Allelochemicals in Parthenium in response to biological activity and the environment

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ABSTRACT

Parthenium (Parthenium hysterophorus L.), a member of Asteraceae, is an obnoxious national weed of wide ecological niches including waste land and agroecosystems. The weed has phenolics, flavonoids, alkaloids, pseudoguaianolides and oils, many of which have been implicated in allelopathy. The phenolics include caffeic acid, vanillic acid, ferulic acid, chlorogenic acid, p-coumaric acid and p-hydroxy benzoic acid. The plant and its parts owe various properties involving allelopathy, phytotoxicity, herbicidal activity, growth regulation / inhibition, including on nitrification and nitrifying bacteria. Among flavonoids are guercetagetin-3, 7-dimethyl ether, 6-hydroxy kempferol-3, 7-dimethyl ether, kaempferol 3-O-glucoside, quercetin 3-O-glucoside, kaempferol-3-O-glucoarabinoside, and lignan (+) syringaresinol. They confer antioxidant activities, scavenging effects on activated carcinogens and mutagens, action on cell cycle progression, altered gene expression, UV-B protection in plants, warding off microbial infections, and protection of plants from herbivores, etc. The alkaloids have been detected but yet to be identified. The pseudoguaianolides identified from the species include parthenin, anhydroparthenin, ambrosin, coronopillin, damsin, hymanin, 6^βhydroxyparthenin, 2^βhydroxycoronopilin, tetraneurin-A, ambrosanolides, charminarone, 6 Bacetoxyhysterone C, deacetyltetraneurin A, hysterin, hysterone E, hysterone D, conchasin A, acetylated pseudoguaianolides, scopoletin (belongs to coumarin), and dihydroxyparthenin. They have diverse activities like cytotoxic, antitumor, antibacterial, antifungal, phytotoxic, antiprotozoan, active against human and animal parasites (including intermediate hosts), insecticidal, moluscicidal, vertebrate feeding deterrence and toxicity, allergic contact dermatitis, mitochondrial oxidative phosphorylation inhibition, allelopathic, anti-inflammatory, and antimalarial. The oils identified from the species include α -pinene, camphene, ßpinene, sabinene, ßmyrcene, ß-terpene, limolene, ßocimene, ocimene, p-cymene, linalool, caryophyllene, humulene, terpinene-4-ol and many



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unidentified compounds. They have been shown to be antifungal, antibacterial, antimicrobial, virucidal, antiparasitical, insecticidal, medicinal, cytotoxic and many find use in cosmetics. Information on role of specific constituents in allelopathic interaction of the species in natural ecosystems still appears to be scarce. Bioherbicidal potential of most of the constituents has not been investigated. These are attractive areas with potential of facilitating development of newer herbicides or pesticides.

Key words : Allelopathy, Allelochemicals, Antifungal, Antimicrobial, Congress grass, Contact dermatitis, Cytotoxic, Environment, Insecticidal, Flavonoids, Growth inhibition, Growth regulation, Herbicidal activity, Microbes and protozoa, Parthenium, *Parthenium hysterophorus*, Phenolics, Pseudoguaianolides, Rhinitis, Skin allergy, Toxicity to animals, Toxicity to plants.

Parthenium (*Parthenium hysterophorus* L.) is commonly known as American feverfew, white top, white head, carrot grass (for resemblance of its leaves with that of carrot) or congress-grass. The species is a herbaceous annual or ephemeral of Asteraceae with world-wide occurrence and is a major crop and pasture weed of India and Australia in particular (Towers *et al.* 1977, Navie *et al.* 1996, Pandey *et al.* 2003, Kohli *et al.* 2006, Sushilkumar and Varshney 2007). It has been asserted that photo- and thermo-insensitivity and adaptability to contrasting ecological conditions enable it to thrive from sea level to altitudes of 3000 m above mean sea level (amsl) (Lomniczi de Upton et al. 1999) in Argentina and to altitudes of more than 2080 m amsl in the Central Himalaya in India (Pandey et al. 2003). In the absence of effective natural enemy, its much publicized than verified probable allelopathic effects on other species and rapid growth allow it to grow luxuriantly all through the year, except in extreme winter, especially with spells of freezing temperatures, and summer drought, suppressing native vegetation and threatening biodiversity (Krishnamurthy et al. 1977, Towers et al. 1977, Kanchan and Javachandra 1979a, b, 1980a, b, Williams and Groves 1980, Jayanth and Bali 1994, Pandey et al. 2003). Abundance of the weed in vacant sites and no man's land may further facilitate its spread to cultivated fields. This may threaten quality and quantity of agricultural production, human and animal health, biodiversity and the environment resulting in serious socio-economic implications (Towers et al. 1977, Narasimhan et al. 1977, Pandey et al. 2003). The biological interactions of the species are due to its allelochemicals comprised of phenolics and terpenoids including sesquiterpene lactone parthenin as a major constituent (Rodriguez et al. 1971, Picman et al. 1979,

Picman *et al.* 1980, Kanchan and Jayachandra 1980b, Picman *et al.* 1981, Das and Das 1995). Economic potential of the secondary metabolites including allelochemical constituents with reference to their bioactivity, except their harmful effects on human, animals, plants, ecosystems and natural biodiversity, largely remains to be speculative, and descriptive rather than drawing practical advantage for use in agriculture and agricultural pest management.

