPP.

glutamine synthetase. Glutamine synthetase inhibition results in a rapid accumulation of ammonia, reduced levels of several amino acids, inhibition of photosynthesis, and finally the death of the plant cell. The metabolism of glufosinate-ammonium in plant cell suspensions and callus cultures of transgenic (*bar*-gene) and nontransgenic sugar beet *Beta vulgaris*, *Daucus carota*, *Digitails purpurea*, and *Datura stramounium* was studied by Müller and co-workers (*49*). The results showed glufosinate-ammonium to be enantioselective. *rac*-Glufosinate, D-glufosinate, and L-glufosinate, as well as the metabolites *N*-acetyl L-glufosinate (**28**) and 3-(hydroxymethylphosphinyl)propionic acid (MPP) (**29**) were ¹⁴C-labeled to trace their transformations. The study suggested that cellular absorption was generally low, but depended on the plant species and enantiomers. The amounts of soluble metabolites generated from *rac*-glufosinate and L-glufosinate were up to 26.7% of the absorbed ¹⁴C in the nontransgenic cell cultures, whereas in the transgenic plant cell, the amounts were 28.2−59.9%. D-Glufosinate was stable.

Another study also compared the transformations of ¹⁴C-labeled *rac*-, L- and D-glufosinate in nontransgenic glufosinate-sensitive plants and in transgenic glufosinate-resistant plants (*50*). After 14 days of incubation, the transformation of *rac*-glufosinate in both nontransgenic and transgenic rape cells remained at a low rate of about 3−10%, whereas it was 20%
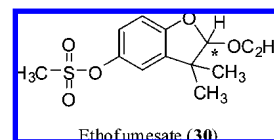

Figure 8. Chemical structure of ethofumesate.

in sensitive corn cells and 43% in transgenic cells; the rate was the same as that for glufosinate in other cells. L-Glufosinate was transformed into the same metabolites as *rac*-glufosinate, and D-glufosinate was not metabolized.

Both studies (*49, 50*) showed that the biotransformations of *rac*-glufosinate, L-glufosinate, and D-glufosinate were different depending on the species of plants. *rac*-Glufosinate and L-glufosinate were metabolized in nontransgenic and transgenic plant cell cultures, whereas D-glufosinate was not metabolized. Müller et al. (*49*) suggested that the absorption rate of D-glufosinate was substantially lower than that of *rac*- or L-glufosinate. The variety used for the experiments was selected for maximum rhizomania resistance, using the *bar*-gene for the selection process.

Heterocyclic Herbicides. Ethofumesate (**30**) is a kind of heterocyclic herbicide that was first described by Pleiffer in 1969 (*51*). It can be used both pre- and postemergence in sugar beet and other root crops, as well as turf, rye grass, and other pasture grasses. Ethofumesate has a chiral center in the furan moiety, so there are two enantiomers (**Figure 8**). Wang et al. (*51*) found preferential degradation of the (−)-enantiomer (UV at 230 nm) in Kentucky bluegrass (*Poa pratensis* L.) and tall fescue (*Festuca arundinacea* Schreb.), with the largest enantiomer ratio (ER, defined as the ratio of (+)-enantiomers to (−)-enantiomers) of about 3. Further investigation is needed to clarify whether there is any process of enantiomeric inversion or enantioselective metabolic pathway.

ENANTIOSELECTIVE EFFECTS OF CHIRAL POPS AND THEIR BIOTRANSFORMATION IN PLANTS

Chlordane. Chlordane, a member of the persistent organic pollutants (POPs), is a synthetic organic pesticide composed of 147 separate components, some of which exhibit optical activities. Chlordane was used as an insecticide, herbicide, and termiticide in the United States before it was banned in 1988. Although chlordane consists of more than 140 different components, chiral *trans*-chlordane (TC), *cis*-chlordane (CC), and achiral *trans*-nonachlor (TN) are present in the highest amounts. In addition, the three compounds persist longer in the environment than many of the minor components. To fully understand the impact of POPs on human health, variations in enantiomeric ratios of pollutants at the interface between terrestrial plants and other environmental compartments must be thoroughly understood. Lee and co-workers (*52*) studied the compositional profile of chlordane in the root, stem, leaves, and fruits of zucchini (*Cucurbita pepo* L.) and compared the soil-to-plant and air-to-plant pathways. This study found that the component fractions of TC, CC, and TN in plant tissues showed significantly different patterns between the two pathways. White et al. (*53*) also confirmed that the chlordane concentration gradient in plant tissues and the enantiomeric ratio were different. In the study of Mattina et al. (*54*), the data for zucchini showed an approximate 5-fold increase in absolute concentration for total TC, an 8-fold concentration increase for total *cis*-chlordane, and a 2.5-fold increase for TN in the root relative to the soil matrix.

