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Phytochemical Investigation of *Parthenium P. Hysterophoros- P.Glomeratum*

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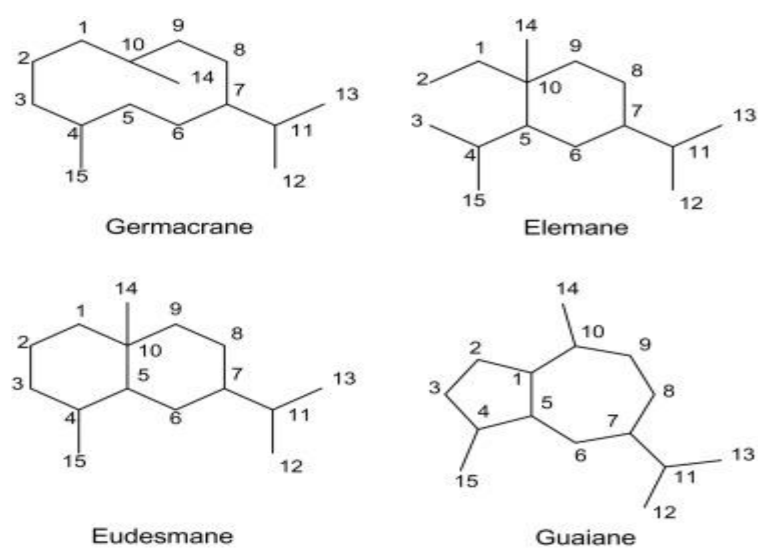
ABSTRACT: From aerial parts of five plants lots of *Parthenium hysterophorus—P. Glomeratum* collected along 72 km in Aligarh Iglas seven known and four new pseudoguaianolides have been found. P-Methoxybenzoic acid was also isolated from plants growing 178 m above sea level. The taxonomic situation of both species is discussed.

KEYWORDS: Parthenium P. Hysterophoros- P.Glomeratum, Aligarh, P-methoxybenzoic acid, sea level

I. INTRODUCTION

Two species of genus *Parthenium*, tribe Heliantheae (Asteraceae) have been described for Argentina: *Parthenium hysterophorus* L. and *P. glomeratum* Rollins 13 [1] *P. hysterophorus*, commonly known as 'altamisa' is a weed, probably originally from America, growing in central and northern Argentina, whereas *P. glomeratum* is found only in the north of the country and was described by Rollins as a new species [2]. The difference between both species is the relatively smaller plant size and the densely agglomerated capitulum (flowering head) of *P. glomeratum*.



Sesquiterpene Lactones

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According to Cabrera [l], *P. glomeratum* would be an extreme form of *P. hyslerophorus* 'one of them is probably only an alpine form' [1]. There is much information about chemical studies carried out on *P. hysterophorus* from different regions of the world [3, 4] and on a sample of *P. glomeratum* from Pampa Blanca, Argentina [3].

Parthenium

Preliminary investigations on the sesquiterpene lactone chemistry in populations of *P. hyslerophorus* from different Argentine geographical regions reported hymenin (1), coronopilin (3). dihydroisoparthenin and hysterin (8) [3, 4], while in samples from other American countries and from other continents, parthenin (2) and tetraneurin A (4) have been identified [4, 5]. *P. glomeratum* yielded hysterin R 1 º OH 2 fi OH R 3 H 4 OAc O g O O 7 O 11 (8) and damsin [3]. According to Rodriguez [3] the sesquiterpene lactone composition in *Parthenium* is characteristic of delimited zones or regions. The present paper deals with taxonomic and phytochemical studies of five populations (Lots I—V) (Table 1) of *P. hysterophorus* and 'or *P. glomeruturn* growing in different geographical regions of Uttar Pradesh India from Aligarh City at 178 m above sea level along 72 km.. Additionally, transplanted plants from 3400 to 1220 m were studied. In the morphological study we analysed the influence of the altitude above sea level over the variation of the plant attributes and the different habitat to which they belong and the individual aspects of one population transplanted to an opposite and contrasting habitat. The phytochemical studies were carried out on the aerial parts after the morphological evaluation

II. RESULTS AND DISCUSSION

The exhaustive morphological analysis of the collected taxa (Plant Lots I—V, see Experimental) led us to the following conclusions: the applied statistic techniques based on the morphology of the vegetative and reproductive organs do not solve the taxonomic problem between *P. hysterophorus* and *P. glomeratum* that could justify the synonymy or the difference between both species.[10] The morphological characters such as plant height, stems and leaves do not provide by themselves conclusive data to establish whether the taxa belong to *P. hvsterophorus* or to

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P. glomeratum. Transplanted plants from 3400 m, after l year adopted shape and size similar to those of *P. hysterophorus* growing at 1220 m. However, the colour and density of flowerheads were intermediate when comparing the transplanted specimen attributes with those of its congeners from the highest and lowest altitude. As is evident, the registered differences of the taxa are largely dependent upon the ecophysiological factors. Seven known sesquiterpene lactones were isolated from the studied plant lots together with the new ambrosanolides 5, 6 (as a mixture), 9 and 10.