Secondary metabolites including allelochemicals

Investigations on natural products chemistry of *Parthenium* have been confined to major nutrients (Dutta *et al.* 1979), phenolics, organic acids, sesquiterpene lactones (Rodriguez *et al.* 1971, Rodriguez *et al.* 1976, Picman *et al.* 1979, Picman *et al.* 1980, Kanchan and Jayachandra 1980b, Picman *et al.* 1981, Das and Das 1995) and leaf oils (Kumamoto *et al.* 1985) (Table 1 and Table 2).

Phenolic acids identified from *Parthenium* plant parts with reference to allelochemic interactions include caffeic acid, vanilic acid, ferulic acid, chlorogenic acid, pcoumaric acid and p-hydroxybenzoic acid and among the organic acids, fumaric acid (Kanchan and Jayachandra 1980b, Das and Das 1995). Among pseudoguaianolides reported are parthenin, coronopilin, damsin, hymanin, 8-

 Table 1. Phenolics and alkaloid secondary metabolites (including allelochemicals) in *Parthenium* and their reported biological activities.

Constituent	Reference	Reported biological activity of the constituent	Reference
Phenolic acids Occurrence: leaf, stem, root, flower, poll- localization is in vacuoles.	en and trichomes,		actors. Usual cellular
 Caffeic acid Vanillic acid Ferulic acid Ferulic acid Chlorogenic acid p-Coumaric acid p-Hydroxy benzoic acid Flavonoids 	Kanchan and Jayacha ndra 1980b. Das and Das 1995	Allelopathy, phytotoxicity, herbicidal activity, growth regulation / inhibition; and nitrifica tion and nitrifying bacteria	Gross 1975, Lodhi and Killingbeck 1980, Patterson 1981, Rice 1984, Mersie and Singh 1988, Pandey 1994b, Pandey <i>et al.</i> 1996b, Pandey and Mishra 2002
 Occurrence: leaf, stem, flower and poller 1. Quercetagetin-3, 7-dimethyl ether 2. 6-Hydroxy kempferol-3, 7-dimethyl ether 3. Kaempferol 3-O-glucoside 4. Quercetin 3-O-glucoside 5. Kaempferol-3-O-glucoarabinoside 6. Lignan (+)- syringaresinol Alkaloids 	n, depending on p Rodriguez <i>et</i> <i>al.</i> 1971, Rodriguez 1977, Towers <i>et al.</i> 1977	lant parts and other factors. Usual cel Antioxidant activities, scavenging effects on activated carcinogens and mutagens, action on cell cycle progression, altered gene expression, UV-B protection in plants, warding off microbial infections, and protection of plants from herbivores, etc.	lular localization is in vacuoles. Harborne and Williams 2000, Rusak <i>et al.</i> 2002
Occurrence: leaf, stem, root, flower. Usu Alkaloids -2 (Unidentified)	al cellular localiza Rodriguez, 1977	ition is in vacuoles. -	-

-, Information not available.

 β -hydroxyparthenin, anhydroparthenin, hysterin, tetraneurin, ambrosanolides and p-methoxybenzoic acid; a sterol β -sitosterol; a triterpenoid betulin; flavonoides quercetagetin-3,7-dimethyl ether, 6-hydroxykempferol 3, 7-dimethyl ether, kaempferol 3-O-glucoside, quercetin 3-O-glucoside and kaempferol-3-O-glucoarabinoside; and a rare lignan (+)-syringaresinol (Rodriguez *et al.* 1971, Rodriguez *et al.* 1976, Picman *et al.* 1980, Towers *et al.* 1977, Kanchan and Jayachandra 1980b, Das and Das 1995, Lomniczi de Upton *et al.* 1999, Venkataiah *et al.* 2003). Occurrence and concentration of various constituents depended on plant parts, geographical distribution and specific populations (Towers *et al.* 1977, Lomniczi de Upton *et al.* 1999). Fresh leaves of *Parthenium* yielded about 0.033% oil which comprised of α -pinene, camphene, β -pinene, sabinene, β -myrcene, α -terpinene, limolene, β -ocimene, ocimene, p-cymene, linalool, caryophyllene, humulene, terpinene-4-ol and many unidentified components (Kumamoto *et al.* 1985). Parthenin and related sesquiterpene lactones form adducts

Talbe 2. Pseudoguaianolide and oils secondary metabolites (including allelochemicals) in Parthenium and their reported biological activities.