DDT. DDT is a well-known pesticide that was widely used in the early 20th century. It was originally synthesized in 1874,

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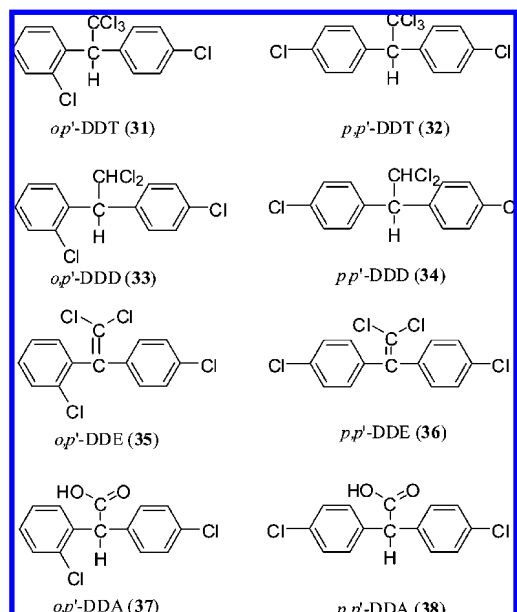*J. Agric. Food Chem.,* Vol. 57, No. 6, 2009 **2093**

Figure 9. Chemical structures of the main analogues of DDT found in the environment.

but its insecticidal properties were not discovered until 1939. It was banned for agricultural use in the United States in 1972 due to its major environmental effects, but it is still used for disease vector control in certain parts of the world. *o,p*′-DDT [1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane] (**31**) comprises up to 25% of technical grade DDT and contains a nonsymmetrically substituted carbon atom, whereas *p,p*′-DDT (**32**) (**Figure 9**) is not chiral. The (−)-enantiomer of *o,p*′-DDT has been shown to be a considerably more active estrogen mimic than the (+)-enantiomer. Garrison et al. (*55*) studied the reductive dechlorination of *o,p*′- and *p,p*′-DDT at the micrograms per milliliter level in the presence of the aquatic plant elodea (*Elodea canadensis*) and the terrestrial plant kudzu (*Pueraria thunbergiana*). The half-lives for the degradation of both *o,p*′- and *p,p*′-DDT by Elodea and kudzu ranged from 1 to 3 days, depending on the growth conditions of the plants. The only products identified were *o,p*′-DDD (**33**) and *p,p*′-DDD (**34**); no DDE (**35**, **36**) or DDA (**37**, **38**) was detected. Phytodegradation experiments using elodea plants and ^{14}C-labeled *p,p*′-DDT indicated that up to 22% of DDT analogues were covalently bound within the plant. The degradation rate in dead plants was the same as that in fresh plants. The reactions with elodea and kudzu were not enantioselective during the formation of *o,p*′-DDD from *o,p*′-DDT. The reductive dehalogenation of *o,p*′-DDT by a partially purified extract of elodea, by the porphyrin hematin, and by human hemoglobin was also shown to be non-enantioselective, with reaction rates similar to those for the whole plant. This evidence indicates that the phytodegradation process may be catalyzed by an achiral enzyme cofactor or another achiral biomolecule.

Together, these studies have demonstrated the biochemical interactions between exogenous chiral chemicals and plants in ecosystems. The interactions may be divided into two types: the enantioselective phytotoxic effects of chiral pollutants on plants and the enantioselective biodegradation of chiral compounds in different species of plants. Nevertheless, the behaviors of chiral compounds in plants are not absolutely enantioselective, for example, that of DDT mentioned above.

CONCLUSION

This review suggests that the phytotoxicities of chiral agrochemicals and the biotransformation processes of enantiomers in plants should be investigated at the chiral level. The enantioselective interactions between chiral compounds and plants differ in terms of not only the chemicals involved but also plant species. As shown in many examples, the complex relationships between chiral agrochemicals and plants seem to be important. The enantioselective toxic effects of chiral pollutants on plants and their enantioselective biotransformation in plants is one such issue. Chiral plant growth regulators can enantioselectively affect the growth of plants, and chiral herbicides and some chiral POPs can have enantioselective toxic effects on plants. On the other hand, these chiral agrochemicals can be enantioselectively metabolized in plants, which is important in the environment. The predominance of one or more enantiomers in plants depends on the species of plant and the characteristics of chemicals and, as yet, cannot be predicted. There is a lack of data that can be used to determine the toxicity criteria of pollutants to plants. Guidelines for the selection of plants for the decontamination of chiral compounds in the environment are also needed. It is noteworthy that the phytochemistry and phytotoxicity of chiral chemicals are still relatively unexplored areas of research. Although enantioselective phytoeffects of chiral chemicals have been observed, the mechanisms underlying these enantioselective effects have not been identified in many cases. It seems that many questions and issues regarding the interactions between chiral compounds and plants remain to be addressed.

ABBREVIATIONS USED

ABA, abscisic acid; ABRH, ABA-responsive heterophylly gene; ACCase, acetyl-CoA carboxylase; AOPP, aryloxy phenoxypropanoic acid herbicides; CC, *cis*-chlordane; DDA, dichlorodiphenylacetic acid; DDD, dichlorodiphenyldichloroethane; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; ER, enantiomer ratio; GA, gibberellin A; IAA, indole-3-acetic acid; IBA, indole-3-butyric acid; ISA, indole-3-succinic acid; MBTU, 1-α-methylbenzyl-3-tolylurea; MCPA, 2-methyl-4-chlorophenoxyacetic; MPP, 3-(hydroxymethylphosphinyl)propionic acid; NAA, naphthleneacetic acid; POPs, persistent organic pollutants; SF, swingtime fuchsia; TC, *trans*-chlordane; TFIBA, 4,4,4-trifluoro-3-(indole-3-)butyric acid; TN, *trans*-nonachlor; VF, variegated fuchsia; 2,4-D, 2,4-dichlorophenoxyacetic; 2,4,5-T, 2,4,5-trichlorophenoxyacetic acid.

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