The Chemistry, Nanoencapsulation and Bioherbicide Use of Allelochemicals

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PREFACE

Most allelopathy books focus only on physiological, ecological, and weed management aspects. This monograph is distinctive from other allelopathy books since it deals with detailed and in-depth chemistry of allelopathy, chemical structures and biochemical modes of actions of allelochemicals, and biochemical pathways related to allelochemicals. Thus, better understanding on principles and applications of allelopathy is achieved.

This monograph exemplifies the organic and analytical chemistry aspects of allelopathy studies conducted in our research laboratory through the isolation, quantification, and characterization of allelochemicals from different plant sources including some weeds, which are viewed as pests of crops, and thus, making them useful and adding value in agriculture. The book is also well-illustrated with diagrams on isolation and quantification of allelochemicals, release of allelochemicals, biosynthetic pathways of allelochemicals, organic synthesis of allelochemicals, and biochemical pathways associated with modes of action of allelochemicals.

This monograph also encompasses the role of allelopathy in addressing dilemmas on synthetic herbicide resistance. Herbicide resistance has been a major problem in weed and crop management due to emergence of weeds that are resistant to synthetic herbicides. Many allelochemicals have multiple sites of action, hence, they can eliminate weeds that have developed resistance to synthetic herbicides. This monograph discusses the use of allelochemicals as potential sources of bioherbicide, a new source of herbicides in the industry which can delay or prevent herbicide resistance.

In addition, the science of nanoencapsulation is a novel field. Studies on nanoencapsulation of synthetic herbicides have been reported. This monograph deals with nanoencapsulation of plant-based allelochemicals for agricultural applications. This monograph is remarkable in underscoring specific examples of allelochemicals studied in our research laboratory that were encapsulated and the assessment of the effect on their stability and herbicide efficacy. Particularly, studies on encapsulation of phenolic allelochemicals extracted from wedelia *(Sphagneticola trilobata* L. Pruski) leaves using gum rosin via emulsification-solvent evaporation and pectin via ionic gelation, and those isolated from mahogany (*Swietenia mahogani* (L.) Jacq.) bark using gum rosin via solvent displacement technique are discussed. The physical chemistry aspect of soil sorption of encapsulated allelochemicals was also touched on by studying the kinetics profile.

Indeed, this monograph is a valuable reference for scientists, researchers, professors, students, and employees in the agrochemical industry. This could also be used as a resource material in educating farmers. Since allelopathy is multidisciplinary, a multitude of specialists from an array of disciplines will benefit and gain positive impact in this monograph such as agriculture, agricultural chemistry, agronomy, analytical chemistry, biochemistry, biology, botany, breeding, environmental chemistry, genetics, horticulture, microbiology, molecular biology, material science, organic chemistry, plant biochemistry, plant pathology, plant ecophysiology and ecology, plant physiology, plant protection, soil chemistry, soil science, and weed science.

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CHAPTER 1

INTRODUCTION TO ALLELOPATHY

1.1 Definition

The word allelopathy was coined in 1937 by an Austrian professor and plant physiologist, Hans Molisch of the University of Vienna, Austria, and it came from two Greek words: (1) 'allelon' which means 'each other,' and (2) 'pathos' which means 'suffering' (Gross, 1999). Hence, allelopathy is the beneficial or detrimental effects of a plant on another plant. Allelopathy is a common biological phenomenon and a form of chemical communication by which one organism produces biochemicals that influence the growth, survival, development, and reproduction of other organisms. These biochemicals are known as allelochemicals, which are secreted into the environment, affecting the growth and development of competing individuals (Krasuska, Bogatek, & Gniazdowska, 2013; Latif et al., 2017). In this monograph, when it mentions allelopathy, we specifically refer to phytoallelopathy (allelopathy specifically towards another plant species) and the chemicals secreted are known as phytoallelochemicals, differentiating it from zooallelopathy (allelopathy towards an animal species) and microbial allelopathy (allelopathy towards a microbial species) (Hickmen et al., 2021).

In 1984, the concept of allelopathy gained interest after Professor Elroy L. Rice published the first monograph on allelopathy in English. In his book, he introduced allelopathy as "the effect(s) of one plant on other plants through the release of chemical compounds in the environment." Noticeably, Molisch and Rice's definitions of allelopathy encompass both positive (growth-promoting) and negative (growth-inhibiting) effects of one plant on another plant, but it may also involve neutral interactions (Bhadoria, 2011; Hierro and Callaway, 2021). Allelopathy is a natural ecological phenomenon in which various organisms affecting other organisms in their vicinity release cytotoxic allelochemicals which are mostly byproducts during different physiological processes in plants in order to compete with surrounding organisms for limited resources. (Rice, 1984; Farooq et al., 2011; Bhadoria, 2011; McCoy, Widhalm, and McNickle, 2022).

Though allelopathy was initially conceived as positive, negative, and neutral interactions, it is presently viewed as a purely negative interaction by most authors, as time progresses. A remarkable mechanism structuring plant communities is competition via allelopathy (Hierro and Callaway, 2021). Aschehoug et al. (2016) considered allelopathy as an interference competition, a form of competition. On the other hand, Ridenour and Callaway (2001) treated allelopathy as a form of interference known as allelopathy interference.

Allelopathy is one of the primary mechanisms of interference competition in plants. Interference competition, a form of direct interference to prevent resource access, is prevalent for physically fighting animals. Generally, most competition occurring in plants is known as resource competition, where one plant simply confiscates the resources away from its neighbors (McCoy, Widhalm, and McNickle, 2022). Weeds are competitive and invasive. In general, an indicator that a plant is allelopathic is when it is invasive (Fig. 1-1). Many weeds are allelopathic, showing characteristics such as spreading prolifically, quickly, and undesirably.

Fig. 1-1. Fields invaded by weeds.