Constituent	Reference	Reported biological activity of the constituent	Reference
Occurring in shoots (mainly leaves an	nd flowering heads), trichomes	and seedlings in their first true leaves	s which bear trichomes,
depending on plant parts and other fa-	ctors. Located in the cytoplasm	n of the plant cells.	
Pseudoguaianolides			
1. Parthenin	Herz and Hogenauer 1961,	Cytotoxic, antitumor,	Fay and Duke 1977,
2. Anhydroparthenin	Romo de Vivar et al. 1966,	antibacterial, antifungal,	Narasimhan <i>et al</i> .
3. Ambrosin	Rodriguez et al. 1976,	phytotoxic, anti-protozoan,	1985, Picman 1986,
4. Coronopilin	Towers et al. 1977,	activity against human and	Pandey 1996b,
5. Damsin	Wickham <i>et al.</i> 1980,	animal parasites (including	Warshaw and Zug
6. Hymanin	Picman et al. 1980, Picmn	intermediate hosts), insecticidal,	1996, Sharma and
7. 8-β-Hydroxyparthenin	et al. 1982, Picman 1986,	moluscicidal, vertebrate feeding	Bhutani 1988, Hooper
8. 2β-Hydroxycoronopilin	Venkataiah et al. 2003,	deterrence and toxicity, allergic	et al. 1990,
9. Tetraneurin-A	Ramesh et al. 2003, Das et	contact dermatitis, mitochondrial	Tafera 2002, Verma
10. Ambrosanolides	al. 2005, Das et al. 2006,	oxidative phosphorylation	et al. 2002,
11. Charminarone	Das et al. 2007	inhibition, allelopathic, anti-	Ramesh et al. 2003,
12. 8-β-Acetoxyhysterone C		inflammatory, and antimalarial	Verma et al. 2004,
13. Deacetyltetraneurin A			Sharma et al. 2005,
14. Hysterin			Lakshmi and Srinivas,
15. Hysterone E			2007,
16. Hysterone D			Regina <i>et al.</i> 2007,
17. Conchasin A			Das et al. 2007,
18. Acetylated pseudoguaianolides			Krenn et al. 2009
19. Scopoletin (belongs to coumarin)			
20. Dihydroxyparthenin			
Oils			
1. α- Pinene	Kumamoto et al. 1985	Antifungal, antibacterial,	Uribe <i>et al.</i> 1985,
2. Camphene		antimicrobial, virucidal,	Lima <i>et al.</i> 1993,
3. β- Pinene		antiparasitical, insecticidal,	Velickovic <i>et al.</i>
4. Sabinene		medicinal and with cosmetic	2002, Damjanoviae -
5. β- Myrcene		applications; and cytotoxic	Vratnica <i>et al.</i> 2008,
6. α- Terpene			Bakkali <i>et al.</i> 2008,
7. Limolene			Ogendo et al. 2008
8. β- Ocimene			
9. Ocimene			
10. p- Cymene			
11. Linelool			
12. Caryophyllene			
13. Humulene			
14. Terpinene -4-ol			
15. Many unidentified compounds			

with cysteine and glutathione (Picman *et al.* 1979). The plant and its residue owe a range of biological activities to constituent phenolics and major sesquiterpene lactone parthenin.

Biological activity of the plant and its constituents including allelochemicals

Medicinal and related uses

Parthenium has been put to use in different parts of the world in different ways. These uses are probably due to the constituent allelochemicals and other constituents in the plant (Table 1 and Table 2). Various medicinal and related uses of *Parthenium* have been reviewed by Towers et al. (1977). Various uses of the species have been summarised in Table 3. The uses had been irrespective of the knowledge of the constituents. It is now that different constituents of the plant have been found to possess various medicinal properties (Table 1 and 2).

Effect on microbes and protozoa

Sesquiterpene lactones and phenolics have been identified as water soluble compounds and the same have been implicated in biological activity including allelopathy of Parthenium plant and its residue (Kanchan and Jayachandra 1980a, b). The plant parts and their extracts suppressed Penicillium spp., inhibited germination of spores of Drechslera rostrata, Fusarium oxysporum, Alternaria alternata, Corynespora cassiicola, Aspergillus fumigatus, A. niger, A. sulphureus and Microsporum gypseum (Luke 1976, Kumar et al. 1979, Shrivastava et al. 1984). Plant extract inhibited mycelial growth and sporulation in pathogen Aspergillus flavus (Lokesha et al. 1986). Parthenium pollen inhibited sporangial germination and zoospore motility in Sclerospora graminicola (Char and Bhat 1975). It showed antifungal property also (Char and Bhat 1975). Leaf and root extracts and constituents parthenin, caffeic acid and anisic acid inhibited nitrogen fixing- and nitrifyingbacteria *Rhizobium phaseoli* and *Azotobacter vinelandii* (Kanchan and Jayachandra 1981). Residue of inflorescence, leaf and root inhibited soil algae (Megharaj *et al.* 1987). Antiamoebic property of parthenin on *Entamoeba hystolytica* using *in vitro* tests was comparable to metronidazole and was effective against experimentally induced hepatic amoebiasis (Sharma and Bhutani 1988). Sesquiterpene lactones isolated from *Parthenium* exhibited activity against a range of gram positive and gram negative bacteria (Montanaro *et al.* 1996).