Table 1: Parthenium weed control at rosette and bolted stages with different herbicidal application at 4 weeks after treatment

Serial number	Herbicides	% Mortality at rosette stage	% Mortality at bolted stage
1	Glyphosate	96	91
2	Metribuzin	87	75
3	2,4-D	71–80	43
4	Bromoxynil + MCPA	57–79	50–61.5
5	Atrazine	56.5	36.5
6	S-metolachor	57.5	41
7	Pendimethalin	42.5	30

Our chemical studies showed (Table l) that coronopilin (3) [6] was common to all the plant lots while hymenin (1) [7] was the major sesquiterpene lactone in Lot I where it was accompanied by its photolytic product confertdiolide (11) [8] and hysterin (8) [9]. Lot II also yielded tetraneurin A (4) [10] as the main constituent and a mixture of the new pseudoguaianolides 1z-hydroxy-4-oxo- 14-0-(2-methyl-butyroyl)-pseudoguaian6b,12-olide (5) and 1 s-hydroxy-4-oxo-14-0-isovaleroyl-pseudoguaian-6b,12-o1ide (6) whose structures will be discussed below. Parthenin (2) [l 1, 12], tetraneurin A (4) [10] and y-methoxybenzoic acid were identified in Lot III while Lot IV produced parthenin (2) [11, 12], chiapin B (7), previously found in P. [rutico.sum [13] and y-methoxybenzoic acid. This acid togcther with hysterin (8) [9] and the new ambrosanolids 4z-0-acetyl-pseudoguaian-6#-o1ide (9) and la-hydroxy-4#-0-acetyl-pseudoguaian-6#,12-olide (10) were isolated from Lot V. Finally, the transplanted members from 3400 to 1220 m yielded coronopilin (3) and parthenin (2) [11, 12]. Known compounds were identified by comparison of their spectral properties with those reported in the literature. Ambrosanolides 5 and 6 were obtained as a 4: 1

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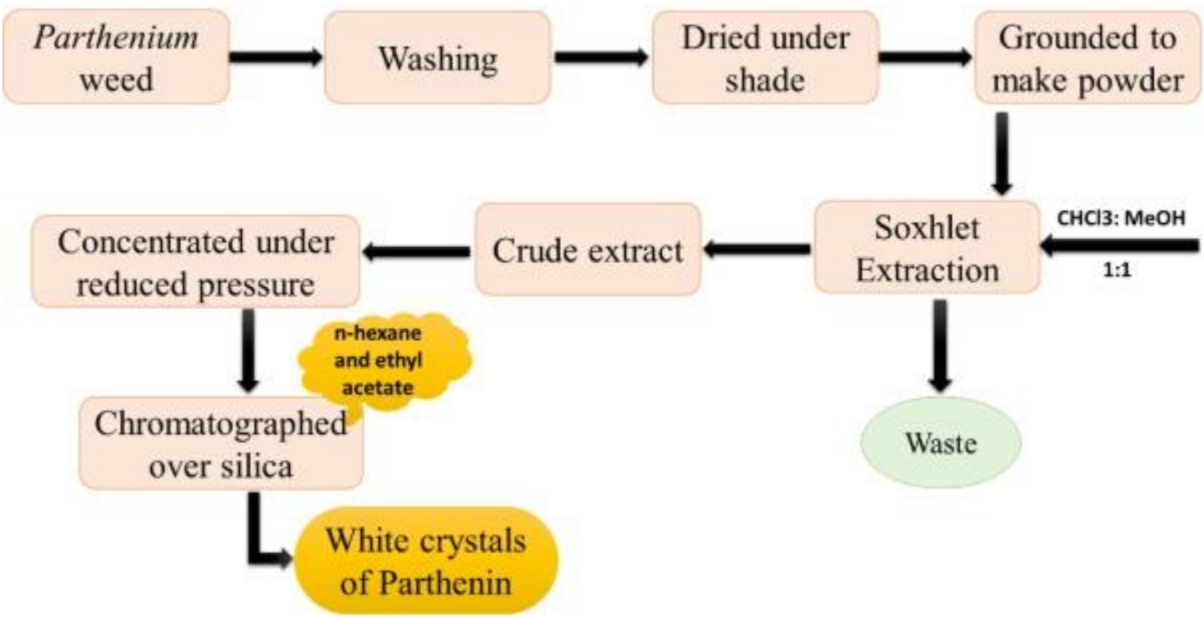
mixture (NMR criteria). El-mass spectrometry of the mixture gave the molecular ion at m/z 364 while the IR spectrum showed an absorption band at 3530 cm ', characteristic of a tertiary hydroxyl group, and a broad signal at 1739 cm ' assigned to the carbonyl groups of the '-lactone moiety and the ester function of the side chain. The 'H NMR spectrum was very close to that of tetraneurin A (4) [10], the only differences were the signals due to the acyl moieties at C-14. The '"C NM R spectrum (Table 3) was in total agreement with that of tetraneurin A (4).