Allelopathy study focuses on the synthesis of biomolecules by one plant, that can induce stress or in some special cases, give benefit to another plant. Hence, this phenomenon could also be viewed as a biochemical interaction among plants. However, allelopathy does not only involve the gross biochemical interactions and their effects on physiological processes but also it deals with the mode of action of these compounds at specific sites of action at the molecular level (Rizvi et al., 1992).

Allelopathic interactions between plants play a significant role in both natural and manipulated ecosystems. Studies of these interactions, particularly in natural ecosystems, provided basis for the science of allelopathy. In a manipulated system, the role of allelopathy in agriculture, investigating the effect of weeds-on-crops, crops-on-weeds, and crops-on-crops interactions, is currently gaining attention for further studies (Kier, 2016).

Allelochemicals have great potential to be developed as nature-based herbicide. They could be isolated and identified, and then they can be used to synthesize active compounds with herbicidal activity. This will lessen the heavy usage of synthetic herbicides (Kruse and Strandberg, 2000). Another promising advantage of allelochemicals is their action against invasive weeds by means of a mechanism not possessed by commercial herbicides, thereby making them ideal lead compounds for the new herbicide discovery (Vyvyan, 2002).

Allelochemicals are advantageous as natural pesticides due to their biodegradability, making them safer and environmentally cleaner in comparison with the synthetic pesticides in the current market. Allelochemicals have relatively low health toxicity and their use can lessen pollution (Kruse and Strandberg, 2000). In addition, allelochemicals are more environmentally friendly because they are higher oxygen- and nitrogen-rich molecules with relatively few halogens. Thus, the environmental half-life of allelochemicals decreases, and thus, accumulation of the compound in soil and eventual effects on non-target organisms are avoided and pollution is reduced (Soltys et al., 2013).

In general, allelochemicals are products of the secondary metabolism and are non-nutritional primary metabolites. These allelocompounds belong to different chemical groups such as triketones, terpenes, benzoquinones, coumarins, flavonoids, terpenoids, strigolactones, phenolic acids, tannins lignin, fatty acids and nonprotein amino acids. Inhibition caused by allelopathy is complicated and can involve the interaction of these classes of chemicals (Ferguson, Rathinasabapathi and Chase, 2016).

In ecology, studies of allelopathy have been significant for three foci, highlighting broad ecological consequences: species distribution, conditionality of interactions, and maintenance of species diversity. Based on evidence, allelopathy affects distributions of local plant species all over the world. Conditionality of allelopathic interactions is a mechanism for invading plants. Maintenance of species diversity is associated with allelopathy since coexistence via intransitive competition and modifications of direct interactions are promoted by allelopathy, where coexistence might be preferable by means of biochemical recognition (Hierro and Callaway, 2021).

1.2 Allelopathic Plants

Allelopathic plants use their allelochemicals as their chemical warfare agents. Table 1-1 presents some examples of allelopathic plants.

Table 1-1. List of some allelopathic plants.

Common name	Scientific name	Type of plant	Example of affected plants	References
Rice	*Oryza sativa* L.	crop	*Echinochloa crus-galli*	Chung et al., 2003; Lee et al., 2004
Wheat	*Triticum aestivum* L.	crop	*Hordeum vulgare*; *Triticum aestivum*	Oueslati, 2003
Pea	*Pisum sativum*	crop	*Lepidium sativum; Lactuca sativa*	Kato-Noguchi, 2003
Tomato	*Lycopersicon esculentum* Mill.	crop	*Lactuca sativa; Vitis* sp.	Kim and Kil, 2001
Congress grass	*Parthenium hysterophorus* L.	weed	*Cyperus iria; Raphanus sativus*, *Solanum lycopersicum*	Motmainna et al., 2021; Bashar et al., 2023
Cogon grass	*Imperata cylindrica*	weed	*Aristida stricta; Pinus elliottii*	Hagan, Jose, and Lin, 2013
Bermuda grass	*Cynodon dactylon* L.	weed	*Festuca arundinacea; Secale cereale*	Liang et al., 2018; Yarnie, Bolouri, and Sahin, 2024
Black walnut	*Juglans nigra*	tree	*Zea mays; Glycine max*	Jose and Gillspie, 1998
Mango	*Mangifera indica* L.	tree	*Citrus jambhiri*	Dalal et al., 2012
Eucalyptus trees	*Eucalyptus spp.*	tree	*Acmena acuminatissima*, *Cryptocarya concinna, Raphanus sativus*	Chu et al., 2014; Zhang et al., 2009
Silvery wormwood	*Artemisia argyi*	herbaceous	*Brassica pekinensis*, *Lactuca sativa*, *Oryza sativa*	Li et al., 2018
Sunflower	*Helianthus annuus* L.)	herbaceous	*Amaranthus albus; Dactyloctenium aegyptium; Lactuca sativa*	Azania et al., 2003; Ravlic et al., 2022

Several crops exhibit allelopathic activity. A well-known example is rice (*Oryza sativa* L.) (Fig. 1-2). Allelopathy in rice is an example of mode of interaction between receptor and donor plants showing either positive effects or negative effects (Chung et al., 2018). Both in the field and laboratory studies, rice cultivars have been found to be allelopathic. For example, 111 rice cultivars have inhibited the growth of *Echinochloa crus-galli* (barnyard grass) (Olofsdotter et al., 1999). The rice variety Duchungjong showed 77.7% higher average growth inhibition of barnyard grass compared to 113 tested rice varieties (Chung et al., 2003). Among the 749 rice cultivars that were tested, japonica rice cultivar exhibited high allelopathic potential against root growth of barnyard grass (Lee et al., 2004).

Fig. 1-2. A typical rice field in the Philippines.