Effect on insects and nematodes

Parthenin and coronopilin have been found to be insect-feeding deterrent and affect insect development or survival, e.g., in confused flour beetle (Tribolium confusum), mosquito (Culex pipiens and Aedes atropalpus), bollworm (Heliothis zea), grasshopper (Melanoplus sanguinipes) (Arnason et al. 1985, Rodriguez and Hedin 1985, Picman 1986). Leaf or whole plant extracts have also been found to be juvinomimetic (Rajendran and Gopalan 1978, 1980) and nematicidal (Gommers 1973) (e.g., on Meloidogyne incognita and Helicotylenchus dihystera, Hasan and Jain 1984) with beneficial effects on crop plants (Bala et al. 1986). The plant extract has insect antifedent and insecticidal activity (e.g., on bruchid Callosobruchus maculatus and cotton pest Spodoptera litura) (Gajendran and Gopalan 1982, Bhaduri et al. 1985, Dhandapani et al. 1985). The plant extract also inhibited cholinesterase of cockroach brain as done by organophosphorus pesticides (Gajendran and Gopalan, 1982).

Effect on and toxicity to live stock and animals

Ingestion of parthenin by feeding on Parthenium

Country/place	Use
Barbados	Flowers and leaves are used for the treatment of inflammation, eczema and skin rashes.
Cuba	Considered as a medicinal plant, used mainly in fever.
Guadeloupe	Used in fever, herpes and rheumatic pains.
Guadeloupe and	Used as a cure for female ailments.
Martinique	

Table 3. Medicinal and related uses of Parthenium (Prepared after Towers et al. 1977)

Guyana	Used in skin eruptions.
Jamaica	Used in resolutive baths, infusions, treatment of wounds, preparation of decoctions for colds, preparation of baths for fleas on dogs and for bush bath in Kingston area and perhaps elsewhere also.
Trinidad	Used along with other herbs in the preparation of bush baths for cleaning of skin.
Mexico	Used as an analgesic in muscular rheumatism, as a remedy against headache and ulcerated sores.
US Virgin Islands	Used for muscular strains, as an analgesic, vermifuge and in heart trouble.
Montgomery, Alaska (US)	Purported to be efficacious as a skin tonic by older people.

Sikkim, India Considered as a medicinal plant (Bennet 1985).

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plants in cattle, buffaloes and other animals may cause illness or death (Narasimhan et al. 1977). Grazing by animals in Parthenium infested areas or due to accidental or compulsive grazing on it during summer (on account of green fodder) may result in significant intake of the species resulting in acute toxicity leading to death (Narisamhan et al. 1977). Grazing of Parthenium by buffaloes and goats in areas infested by this weed in India often results in bitter milk problem (Picman 1986). Terpenoids have been found to be toxic and in extreme cases of excessive ingestion of the toxin the animals may develop serious toxicity leading to death. Parthenin has been found to be molluscicidal (Picman 1986). Other effects on animals may include sensitization of body organs upon rubbing or touching the plants (Mahadevappa 1997). The terpenoids and other constituents have been attributed to be toxic.

Parthenium causes direct losses to the grazing industry in Australia (Adkins et al. 1997) and can reduce beef production considerably (Chippendale and Panetta 1994). While grazing in Parthenium infested areas, animals may suffer from allergic skin reactions; although unpalatable, animals like cattle, sheep and goats eat it when green forage is scarce. This results in the production of taints in mutton or even death of the animal if consumed in large amounts (Tudor et al. 1981). Sesquiterpene lactones cause toxicity by directly affecting functions of various organs, e.g., by acting as a cardiac depressant as reported in *in vitro* and *in vivo* situations, by involvement in reactions with sulphydryl groups of key enzymes and by affecting microbial composition of rumen (Picman 1986). Symptoms of toxicity of Parthenium feeding to cattle and buffaloes include diarrhoea in a day's time (which subsides in 3-4 days), anorexia, pruritus, alopecia and dermatitis and subsequent death in 8-30 days (Narasimhan et al. 1977, Kadhane et al. 1992). Other symptoms were itching followed by the appearance of erythematous eruptions involving the tip and base of ears and all along the neck. This may gradually extend on either side of thoracic region, dorsal aspects of the abdomen and the lesions extending to knee, hook joints and the brisket region (Narasimhan et al. 1977). The toxicity involved massive ulceration and necrosis in internal organs affecting mouth, gastrointestinal tract, liver, and kidney, congestion in lungs and extensive haemorrhagic zones in kidney. Discontinuation of Parthenium feeding resulted in improvement in health and marked regeneration of ulceration (Narasimhan et al. 1977).