The EI mass spectrum of ambrosanolide 9 gave the molecular ion at m/z 292 while the IR spectrum showed a broad absorption band at 1749 cm* ' assigned to the carbonyl groups of the conjugated '- lactone and the acetyl moiety. The 'H NMR spectrum (Table 2) was assigned by analogy with hysterin (8) [9] while the "C NMR spectrum (Table 3) confirmed the proposed structure. The positive ion FAB mass spectrum of ambrosanolide (10) showed the [M + l]* ion at m z 309 suggesting an extra oxygen with respect to 9. The 'H NMR spectrum (Table 2) was similar to those of hysterin (8) and ambrosanolide (9). However, there were noticeable deshielding effects on both the H-4 and H6 signals. This effect may be explained because of the opposite stereochemistry at C-4 of ambrosanolide (10) that would imply the absence of the anisotropic effect on H-6 caused by the #-orientation of the acetyl group as it has been demonstrated for tetaneurin E and related compounds [14]. The singlet at 6 85.9 in the "C NM R (Table 3) confirmed the presence of the tertiary hydroxyl group at C-1

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Summary Table 2 of *P. hysterosporous*

Introduced to	Introduced from	Year	Reasons	Introduced by	Established in wild through	
					Natural reproduction	Continuous restocking
Australia		1950s			Yes	No
Ethiopia		1960s			No	No
India	USA	1950s			Yes	No
Kenya		1970s			Yes	No
Queensland		1958	Seed trade (pathway cause)		Yes	No
South Africa		1880			Yes	No
Pakistan		1980s	Hitchhiker (pathway cause)		Yes	No
Nepal		1967	Hitchhiker (pathway cause)		Yes	No
Sri Lanka		1999			Yes	No

Full proof of the skeleton of ambrosanolide (10) was achieved by a combination of homonuclear H-H COSY. NOESY and 'H-"C HETCOR experiments. The NOESY spectrum of abrosanolide (10) (Table 4) showed a nOe between H-4 and H-6 indicating that the acetyl moiety is in a #-orientation. Other features in this spectrum showed the spatial vicinity of H- 14/'H2b. H- l5,'H-2b, H-15,'H-3b. H-15,/H-8§ and HI 3 /'H-8«. [7,8]Finally, the HETCOR experiment allowed the unambiguous assignments reported in Tables 2 and 3. Our chemical results are in good agreement with the proposal of Rodriguez that 'the distribution of secondary products in Parthenium is probably a result of adaptive responses to various physical and biotic factors in the environment' [3]. On the other hand, evaluation of both the taxonomic and photochemical studies suggests that *P. glomeratum*, described as an autonomous and independent species could be an alpine form of *P. hysterophorus* as suggested by Cabrera [I}

Experimental

General. Mps are uncorr. CC were performed on silica gel 60 (7W230 mesh); TLC was carried out on precoated Silica ge1 60 F,,, plates (Merck). Detection was achieved by viewing under UV light and spraying with H SO, soln as reagent followed by heating. Plant material. The plant lots were collected in December 1990 and identified by AK Singh. Voucher specimens are deposited at the Department of Chemistry RBS College Agra. The plant material was collected along the side road Aligarh to iglas road(Uttar Pradesh) as follows: Lot I, City at 178 m (Iglas A); Lot II, at 162 m (Iglas 2); Lot III, at 167m (Iglas 3); Lot IV, from Iglas 4 &(Iglas 5); Lot V, from 330to 340 m Aligar Iglas (UP).One of these specimens was transplanted and cultivated at 122 m (Aligarh to Raya)[9]

General extraction procedure:- Air dried aboveground parts were exhaustively extracted with CHCI . The residue obtained after evapn of the solvent was dissolved in hot EtOH and a soln of 4% Pb(AcO), was added. After standing