Numerous rice allelochemicals have been analyzed in root exudates of rice and decomposing rice residues. Several of these allelochemicals interact with the environment (Amb and Ashliwalia, 2016). Cytokinins, diterpenoids, fatty acids, flavones, glucopyranosides, indoles, momilactones (A and B), oryzalexins, phenols, phenolic acids, resorcinols, and stigmastanols are the several phytotoxins that have been identified in rice extracts (Khanh et al., 2007). In addition, benzoxazinoids and phenylalkanoic acids have also been found in rice extracts (Belz, 2007). The most common allelochemicals in rice are phenolics and momilactones (Rahman et al., 2022). The studies on momilactones could be a basis for sustainable weed management (Serra, Shanmuganathan, and Becker, 2021).

Wheat (*Triticum aestivum* L.) is another allelopathic crop. Various allelochemicals have been isolated from wheat (Khamare, Chen, and Marble, 2022). Polyphenols, hydroxamic acids, and short-chain fatty acids are the main categories of allelochemicals present in wheat (Yongqing, 2005; Krogh et al., 2006). The allelopathic activity of wheat's residues, straw, seedlings, and aqueous extract have already been extensively studied (Wu et al., 2000; Farhena Aslam 2016). Diluted extracts of roots, leaves, and stems of two durum wheat varieties viz., Karim and Om rabii showed allelopathic potential affecting *Hordeum vulgare* variety Manel (barley) and *Triticum Aestivum* variety Ariana (bread wheat) (Oueslati, 2003). Thus, wheat could be utilized as an allelopathic cover crop for weed control in different cropping systems (Yongqing, 2005).

Pea (*Pisum sativum*) has been investigated for its allelopathic potential. Kato-Noguchi (2003) reported that the putative allelochemical compound in pea residue is pisatin, based on structural elucidation supported by MS, IR, and Proton NMR spectral data. At concentrations higher than 10 and 30 micromolar, pisatin exhibited growth inhibition of cress (*Lepidium sativum* L.) and lettuce (*Lactuca sativa* L.) seedling. These findings suggested that pea residue has growth inhibitory activity.

Tomato plant (*Lycopersicon esculentum* Mill.) secreted allelochemicals on different receptor plants, such as *Lactuca sativa* and vitis. Forty phytotoxic compounds identified in the essential oil of tomato using GC/MS include trans-2-hexenal, α-terpineol, linalool, phenylacetaldehyde, methylsalicylic acid, and tetradecanoic acid. The presence of those compounds implies that tomato is allelopathic (Kim and Kil, 2001).

Various weed species have also been recognized as allelopathic. Kalisz et al. (2021) reported that 51–67% of these invasive plants are allelopathic. For instance, congress grass or gajjar grass (*Parthenium hysterophorus* L.) has been a problematic weed in agriculture, animal husbandry, ecology, and the environment (Kohli and Rani, 1994). Motmainna et al. (2021) reported that *P. hysterophorus* extract at 100 g L^{-1} mostly injured *Cyperus iria*. Likewise, Bashar et al. (2023) showed that *Raphanus sativus*, *Solanum lycopersicum*, *Capsicum frutescens*, *Abelmoschus esculentus*, *Daucus carota*, *Digitaria sanguinalis*, and *Eleusine indica* were highly susceptible to *P. hysterophorus* allelochemicals. Parthenin, a sesquiterpene lactone of pseudoguanolide, is the major allelochemical present in gajjar grass (de la Fuente et al., 2000). Similarly, the allelopathic effect of whitetop (*Lepidium draba*) is mainly due to the presence of parthenin in various parts of the plant (Kohli et al., 1993; de la Fuente et al., 2000).

On the other hand, cogon grass (*Imperata cylindrica*), present in all continents and is viewed a weedy pest in 73 countries, is an aggressive colonizer considered as one of the top ten world's worst weeds and is included among the world's top 100 worst invasive alien species (Sellers et al., 2018; Kato-Noguchi, 2022). Inhibition of germination and growth has been reported negative effect of extracts, leachates, root exudates, decomposing residues and rhizosphere soil of cogon grass on a large number of plant species (Kato-Noguchi. 2022). Fatty acids, terpenoids, simple phenolics, benzoic acids, phenolic acids, phenolic aldehydes, phenylpropanoids, flavonoids, quinones, and alkaloids are the allelochemicals present in cogon grass (Kato-Noguchi, 2022). Based on reduction in mycorrhizal colonization and total mycorrhizal root length, *Aristida stricta* Michx. var. beyrichiana and *Pinus elliottii* (tree) were adversely affected by rhizochemicals from cogon grass (Hagan, Jose, and Lin, 2013). One of the key mechanisms why cogon grass is invasive is the production of allelochemicals in its root system, lessening the competitive ability of neighboring plants (Sellers et al., 2018).

Bermuda grass (*Cynodon dactylon* L.) 'Baoding' has been found to contain 23 allelochemicals in root exudates with 50.31% esters and 17.03% alkanes, based on GC-MS analysis. Among the compounds detected, 3-phenylpropyl 4-methylbenzoate had the highest level (34.73%). At 1.50 mg/mL of concentration of root exudates of Bermuda grass, seed germination, biomass, and physiological elements of 6-tall fescue (*Festuca arundinacea*) cultivars were inhibited (Liang et al., 2018). Increasing extract concentrations of Bermuda grass caused decrease in seedling growth, coleoptile length, radical length, coleoptile weight, and radical weight of basil (*Ocimum basilicum* L.) and common purslane (*Portulaca oleracea* L.) (Golparvar et al., 2015). Yarnie, Bolouri, and Sahin (2024) reported that Bermuda grass extract with a concentration of 30%, caused inhibition of rye (*Secale cereale* L.) callus induction to 50%, indicating that the allelopathic potential of Bermudagrass extracts could be tapped in the production of bioherbicides.

Plant allelopathy is also associated with trees. This is crucial so that when one tree is planted besides another tree, the allelopathic potential of trees should be considered. Often cited as an example of allelopathic tree is the black walnut *(Juglans nigra),* which releases juglone, an allelochemical affecting some plant species greatly (Jose, 2002). Juglone had been found to exhibit significant inhibitory effects on shoot and root relative growth rates of corn (*Zea mays* L.) and soybean (*Glycine max* L. Merr.) seedlings (Jose and Gillspie, 1998).