Effect on and toxicity to human beings

Exposure to the weed may cause hay fever, asthma or dermatitis and these can also be caused by dust and debris from the plant as well as pollen (Mitchell 1975, Mitchell and Calnan 1978, McFadyen 1995). Sesquiterpene lactone and other constituents in Parthenium may cause contact dermatitis. The highest concentrations of sesquiterpene lactones are found in trichomes which are present on stems, the underside of leaves and in flowering heads (Warshaw and Zug 1996). Direct contact with Parthenium plants, disseminated dried parts, trichomes or pollen containing major sesquiterpene lactone parthenin and perhaps other constituents including coronopillin, tetraneurin-A and related pseudoguainolides may cause allergic contact dermatitis. Dermatitis is a much more serious problem in India than America as the plant growth is vigorous and contains large amount of sesquiterpene lactones including parthenin, which are absent in the plants in South America (Lonkar et al. 1976, Towers et al. 1977). The dermatitis may appear in various patterns. A typical airborne contact dermatitis may involve eyelids, nasolabial folds, photodermatitis involving the eyelids, nasolabial folds, areas under the chin, and behind the ears, atopic dermatitis, seborrhetic dermatitis, exfoliative dermatitis and photoseustive lichenoid dermatitis (Warshaw and Zua 1996, Lakshmi and Srinivas 2007). Handling of the weed during farming and garden operations may result in hand dermatitis. Inhalation of pollens can cause allergic rhinitis which can develop into bronchitis or asthma if the pollens enter the respiratory tract during breathing.

The pollen may affect the exposed skin surface of sensitive individuals (Lonkar et al. 1974, Subba Rao et al. 1977, Prakash et al. 1978, Warshaw and Zug, 1996). Air borne pollen carried either as individual grains or in the form of clumps (2-80 grains) causes severe allergic rhinitis in sensitive individuals (Rao et al. 1985). The pollen of Parthenium was found to be a potential source of allergic rhinitis. A clinical survey (Rao et al. 1985) showed that 34% of the patients suffering from rhinitis and 12% suffering from bronchial asthma gave positive skin-prick test reaction to the *Parthenium* pollen antigen extracts. Parthenium specific IgE was detected in sera of sixteen out of twenty four patients suffering form seasonal rhinitis. There was 66% correlation between skin test and radioallergosorbant test. There are indications that with the sustained spread and widespread growth of Parthenium in India, large sections of the population are getting increasingly sensitized (Shriramarao et al. 1991). This may intensify the problem to human health and exacerbate consequent socio-economic implications.

Parthenium is a serious threat to human health and environment (Towers and Rao 1992, McFadyen 1995). In India, 4-7% of human population studied suffered from recognisable clinical symptoms associated with *Parthenium* rhinitis, while 42-52% have been reported to be sensitized without showing obvious symptoms (Towers and Rao 1992). In Australia, health risks by Parthenium included hay-fever and skin problems and about 20% of the exposed population developed asthma (McFadyen 1995). Repeated contacts with the weed or its disseminated parts either directly or through the environment may cause allergic eruptions in sensitized individuals on exposed parts of the body. Commonly affected body parts include upper eyelids, sides of the neck, parts of face, V of neck, fronts of elbows and backs of knees (Towers et al. 1977). The eczematous dermatitis may affect face, antecubital and popliteal fossae, the V of neck, and hands. This may progress to chronic ailment with lichenification and spread to affect the wrists, forearms, upper trunk, and sometimes partially generalised and universal (Towers et al. 1977). Secondary changes may involve impetiginization, fissuring of the skin and various pigmentary changes with further increase in the disease on exposure to sunlight (Lonkar et al. 1974).

Contact of skin with low molecular weight chemicals and sensitization of blood lymphocytes may result in contact dermatitis and contact of the nasal mucous membranes with high molecular weight chemicals like proteins of plant pollen may cause allergic rhinitis (hay fever) (Towers *et al.* 1977, Sriramarao *et al.* 1993). Sesquiterpene lactones require exocyclic methylene group on the γ - lactone ring for immunological reactivity of these compounds (Mitchell 1975). Sesquiterpene lactones form complexes with amino acids, polypeptides, and proteins mainly through their sulphydryl groups (Dupuis *et al.* 1974, Picman *et al.* 1979, Dupuis *et al.* 1980).

Effect and toxicity on plants

The allelochemicals present in the *Parthenium* have been implicated in regulation to its own populations and shown to affect both the crops and other higher plants including weeds.

Autotoxicity

Investigations (Picman and Picman 1984, Kumari and Kohli 1987) have shown autotoxicity in *Parthenium*. Picman and Picman (1984) have shown role of the autotoxic effect of water soluble secondary plant metabolites, sesquiterpene lactones and phenolic acids present in the *Partheinium* in regulating its own population. The germinaion rates of achenes of *Parthenium* increased with increasing distance between them (decreasing achene density) and increasing washing period preceding the germination tests. The inhibition of germination processes by water soluble autotoxins was temporary and its duration was determined by the concentration of the allelochemicals in the environment. In another study (Kumari and Kohli 1987), the leachates derived from the plant decreased percent cell survival and chlorophyll content. Leachates from leaves were more toxic to *Parthenium* when applied to the foliage as compared to when applied through the roots. The polar allelochemicals were highly effective in preventing rooting and sprouting of stem cuttings and in reducing the regeneration potential of mature *Parthenium* plants. Sesquiterpene lactones, parthenin and coronopilin, constituents found in large amounts in *Parthenium* (Picman and Picman 1984) were autotoxic to seedlings and older plants at 0.1%. The investigators suggested that in *Parthenium*, the water soluble plant metabolites would play an important role not only in allelopathy and defence against herbivorous predators and diseases but also as autotoxins in its population regulation and the timing of the germination.