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overnight the ppt. was filtered and the organic solvent evapd and the aq. soln extracted with CH3CI . The organic layer was dried over N a2SO4, and the solvent evaporated under red. press to yield a gummy residue

Table 3: Plant trade

Plant parts liable to carry the pest in trade/transport	Pest stages	Visibility of pest or symptoms
Growing medium accompanying plants	weeds/seeds	Pest or symptoms not visible to the naked eye but usually visible under light microscope
Stems (above ground)/Shoots/Trunks/Branches	weeds/seeds	Pest or symptoms usually visible to the naked eye
True seeds (inc. grain)	weeds/seeds	Pest or symptoms usually visible to the naked eye

Isolation and Purification- The residues obtained as described above were fractionated by CC, eluted with benzene and the polarity increased with EtOAc and Me,CO. Further purification of the fractions were achieved by dry column chromatography and,'or on Sephadex LH-20. Light infestations of *Parthenium hysterophorus* in cultivated fields may be hoed or weeded by hand if labour is available at acceptable cost[12,13].Generally the application of herbicides is expensive and often harmful; Paraquat sprays may be applied while the weeds are young. Glyphosate is not effective against this species.The most satisfactory and promising means of practical long-term control are biological. Several species that feed on the weed are variously in use or on trial in various countries. The best-established control organism so far is a beetle native to Mexico, *Zygogramma bicolorata* (Mexican Beetle), which was first introduced to India in 1984. It since has become widespread and well-established on the subcontinent. It defoliates and often kills the weed, and its damage to the young flowering tops reduces seed production.In various countries, such as Australia and South Africa, several other biocontrol agents have been released or are under evaluation. These include at least two more species of beetles that have been released in South Africa, a stem boring weevil *Listronotus setosipennis*, and a seed weevil Smicronyx lutulentus.[24]Also in South Africa, rust fungi have been of some use: the winter rust *Puccinia abrupta* var. *partheniicola* plus the summer rust *Puccinia xanthii*. In Australia, apart from the foregoing, yet other biocontrol agents have been employed or evaluated on *Parthenium hysterophorus*, to a total of 11 species since 1980. Of those eleven, nine appear to have established in various regions. The two with the greatest effect seem to be the *Parthenium* beetle *Zygogramma bicolorata* and a stem-galling moth *Epiblema strenuana*. However, other species that appear to have established usefully include a leaf-mining moth, Bucculatrix parthenica; a stem-galling weevil, *Conotrachelus albocinereus*; and a root-boring moth *Carmenta ithacae*.[10,11]

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Table-4: *Parthenium* infestation levels

Parthenium weed infestation levels	Grasses	Non-grasses	Parthenium weed
No	25.75 (663.0)	12.13 (146.6)	1.46 (1.6)
Very low	10.99 (120.4)	13.16 (172.6)	2.91 (8.0)
Low	10.65 (113.0)	17.17 (294.3)	15.67 (245.1)
Moderate	9.43 (88.5)	16.50 (272.3)	30.17 (910.0)
High	10.77 (115.5)	13.48 (181.2)	39.78 (1582.0)
$LSD_{5\%}$	6.57	NS	6.65

[1]Values in bracket are original density while those out of the bracket are square root transformed; NS = non-significant

Parthenium hysterophorus invades disturbed land, including roadsides. It infests pastures and farmland, causing often disastrous loss of yield, as reflected in common names such as famine weed. In some areas, heavy outbreaks have been ubiquitous, affecting livestock and crop production, and human health.[14][15]The plant produces allelopathic chemicals that suppress crop and pasture plants, and allergens that affect humans and livestock. It also frequently causes pollen allergies.A study published further showed that the plant could promote malaria by supplying much appreciated food and shelter to mosquitoes in Eastern Africa.It is being investigated as a means of removing heavy metals and dyes from the environment, control of aquatic weeds, commercial enzyme production, an additive in manure for biogas production, as a biopesticide, and as green manure and compost.The species has been listed as an invasive alien species of Union Concern. This means it is illegal to import or sell this species in the whole of the European Union. Contact with the plant causes dermatitis and respiratory malfunction in humans, and dermatitis in cattle and domestic animals. The main substance responsible is parthenin, which is dangerously toxic. It also is responsible for bitter milk disease in livestock when their fodder is polluted with *Parthenium* leaves.Among other allelopathic effects of the species, the presence of *Parthenium* pollen grains inhibits fruit set in tomato, brinjal, beans, and a number of other crop plants.[16]

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