Kato-Noguchi and Kurniadie (2020) reported that mango (*Mangifera indica* L.) (Fig. 1-3) is allelopathic, with its leaves containing phytotoxic substances such as coumaric, vanillic, caffeic, cinnamic, gallic and protocatechuic acids, and methyl gallate and quercetin-3-O-α-glucopyranosyl-(1→2)-β-D-glucopyranoside. When *Citrus jambhiri* Lush. were planted into the soil obtained from mango orchard, the growth of shoots, roots, and leaves of *C. jambhiri* was suppressed (Dalal et al., 2012). This allelopathy study revealed the potential use of mango as a weed management strategy in home gardens and other agriculture settings to lessen the use of commercially available synthetic herbicides. (Kato-Noguchi and Kurniadie, 2020).

Fig. 1-3. Mango tree and mango leaves.

On the other hand, eucalyptus trees (*Eucalyptus spp*.) are also widely known to be allelopathic, releasing volatile allelochemicals that can inhibit the growth of nearby plants. Eucalyptus extracts caused significant reduction in germination rate of *Delonix regia* during the early treatment period, and significant seedling height suppression of *Schima superba* and *Michelia macclurel* (Zhang and Fu, 2009). *Eucalyptus urophylla* was reported to inhibit the growth of native tree species such as *Acmena acuminatissima*, *Cryptocarya concinna,* and *Pterospermum lanceaefolium* (Chu et al., 2014). Moreover, Zhang et al. (2009) revealed that aqueous extract of *Eucalyptus grandis* root inhibited the germination and early seedling growth of *Raphanus sativus*, *Phaseolus aureus*, and *Lolium perenne*. Based on GC–MS analysis, greater amounts of allelochemicals were detected in the rhizosphere soil and roots of younger *E. grandis* plantation, indicating that the allelopathic compounds in roots and rhizosphere soil may play significant roles in *E. grandis* plantation allelopathy.

Allelopathic shrubs and herbaceous plants also exist. Water-soluble extracts of silvery wormwood (*Artemisia argyi)*, a perennial herbaceous plant popular in Asia, showed the strongest allelopathic inhibitory effects on different plants under incubator conditions, as analyzed using ultra high-performance liquid chromatography-quadrupole-time of flight-high resolution mass spectrometry (UPLC-Q-TOF-MS) (Li et al., 2018). The study showed that *A. argyi* inhibited both dicotyledons and monocotyledons not only by seed germination but also by seedling growth of *Brassica pekinensis*, *Lactuca sativa*, *Oryza sativa*, *Portulaca oleracea*, *Oxalis corniculata,* and *Setaria viridis* in pot experiments. Additionally, the field trial revealed that *A. argyi* significantly caused growth inhibition of weeds in *Chrysanthemum morifolium* field, without harming *C. morifolium*. This study provides scientific evidence for the research and development of environmentally friendly, nature-based herbicides (Li et al., 2018).

Sunflower (*Helianthus annuus* L.) exhibited inhibitory effect of its soil-incorporated fresh or dry biomass on the seed germination and seedling growth of *Amaranthus albus, Amaranthus viridis, Agropyron repens, Ambrosia artemsiifolia, Avena fatua, Celosia crustata, Chenopodium album, Chloris barbara, Cynodon dactylon, Digitaria sanguinalis, Dactyloctenium aegyptium, Digitaria ciliaris, Echinochloa crus-galli, Flaveria australasica, Parthenium hysterophorus, Portulaca oleracea, Sida spinosa, Trianthema portulacastrum,* and *Veronica perisca* (Azania et al., 2003). Aqueous extracts from dry sunflower leaves inhibited seed germination of lettuce, and reduced root length up to 85% (Ravlic et al., 2022). Sunflower residues can suppress the growth of weeds through spreading it in the form of a layer over the soil surface or mixing it in the soil (Jabran, 2017). Thus, sunflower extracts could be useful in weed management for sustainable agriculture (Azania et al., 2003)

1.3 Applications of Allelopathy

Allelopathy offers huge applications in the field of agriculture. Strategies have been implemented to incorporate it as part of Integrated Pest Management (IPM) and to reduce growth of weeds and increase crop yield. Inclusion of allelopathy as a tool in integrated weed management strategies could reduce application of synthetic herbicides (Khamare, Chen, and Marble, 2022). Allelochemicals are environmentally friendly weed control agents useful in sustainable farming (Palanivel et al., 2021).

Crop allelopathy has gained the interest of many scientists, researchers, and specialists on this field. On the global scale, tremendous efforts have been carried out to conduct research on how to utilize allelopathic crop plants for improved agricultural practices.

To be an allelopathic crop, four criteria should be met: (1) has patterns of vegetation around the crop itself, (2) has effects on the growth of other crops or the same crop growth when planted in succession, (3) creates soil sickness problems because of the accumulation of allelochemicals in the soil, and (4) makes and secretes bioactive allelochemicals into the environment (Duke, 2015; Scavo and Mauromicale, 2021). In view of these criteria, rice allelopathy as a basis for sustainable weed management has been extensively studied since rice has strong allelopathic property (Serra, Shanmuganathan, and Becker, 2021).

This monograph entails to cover the relevant role of allelopathy in the formulation of bioherbicides for sustainable weed management and for addressing concerns on herbicide resistance (see chapters 2, 7, and 10). The organic chemistry, analytical chemistry, and biochemistry aspects of allelochemicals are explored and well-discussed (see chapters 3 through 6 and 8). This book also presents the application of nanotechnology in creating nanoencapsulated bioherbicide for efficient and stable delivery of allelochemicals (see chapters 9 and 10).