Effect on and toxicity to other plants

Parthenium affected most field grown economically important plants including wheat, barley, ragi (Eleusine coracana) (Kanchan and Jayachandra 1979a, b, Shrivastava et al. 1985), groundnut (Arachis hypogea), Crotalaria juncea and Phaseolus mungo (Sarma et al. 1976), French beans (Phaseolus vulgaris) (Kanchan and Jayachandra 1979a,b), tomato (Lycopersicum esculentum) (Mersie and Singh 1988), cowpea (Vigna sinensis), bajra (Pennisetum typhoideum) (stimulated the growth in bajra) (Kanchan and Jayachandra 1979b) and Brassica compestris (Kumari et al. 1985) reportedly through allelopathy. The allelopathy was attributed to release of phenolics and sesquiterpene lactones from the plants into the soil through leaching, exudation from the roots, as result of death and decay of the plant, and from its residue (Kanchan and Jayachandra 1979a, b). Parthenium pollen inhibited germination of pollen and pollen tube growth of test species (Crotalaria palida and Desmodium heterocarpon) and caused withering of flowers and reduction of leaf chlorophyll content (Kanchan and Jayachandra 1980c). The pollen allelopathy has been attributed to the constituent allelochemicals mainly terpenoids parthenin and coronopilin (Picman 1986). Parthenin inhibited germination and seedling growth of Crotalaria mucronata, Cassia tora, Cassia obtusifolia and barley (Hordeum vulgare). In these instances inhibition of root growth was more prominent (Khosla and Sobti 1981). Parthenin was phytotoxic to Cyperus rotundus (Khosla et al. 1980). Parthenin also inhibited germination in Phaseolus radiata (Kohli et al. 1993). Its allelochemical potential erects a potential threat to the natural biodiversity (Ramakrishnan 1991). Not only this, Parthenium has been reported to inhibit its own seed germination, and the constituents parthenin and coronopilin to be toxic to its seedlings and adult plants (Picman 1986). Residue of the plant parts and constituent allelochemicals including phenolics and major

sesquiterpene lactone parthenin showed herbicidal property towards nine aquatic weeds (Pandey et al. 1993a, b, Pandey 1994a, b, Pandey 1996a, b). Parthenin and its pyrolysed and photo-derivatives exhibited growth regulatory effects greater than that of indole-3-acetic acid in tests based on the growth and morphogenetic response of hypocotyl cuttings of *Phaselous aureus (Vigna radiata)* (Batish et al. 1997). Parthenium leaf extract was phytotoxic and affected cytomorphological behaviour of sunflower (Helianthus annuus) (Kumar and Gautam 2008). The lower concentration of decomposed Parthenium leaves enhanced growth while higher doses suppressed both growth and morphology of sunflower (Helianthus annuus). Pollen mother cells showed abnormality with increasing concentration of the allelochemicals. Better understanding of the allelochemicals interaction was envisaged for the betterment of crops.

Constituent phenolics and major sesquiterpene lactone parthenin showed toxicity to seed germination, and seedling growth in terrestrial plants, as well as subsequent growth of both terrestrial (e.g., Kanchan and Jayachandra 1979a, Mersie and Singh 1987, 1988) and aquatic plants (Pandey et al. 1993a, b, Pandey 1994a, b, Pandey 1996b). Some of the constituent phenolic acids have been shown to be inhibitory at low and lethal at slightly higher concentrations (Pandey 1996b). Likewise, sesquiterpene lactone parthenin has been shown to be phytotoxic to aquatic weeds. Typical toxicity symptoms of these allelochemicals include root dysfunction together with sustained evapotranspiratory loss of water, reduction in water absorption and/or use, decline in dehydrogenase activity in the roots, loss of chlorophylls and carotenoids, and massive damage to cellular membranes of roots resulting in rapid loss of biomass due to desiccation following death and decay of the treated plants (Pandey et al. 1993a, b, Pandey 1994a, b, Pandey 1996a, b). It has been suggested that the toxicity involved changes in macromolecules proteins, nucleic acids and lipids which manifested in massive damage to cellular membranes and loss of enzyme (e.g., dehydrogenases) activity. Sesquiterpene lactones react with SH groups of cysteine, glutathione, and many proteins (Picman 1986), and also some are novel uncouplers of oxidative phosphorylation (Chefurka 1978).