CHAPTER 2

ALLELOPATHY AND WEED MANAGEMENT

2.1 Weed Management and Sustainable Agriculture

Globally, weeds, as plants that are competitive, persistent, pernicious, and have a negative effect on desired crops, are one of the most difficult dilemmas and yield-limiting biotic constraints in agricultural production due to their competition with crops. There are about 250,000 species of plants in the world and 3% of these or about 8,000 behave as weeds. As the world's population has been escalating, world food production should be protected from significant yield loss caused by weed competition (Chauhan, 2020). Weeds compete with crops resulting in significant reduction in yield by sharing light, air, water, nutrients, and space (Sathishkumar et al., 2020). Weeds hinder crop growth and development, causing yield loss greater than any other pest in crop production (Khamare, Chen, and Marble, 2022).

Weed management is most effective when it involves an integrated approach. Cultural, biological, mechanical, and chemical control methods have been implemented to reduce weed growth and maximize crop yield. Conventional weed management involves only the use of herbicides, making it insufficient due to the rise of herbicide-resistant weeds. The emerging weed management that is being implemented in agriculture is called the integrated weed management (IWM), the sustainable use of available methods in the agricultural sector to reduce weed pressure or control and manage them without reducing farm income and without causing damage to the environment. IWM is a multidisciplinary approach with the primary goal of preventing weeds, enhancing crop competition, and reducing weed density. The success in implementation of IWM greatly depends on the predictive simulation models of weed occurrence (Swanton et al., 2000; Knezevic, Jhala, and Datta, 2017). Comprehension of all the existing chemical, biological, and physical interactions between the plant and the weed is essential in devising a specific method for weed management (Lengai et al. 2020).

Weeds could be controlled by mechanical weeding or by application of herbicides. However, manual removal of weeds is laborious and expensive while use of herbicides has caused serious ecological implications. Thus, allelopathy could be an alternative method to manual weed management practices and indiscriminate use of herbicides (Sathishkumar et al., 2020).

Management of weeds coupled with sustainable agriculture is of great advantage. According to Motmainna et al. (2023), sustainable agriculture pertains to "management procedures that work with natural processes to conserve all resources, minimize waste and environmental impact, prevent problems and promote agroecosystem resilience, self-regulation and sustained production for the nourishment and fulfilment of all." Sustainable agriculture centers on ensuring global food security by means of innovative and environmentally friendly techniques for pest control (Arora, Husain, and Prasad, 2024). In view of the principles of sustainable weed management, allelopathy could be adopted as an eco-friendly method of controlling weeds. Natural products have been proposed as a weed control agent substituting synthetic herbicides (Diaz-Franco er al., 2023). Among these natural products are allelochemicals secreted by plants (Ain et al., 2023). To reach the goal of sustainable agriculture, rigorous research on plant breeding, soil fertility and tillage, crop protection, and cropping systems is indispensable (Tahat et al., 2020).

Allelopathy can be utilized as a weed management tool. This can reduce the use of synthetic pesticide in sustainable agricultural production (Ravlic et al., 2022). Various investigations have been conducted in using the phenomenon of allelopathy as an effective and environmentally friendly weed management tool that can be incorporated in a sustainable, ecological, and integrated weed management system (Khamare, Chen, and Marble, 2022). As a weed management tool intended for solving problems in agriculture and improving growth and crop production, allelopathy has been used in crop rotations, intercropping, crop residue incorporation, and aqueous extracts applications—strategies that are highly flexible and can boost efficiency, blending them with integrated weed management strategy. (Hussain and Abbas, 2021; Scavo and Mauromicale, 2021).

Allelopathy-inspired weed management solutions are highly adaptable and changeable depending on the particular characteristics of the context including pedo-climatic conditions, weed species, agricultural practices used, economic constraints, and farmer's expectations. Allelopathy can be utilized in various cropping systems, in organic farming and in conservative, minimum, and no-tillage agricultural systems (Scavo and Mauromicale, 2021).

Allelochemicals could be developed as bioherbicides that can control even herbicide-resistant weed biotypes. The discovery of invasive and fast-growing weeds could be tapped as a potential source of bioherbicide, for example, the bioherbicidal utilization of *Sphagneticola trilobata* L. Pruski, commonly known as wedelia (Fig. 2-1) is discussed in chapter 10. Prior to commercialization, providing a time-saving alternative route in novel development of herbicides with new or multiple modes of action is the determination of identity of new allelochemicals with phytotoxicity to herbicide-resistant weed populations (see chapter 7) (Hickman et al., 2023) Isolation, characterization, and quantification of available allelochemicals are also important steps in the discovery of potent allelochemicals with bioherbicidal potential (see chapter 8). Thus, such development of herbicides could be exploited in addressing herbicide resistance associated with target-site adaptations (Gressel, 2020; Hachisu, 2021).

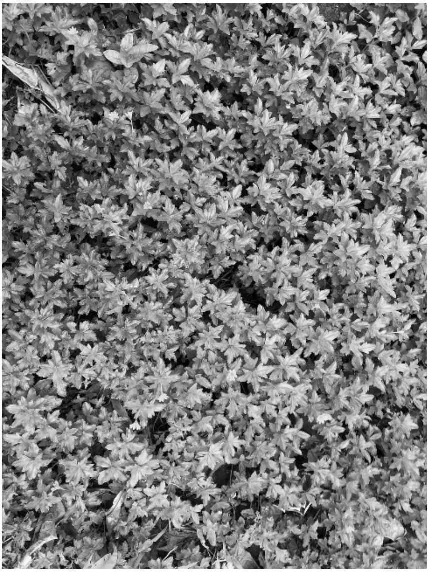

Fig. 2-1. Wedelia is an invasive weed with bioherbicidal potential.