Allelopathic inhibition

The allelochemicals of the *Parthenium* may pose agricultural hazards directly by inhibiting the crop or desired species or may manifest through affecting communication of roots with their environment and consequential biological, biochemical and biophysical interactions. *Parthenium* plant, plant parts and their residue extracts and the constituent allelochemicals have been shown to be inhibitory to plants. This includes inhibition of seed germination, and seedling and plant growth both in the laboratory and under field conditions in a variety of plant species including almost all major crop plants (e.g., Kanchan and Jayachandra 1979a, b, Mersie and Singh 1987, Tefera 2002, Regina *et al.* 2007). Recent report (Belz *et al.* 2009) exhibited low soil phytotoxicity of parthenin and showed that it did not accumulate over time. Along with the reduction in bioavailability and development of hormetic effects, results suggested that for parthenin to have detrimental allelopathic effects, it required its high densities that would result in high soil levels of parthenin and soil conditions that favored the persistence of parthenin for ecological significance.

The species produces large quantity of pollen. Deposition of Parthenium pollen on floral parts of other plants may inhibit pollen germination as well as growth of their pollen tube, affecting pollination, fruit set and the yields (Kanchan and Jayachandra 1980c). Pollen grains deposited on leaves of other species in large quantities also reduced the chlorophyll content of the test species. Studies implicate that parthenin may affect early growth of mung bean by impairing metabolic activities such as cellular respiration, protein content and enzyme activities. Such studies can help to further understand the mode of action of parthenin with a view to its possible utilization for future weed management programmes (Batish et al. 2001). Thus, Parthenium threatens agriculture by being a weed, a strongly allelopathic species and a species with pollen allelopathy. Information on role of specific constituents in allelopathic interaction of the species in natural ecosystems still appears to be scarce. Bioherbicidal potential of most of the allelochemical constituents has not been investigated. These are attractive areas with potential of facilitating development of newer and future herbicides or pesticides.

Possible addition into soil through the plant and plant parts residue and their constituent allelochemicals and exudation through roots and consequential impact on rhizosphere biology

The understanding of the biology, biochemistry, and genetic development of roots has considerably improved during the last decade (Smith and Fedoroff 1995, Flores *et al.* 1999, Benfey and Scheres 2000). The processes mediated by roots in the rhizosphere such as the secretion of root border cells and root exudates are not yet well understood (Hawes *et al.* 2000). The classical roles of roots are providing mechanical support and allowing water/nutrient uptake. The roots also perform certain specialized roles, including the ability to synthesize, accumulate, and secrete a diverse array of compounds

(Flores et al. 1999). Given the complexity and biodiversity of the underground world, roots are clearly not passive targets for soil organisms. The compounds including those implicated in allelopathy secreted by plant roots serve important roles as chemical attractants and repellants in the rhizosphere, the narrow zone of soil immediately surrounding the root system (Estabrook and Yoder 1998, Bais et al. 2001). The chemicals secreted into the soil by roots are broadly referred to as root exudates. Through the exudation of a wide variety of compounds, roots may regulate the soil microbial community in their immediate vicinity, cope with herbivores, encourage beneficial symbioses, change the chemical and physical properties of the soil, and inhibit the growth of competing plant species (Nardi et al. 2000). The ability to secrete a vast array of compounds into the rhizosphere is one of the most remarkable metabolic features of plant roots, with nearly 5% to 21% of all photosynthetically fixed carbon being transferred to the rhizosphere through root exudates (Marschner 1995). The allelochemicals may influence root-rhizosphere communication, root microbe communication, and root insect communication. The root exudates including allelochemicals may alter soil characteristics through biological, biochemical and biophysical interactions (Walker et al. 2003). Depending on the net result of the interactions, the allelochemicals may play decisive role in final crop yields.

Herbicidal potential of the allelochemicals

Investigations (Pandey et al. 1993a, b, Pandey 1994a, b, Pandey 1996a, b) have overwhelmingly shown herbicidal potential of the plant parts and constituent allelochemicals of the Parthenium on aquatic weeds. Allelochemicals of Parthenium, phenolics and terpenoids, the major terpenoid being sesquiterpene lactone parthenin, have herbicidal potential for aquatic weeds, especially to submerged aquatic weeds (Pandey 1995a, b). The parthenin was toxic at 50 ppm to the floating aquatic weeds pistia (Pistia stratiotes L.) and lemna (Lemna pausicostata Hegelm.) and at 100 ppm to water hyacinth (Eichhornia crassipes Mart Solmns.), salvinia (Salvinia molesta Mitchell), azolla (Azolla nilotica Decne.), and spirodella (Spirodella polyrhiza L. Schleid). The lethal dose for the submerged weeds najas (Najas graminea Del.), ceratophyllun (Ceratophyllum demersun L.), and hydrilla (Hydrilla verticillata L. f. Royle) was 25 ppm (Pandey 1996a). The submerged aquatic weeds were more sensitive to parthenin. Water hyacinth was used as a representative for studying the phytotoxicity of parthenin on aquatic weeds. Inhibition of water hyacinth by parthenin was associated with decline in water use, root dysfunction, excessive leakage of solutes from roots indicative of massive damage to cellular membranes, loss of dehydrogenase activity in the roots, and loss of chlorophyll in the leaves. Plant death occurred in a period of one to two weeks. Parthenin phytotoxicity is gradually lost in an aquatic environment as a lethal dose became non-lethal in about 30 days under outdoor conditions. Possible build-up of a toxin concentration may affect population dynamics and a shift in the aquatic weed flora in the immediate area of Parthenium stands. Accumulation of the toxin in an aquatic environment, however, at a level sufficient to produce such changes in a natural ecosystem as a consequence of rain washing Parthenium plants and leaching of toxin from their residue appears to be unlikely. Investigators have tried ecofriendly weed management through incorporation of parthenium under puddle conditions (Prabukumar and Uthayakumar 2006). Application of the botanical reduced weed incidence and showed potential weed management efficiency.