Allelopathy could also be used in designing biotechnologies focusing on the development of transgenic allelopathy in crops. Different genes are associated with plant allelochemicals (Singh et al., 2021). In the past 20 years, biotechnology applications have gained the attention of researchers and scientists through genetic engineering (GE) techniques including the analysis of quantitative trait loci (QTLs) based on restriction fragment length polymorphism (RFLP), amplified fragment length polymorphism (AFLP), and microsatellite markers employed in identifying the crop allelopathic activity-conferring genetic markers (Joshi et al., 2019; Scavo and Mauromicale, 2021). QTLs linked to allelochemicals have been genetically mapped and modes of action and molecular mechanisms of allelopathy have been investigated in relevance to weed management (Palanovel et al., 2021). One important step is the selection of allelopathic cultivars, which has been investigated through screening methods. In the study of Ladhari et al. (2020), thirteen fig (*Ficus carica* L.) cultivars were screened for their allelopathic activity and allelochemical concentration, and the findings revealed that the degree of inhibition depends on the cultivars and phytochemical profiles. The recent advances in analytical chemistry, metabolomics, biotechnology, and genetics have contributed in identifying, isolating, and purifying of novel allelochemicals, and in making commercial cultivars with embodied or initiated allelopathic traits coupled with competitive components (fast seedling emergence, high growth rate, early vigor, root development, and wide leaf area) is the recent GE future perspective (Scavo and Mauromicale, 2021).

Intensifying the inherent capability of crops in competing with neighboring plants is one of the relevant strategies in reducing crop yield losses. In using allelopathy for weed control, it is important that the donor plant is fully resistant to its allelochemical. These allelopathic plants can be implemented within integrated pest management methods (Kiely, Randall, and Kaczorowska-Dolowry, 2023). The use of allelopathic crops could also be a resource in managing herbicide-resistant weeds (Hickman et al., 2023). The breeding of allelopathic crops for weed management could also be enhanced through genetic engineering techniques (Kong et al., 2019; Aci et al., 2022). The genetic regions associated with sorgoleone biosynthesis in sorghum has been investigated for future use in enhancing these genes for higher allelopathic potential (Shehzad & Okuno, 2020).

Poaceae plants are widely reported as allelopathic. Among the most studied allelopathic crops are rice (*Oryza sativa* L.), rye (*Secale cereale* L.), common (*Triticum aestivum* L.) and durum wheat (*T. durum*), sorghum (*Sorghum* spp.), barley (*Hordeum vulgare* L.), and oat (*Avena sativa* L.) (Scavo and Mauromicale, 2021). Some allelopathy studies related to rice are elaborated in the previous chapter. Since rice is one of the world's major staple crops, it can be utilized as an allelopathic crop for weed management (Serra, Shanmuganathan, and Becker, 2021). Kato-Noguchi et al. (2013) showed that the rice allelochemical momilactone B inhibits both growth and germination of weeds, which was evidently revealed when *A. thaliana* seeds put on filter paper with varying concentrations of momilactone B exhibited a germination IC_{50} of 48.4 μM, which was considerably greater than those measured for root and hypocotyl growth inhibition in *A. thaliana.* Though it is well-known that momilactone B interferes with plant growth and development, its mode of action is largely unknown (Serra, Shanmuganathan, and Becker, 2021). Wu et al. (2020) investigated the effect of momilactone B on *A. thaliana* at the transcriptional level and their findings showed that momilactone B inhibits root growth and development by disrupting abscisic acid (ABA) and auxin homeostasis and hormone signalling.

Information dissemination to farmers is necessary to educate them about allelopathy and allelochemicals in layman's terms. The potential avenues of application for allelopathy should be bridged from the scientist's laboratory to the farmer's field. Development and identification of allelopathic crops is not sufficient, evidence shows that their potential benefits are not widely known among farmers, or that farmers are still reluctant to use such knowledge practically (Scavo and Mauromicale, 2021; Hickman et al., 2023) Thus, helping advisors and farmers in assessing whether allelopathy can be effectively implemented into an eco-friendly weed management strategy is essential (Scavo and Mauromicale, 2021).

2.2 Allelopathy and Intercropping

Intercropping, the practice of planting compatible crops together simultaneously in the same field, is an environmentally friendly strategy in weed interference (Khamare, Chen, and Marble, 2022). Intercropping systems are beneficial, offering greater crop yield and quality, causing fewer pest-related problems than monoculture systems, and enhancing biodiversity and natural soil fertility (Glaze-Corcoran et al., 2020; Hussain and Abbas, 2021). Intercropping can favorably change the microbial communities around the rhizosphere and this was observed when wheat was intercropped with faba bean compared to wheat monoculture only. Similarly, alteration in rhizobial communities took place when maize was intercropped with chickpea and soybean (He et al., 2013).

Allowing more interactions between crops and facilitating their cultivation, strip intercropping is the most embraced method in field experiments on allelopathy (Scavo, Restuccia, and Mauromicale, 2018). The most common example of allelopathic intercropping is cereal–legume intercropping, paving the way for high numbers of allelopathic crop appropriate for cover cropping both in the Poaceae and Fabaceae families (Scavo and Mauromicale, 2021).

Allelopathic plants could be utilized as trap crops in intercropping systems used to manage competitive weeds. Twelve intercrops in cotton in a span of 5 years resulted in 43–71% average reduction of weed growth and

91–96% reduction of weed biomass relative to control, with sun hemp (*Crotalaria juncea* L.) exhibiting the greatest phytotoxicity and significant inhibition of purple nutsedge (*Cyperus rotundus* L.) and smooth joyweed (*Alternanthera paronychioides* A. St.-Hil.) (Blaise et al., 2020). Comparing the combinations of various allelopathic crop species and spatial arrangements on grain production and weed control in soybean, Cheriere et al. (2020) indicated that a trade-off between soybean production and weed control occurred with sunflower showing the lowest yield but with the highest weed control level, suggesting that farmers could handle a trade-off by combining associated species choice and spatial arrangement, for instance growing alternate rows in sorghum and buckwheat intercrops.

Intercropping *Camellia oleifera* with *Arachis hypogaea* L. in southern China showed inhibitory effects of *C. oleifera* extracts on seed germination and growth of *A. hypogaea,* with the fruit shell exhibiting the greatest inhibitory effect. GC-MS analysis revealed that the identified allelopathic substances inhibiting *A. hypogaea* germination and growth are 2,4-di-*tert*-butylphenol, hexanal, and benzaldehyde (Wen et al., 2023).

When cowpea was intercropped with maize, the growth of jungle rice, purslane, jute mallow (*Chorchorus olitorius* L.), and Egyptian crowfoot grass (*Dactyloctenium aegyptium* (L.) Willd.) was reduced (Saudy, 2015).

When pea (*Pisum sativum* L.) was intercultivated with barley (*Hordeum vulgare* L.), sorghum with pea (*Vigna unguiculata* (L.) Walp.), and wheat with chickpea (*Cicer arietinum* L.), intercropping resulted in suppression of weed intensity and improvement in yield (Abbas et al. 2021). Likewise, when wheat was intercropped with white clover along with high nitrogen availability, weed shoot dry matter was reduced, cover crop biomass was enhanced, nitrogen accumulation improved, and wheat yield and protein content increased (Vrignon-Brenas et al., 2018).

Appropriate intercropping ratios are to be selected in enhancing weed control. Rad et al. (2020) reported that intercropping sorghum with varying ratios of hairy vetch (*Vicia villosa* Roth) and lathyrus (*Lathyrus sativus* L.) and employing three various strategies of no weed control, full weed control, and hand weeding revealed that the greatest sorghum yield was exhibited with sorghum and 33% hairy vetch, the least in sorghum and 100% lathyrus, and the highest weeding efficiency in sorghum with 100% lathyrus (Rad et al., 2020). When white clover (*T. repens*) intercropping was combined simultaneously with high nitrogen availability, Brenas et al. (2018) found that significant increase in cover crop biomass, decrease in weed shoots' dry matter, improvement in nitrogen accumulation, and maintaining high wheat yields and protein content occurred.

2.3 Allelopathy and Crop Rotation

Crop rotation—the strategy of planting various crops in the same field systematically and sequentially over a growing season—has been advantageous owing to sustaining soil structure, increasing organic matter, and decreasing soil erosion associated with monoculture system. Allelopathic crops introduce allelochemicals in the soil, thereby causing reduction in weeds for the subsequent crop (Khamare, Chen, and Marble, 2022).

Combining crop cultivars is more advantageous than using a single uniform species. When use of species or cultivar mixtures is adopted, weed suppression is enhanced owing to resource competition and allelopathy—both phenomena taken advantage of by plants in detecting and modifying their responses to neighboring plants (Yang et al., 2018; Smith et al., 2020; Hickman et al., 2023). Despite lowered exudation of allelochemicals, relatively closely related rice cultivars possess greater effectivity in competitive inhibition of paddy weeds (Xu et al., 2021). Hussain et al. (2022) mentioned that plants more functionally analogous to the allelopathic species will stir a greater allelopathic feedback, indicating that proper combination of crops or cultivars may have potential to enhance and increase weed suppression through allelopathy (Hickman et al., 2023).

Additional weed control can be boosted by utilizing allelopathic crops as smothering crops growing rapidly with thick canopy, such as sudan grass (*Sorghum sudanense* L.), common buckwheat (*Fagopyrum esculentum* Moench), rye, barley, sunflower, and sweet clover (Cheema et al., 2012). After the harvest of rice cultivar PI312777 exhibiting allelopathic activity, the growth of barnyard grass in soil was inhibited compared to the soil where non-allelopathic rice cultivar was planted (Dmitrovic et al., 2015).

Crop rotation can be incorporated in an integrated weed management system (IWMS). When included in such system, crop rotation affords the best results, preventing against weed establishment and reducing of the soil seedbank (Scavo and Mauromicale, 2020). Control of weeds in the current and next crops can be achieved when an allelopathic crop is incorporated within rotational sequences, with the release of allelochemicals into the soil via root exudation, decomposition of plant residues, and leaching from plant foliage (Scavo and Mauromicale, 2021). Allelochemicals secreted into the rhizosphere can directly or indirectly be converted by microbes into more active, less active, or entirely inactive metabolites that can suppress seed germination and lessen weed density and biomass (Scavo, Abbate, and Mauromicale, 2019).

The desirable effects of allelopathic crops within crop rotations are greatly pronounced in conservative agricultural systems (Scavo and Mauromicale, 2021). Sorghum-wheat rotation exhibited the highest weed-suppressive effect (in terms of density and dry biomass reduction) in all tillage systems due to build up of sorgoleone allelochemicals in the soil.

The use of crop rotation in weed management can reduce the dependency on synthetic herbicides. Hence, diversification of crop rotations can be promoted to inhibit weeds (Scavo and Mauromicale, 2021). In the meta-analysis across studies conducted by Weisberger et al. (2019), employing simple and more diverse crop rotations with involvement of allelopathic crops (wheat, oat, corn, alfalfa, sunflower, etc.) lowered weed density by 49% compared to simple sequences. When cultivated cardoon or globe artichoke was included for 2–3 years in Mediterranean crop rotations, the size of the weed seedbank was minimized and formation of soil eubacterial communities was enhanced.

2.4 Allelopathy and Mulching

Mulching is the process of incorporating any material to soil surface for weed growth reduction, soil moisture improvement, and surface runoff reduction (Adekalu et al., 2007; Chalker-Scott, 2007). Surface-applied or soil-incorporated mulching can also cause inhibition of weed germination and growth through light exclusion by serving as a physical barrier and lowering accessible moisture in the top layer (Richardson et al., 2008; Marble, 2015; Jordan et al., 2010; Gerhards and Schappert, 2020). Due to allelochemicals present in residues from allelopathic plants used as mulch, allelopathic mulch can be used in managing weeds, improving crop yield, and enhancing soil quality (Khamare, Chen, and Marble, 2022).

Allelopathic crop mulch is a useful weed management technique that can cause significant weed growth reduction. Addition of sorghum, sunflower, and brassica residues into the soil inhibited sprouting and seedling growth of purple nutsedge and horse purslane (Matloob et al., 2010). Interestingly, crop residues of sorghum, sunflower, and brassica controlled the growth of horse purslane and purple nutsedge better than individual application of these crop residues (Khaliq et al., 2011).