Various phenolics constituents of *Parthenium* may show herbicidal activity at various concentrations depending on species and other environmental conditions. The coumarins and phenolics compounds derived from cinnamic and benzoic acids interfere to some degree with many vital plant processes, including cell division, mineral uptake, stomatal function, water balance, respiration, photosynthesis, protein and chlorophyll synthesis, and phytohormone activity (Eihnellig 1995), and may exert oxidative stress (Pandey *et al.* 2005).

Parthenin has been shown to have herbicidal activity on two weedy species, *Avena fatua* and *Bidens pilosa* (Batish *et al.* 2002). It inhibited root and shoot length and seedling dry weight. Root growth was more affected than shoot growth. Similar observations were made when the test weeds were grown in soil amended with different concentrations of parthenin. In addition to growth, there was a reduction of chlorophyll content in the growing seedlings. It also caused water loss in the weedy species. The study, therefore, revealed that parthenin exerted an inhibitory effect on the growth and development of both the weeds. Similarly, parthenin has been reported to affect early growth and physiology of *Ageratum conyzoides* (Singh *et al.* 2002).

Among the other potential herbicidal allelochemicals is p-hydroxybenzoic acid (Pandey 1996b). However, herbicidal activity of most of the constituents on weeds of aquatic and terrestrial ecosystems needs to be investigated. Much remains to be known if there are constituents alone or in combinations as such or after chemical modifications able to prove lethal at 50 ppb to 5-10 ppm for direct us for the management of the aquatic weeds as substitutes for synthetic herbicides threatening environmental safety. The viable option would be identifying potential novel natural molecules and exploring them as such, in combinations and after chemical modifications for use as environment friendly herbicides.

Potential impact on the environment

The constituents including allelochemicals present in the plant may facilitate the aggressive exotic weed in establishing especially in newer ecological niches and to continue its spread over time and space in various ways. The contribution of the constituents including allelochemicals to this has not been ascertained and it is difficult to estimate their relative contribution in this process. The phenolics and terpenoid constituents might be conferring disease resistance, making the plant unpalatable and toxic to avoid grazing, feeding by insects and use by other species conferring it a competitive edge for success in establishment. The overall consequences of manifestations of the constituents including allelochemicals may culminate in upsetting of ecological equilibrium affecting the most native plant communities. In the absence of immune systems or effective enemies and other biological control mechanisms adapted to counteract the species, its population may explode. The resultant reduction in the resources available for the native species due to interferences (competition and/or allelopathy) may endanger or reduce the flora and fauna biodiversity. Native plants form the basic biological matrix of all communities, and the growth forms of plants are important components of community structure. The exotic invasive weeds like Parthenium may often completely alter structure when in monocultures thereby deteriorating the ecosystems and interfere with the benefits of the ecosystems to humans. The constituents of the weed including allelochemicals make the species one of the most troublesome and noxious weeds of urban and rural India, threatening the native vegetation and agriculture, causing human and animal health problems, and may cause fodder scarcity in addition to being unpalatable and toxic to livestock. Prolific growth, large amount of pollen and large number of seed production, and resultant pouncing of the plant parts and in fact, its constituents including allelochemicals into the environment may i. enrich soil seed bank with its seeds and perpetuate the weed problem including in agroecosystems both in rabi and kharif seasons, ii. reduce production including those of agricultural and horticultural crops by the weed incidence and by allelopathy, possibly by excessive circumstantial plant parts residues and their constituent allelochemicals accumulation, if it occurred, and by its pollen (pollen allelopathy caused by inhibition of germination of pollen of other species in their stigma due to presence and release of such inhibitory allelochemicals by Parthenium pollen), iii. may reduce quality and quantity of usable biomass production of native species in wastelands and pastures, iv. threaten natural biodiversity and cause extinction of native flora and affect communities and dynamics of natural vegetation and ecosystems, v. cause toxicity to grazing animals especially due to its constituent allelochemicals parthenin and other sesquiterpenoids toxic constituents, thereby reducing both quality and quantity of live stock and live stock products production, vi. cause contact allergies to sensitive animals and human rubbing across its plants and/or coming across its plant parts, and vii. reduce quality of air by pollution with its pollen and may cause various health problems including rhinitis in sensitive individuals. Thus, the weed, by way of its constituents, may deteriorate the environment and may have psychosocio-economic implications (Pandey 2001).

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