Surface-applied mulches are preventive weed control agents. They alter the soil weed seedbank, weed emergence, and establishment (Scavo and Mauromicale, 2020). The soil weed seedbank significantly decayed and wheat yield rose after the application of sunflower, rice, corn, and sorghum mulches in a two-year field trial (Abbas et al. 2018). Combination of allelopathic crop mulches and post-emergence herbicide mixtures at low doses offered an effective control of *Phalaris minor* Retz, thereby decreasing the occurrence of herbicide-resistance in *P. minor.* Studying the effect of *Trifolium subterraneum* cover cropping (with or without burying dead mulches into the soil) on the quali-quantitative composition of the soil weed seedbank in an apricot (*Prunus armeniaca* L.) orchard. Scavo et al. (2020) found that green manuring of *T. subterraneum* was more effective than dead mulching in reducing the size of the soil weed seedbank.

2.5 Allelopathy and Cover crops

Cover crops, also called living mulch, green manure, smother crop, or catch crop, are planted to take the place of weeds growing in between crop rows. Cover cropping is a substitute to tillage for weed suppression, reducing the use of synthetic herbicide (Samarajeewa et al., 2006; Mennan et al., 2020). Among the ecological advantages of cover cropping are the following: (1) reducing weeds; (2) conserving soil; (3) improving soil fertility; (4) attracting beneficial insects; (5) maintaining soil moisture, reducing soil erosion; (6) minimizing nutrient leaching; (7) enhancing of soil organic matter levels and microbial activities; and (8) improving of soil structure and hydraulic properties (Gerhards and Schappert, 2020; Mennan et al., 2020).

In general, cover crop phytotoxicity is directly proportional to biomass production. In other words, the higher the biomass production and biological length, the higher the phytotoxicity of cover crop (Restuccia et al., 2020). Other factors to be considered in cover cropping are those related to soil properties such as texture, structure, pH, organic matter level, and ion exchange capacity. These factors influence retention of allelochemicals, their transport, and their availability (Scavo et al., 2019). Moreover, the degree of effective weed control in cover crop management progresses as seeding rate, amount, and duration of plant residue increase (Mennan et al., 2020).

Use of cover crops can also be implemented in IWMS. Cover cropping can also be utilized in low-input agriculture and organic farming to manage the soil weed seedbank and avoid weed emergence (Scavo and Mauromicale, 2020). Suppressing weed growth through allelopathy, cover crops serve as a living mulch at first, obstructing empty space where weeds can emerge (Osipitan et al., 2019; Mennan et al., 2020). Examples of relevant cover crops with allelopathic potential are sunhemp (*Crotalaria juncea* L.), yellow sweet clover (*Melilotus officinalis* (L.) Pall.), sorghum, cowpea, alfalfa, ryegrass, barley, oat, buckwheat (*Fagopyrum esculentum* Moench.), the Brassicaceae black mustard, field mustard (*B. rapa*), rapeseed

(*B. napus*), white mustard (*Sinapis alba* L.), legumes alfalfa, hairy vetch (*Vicia villosa* Roth), common vetch (*V. sativa*), velvet bean (*Mucuna pruriens* ((L.)) DC.), cowpea (*Vigna unguiculata* ((L.)) Walp.), crimson clover (*Trifolium incarnatum* L.), subterranean clover (*T. subterraneum*), red clover (*T. pratense*) and Egyptian clover (*T. alexandrinum*), white mustard (*Sinapis alba* L.), wheat, and cereal rye (*Secale cereale* L.) (Farooq et al., 2011; Tursun et al., 2018; Scavo and Mauromicale, 2021). In addition, *Camelina sativa* (L.) Crantz (camelina) cover crops have been effective in stimulating growth and yields in corn and soybeans (Ghidoli et al., 2023).

Sturm et al. (2018) reported that allelopathic effects were species-specific. The authors employed active carbon for immobilization of allelochemicals in a glasshouse experiment and results revealed that the weed *Stellaria media* (L.) Vill. had a greater sensitivity to allelopathy than *Alopecurus myosuroides* Huds. and volunteer wheat (*T. aestivum*). Thus, they have the following conclusions: (1) allelopathy contributes in overall suppression of weeds, in addition to greater contribution played by competition; and (2) an allelopathic cover crop should have competitive prerequisites to enhance the efficiency of its weed control such as rapid germination, fast development, dense canopy, and high soil coverage.

Though cover cropping and green manuring are generally viewed as distinct and separate methods, they can be treated as synonymous (Scavo and Mauromicale, 2020; Mennan et al., 2020) Recently, various researches have concentrated on inclusion of allelopathic plant residues into the soil including green manuring for control of weeds under field conditions (Scavo and Mauromicale, 2021). Based on the report of Puig et al. (2019) on the allelopathic activity of leaf green manure of *Eucalyptus globulus* Labill. in corn fields for two seasons and in two different locations, *Eucalyptus* green manure caused significant weed biomass reduction of *Digitaria sanguinalis* (L.) Scop. and *Chenopodium album* L. chiefly at early stages of corn establishment, without affecting corn. *E. globulus* green manure also heightened the soil pH, cation exchange capacity, and microbial biomass carbon. Likewise, studying barley (*H. vulgare*) and vetch (*V. sativa*) green manure in a long-term field experiment involving corn and sunflower, Alonso-Ayuso et al. (2018) reported that substituting a winter fallow by cover crops showed beneficial effects on weed density, diversity, and soil seedbank, with both cover crops exhibiting a weed density reduction of 51–63% in spring. Also, barley green manure inhibited winter weeds better than vetch, but no effect was observed on the weed seedbank size after 10 years of cover cropping.

Mixing cover crops has positive synergistic effect on weed control. Several reports have evidently demonstrated the greater effectiveness in