International Journal of Global Innovations and Modern Research
Abbreviated Key Title: IJGIMR
ISSN (Online): 3108-1789
Published By Books Arcade, Delhi, India.

OPEN ACCESS

Volume-1 | Issue-1 | January - June 2026 | DOI: https://doi.org/10.66304/IJGIMR.2026.v1i1.20

ORIGINAL ARTICLE

Juvenile Hormone-Like Substances: Part XXXIII Search for Greener Pesticides: Eco-Friendly Approach Towards Pests' Management

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ABSTRACT

The incessant increase of inhabitants around the world necessitates sustainable resources of food. Agriculture is the main torrential strength for broad-based economic growth in developing nations where nutrition obligation is particularly life-threatening because of the sluggish rate of net food production. Pesticides have a decisive part to play in our survival for fruitage defense and in evading the dispersal of destructive parasites instigating human ailments like malaria etc. Because of commercial, health and particularly, ecological motives, the designing of more specific and operative compounds that could regulate such parasites, is equally a significant mission in agricultural, environmental sciences besides in the cooperative world. Practice of exceedingly noxious traditional pesticides for numerous ages repeatedly has led to severe adverse results, in the atmosphere like assassination of inoffensive class; both florae and faunae, thereby generating disparity in biodiversity which ultimately leads to adverse effects in the ecology. Synthesis, approach of action and ecological profile of juvenile hormone analogues (JHA) having different functional groups, hetero atoms and varied length of the side chain, as green substitutes aimed at synthesis of insect repellent/ pesticides have been studied.

Keywords: Juvenile Hormone Analogues, DDT, Potential Pesticides, Chemosterilization, Sulphonamide.

Funding: This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

INTRODUCTION

Initially, the first skilled insecticides were brought into notice and use in the mid of the twentieth century. Previously, the pests were mostly regulated/ managed by inorganic compounds like S, arsenicals, HCN or cryolite, some of which are still being used notwithstanding of their high destructiveness nature to living organisms. After that organochlorine, organophosphorus and carbamate insecticides were familiarized which revealed promising[1] change in agrochemical science as these seductively fetched down the crop decline due to insect and pests bustle.

The introduction of DDT as organochlorine insecticide with diverse range of insecticidal accomplishment and with a practical widespread outstanding activity[2] carried a worth augmentation in the agriculture production. With the time span of years, chlorine derivatives of above insecticides were revealed to reason unadorned antagonistic ecological reparations, both in earthly and marine ecosystem[3]. Their long perseverance formed an accrual of organo-chlorine pesticides in flora and fauna via the nutrition cable thereby majority of them were barred in many countries[3], though DDT is steadily in practice in some of the nations wherever malaria is an endemic[4]. Latest literature survey revealed that long-lasting contact with DDT stays allied with nervous impairments[5], enhanced ageing[6] and chest cancer[7]. Organophosphorus insecticides established to be the steady and active insect regulator agents. They distress the nervous system by phosphorylation of acetyl cholinesterase, prompting breathing muscle weakness and neuromuscular dysfunction[8]. Carbamates are still in usage and are selective against embattled species[9].These are noxious against some useful species like Apis mellifera. Carbamates have short perseverance in the earth, floras and the environment[3].

Above all these antagonistic ecological features, even at the present time, some inhabitants of pests remained unaffected by organic chlorine, organic phosphorus and some of the carbamate congaing insecticides[10]. For example, 98 species of insects as well as Anopheles vector causing malaria, Pediculus humans, the human body louse, infectious agent of epidemic plague and some more parasitic insects, eighteen classes of Culex flies and some more species have been reported to developed resistant to one of the earliest-born and uppermost effective natural occurring and man-made compound 2, 2-bis-(p-chlorophenyl)-1, 1, 1-trichloroethane, DDT[11]. Additional, 27 type of agricultural pests and more such damaging species as the pink boll worm, P. gossypiella of family Gelechiidae, cabbage looper and some corn earworms have also recognized DDT[12] resistance. In the mandate towards finding solution to this problem, it might be stimulating procedures to have novel pesticides through a different mechanism.

Also, the practice of 2, 4-D, *i.e.*, (2, 4-dichloro phenoxy acetic acid), a volatile herbicide, by corn cultivators is considered to decrease the production of grapes in the connecting zone to a range of around 95%. Accordingly, the chief target of insecticide study remains the extension of innovative, careful besides extremely operative compounds which root no ill-treatment toward living well-being and the environment[13].

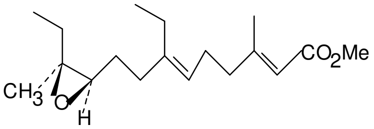
JUVENILE HORMONES AND JUVENILE HORMONE ANALOGUES – AS POTENTIAL GREENER PESTICIDES

Juvenile hormones have been designated as *Potential insecticides*[14]and *Third generation pesticides*[15] since they prevent the metamorphosis and preserve the larval stage in insects. JH and JHA will regulate the insect problem by developmental ailments like feminine sterility, ovicidal belongings, adult emergence disappointments, defects in mating and purpose of some structures to final incapability of pairing and impregnation. The JH causes progressive ailments in insects after their interface with the treated plants[16]. Also, JH will not regulate the insect problem by lethal action but by physiological action and their ruin products are not detrimental to warm blooded creatures, the ecological contamination will be insignificant in their practice. The learning of insect hormones has implicit a countless repute since the prospect of their use as pesticides and insecticides. Insect Juvenile Hormones is a type of organic substances that regulate the post-embryonic growth of pests since egg to their mature phase. They stand concealed by endocrine glands, the Corpora allata. These JH have been categorized by certain size and shape of the molecule, occurrence of certain précised functional groups and substituents in the molecule. All compounds whether naturally occurring or synthetic, which can distress or regulate the progress and developmental progressions in insects or which may be able to reveal the physiological features of Juvenile Hormones (JH), may be termed as Juvenile Hormone Analogue (JHA) or JH Mimics or generally Juvenoids.

The existence of JH was first pronounced[17] by Sir Vincent Wigglesworth in 1934, yet, however in 1956, William[14]prepared lipid compound from the abdomen of the mature masculine Cecropia moth that revealed a high JH activity. Generally, the juvenoids may be classified into two classes:

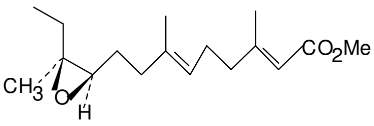
1. Acyclic
2. Cyclic

The most important acyclic JH inaccessible from natural sources[18] are JH-1 (Cecropia C_{18}-JH); (1.1), JH-II (Cecropia C_{17}-JH); (1.2); and JH-III (Manduca C_{16-}-JH); (1.3).



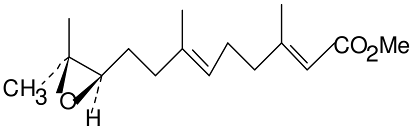
JH-I

(1.1)



JH-II

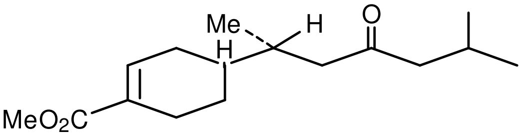
(1.2)



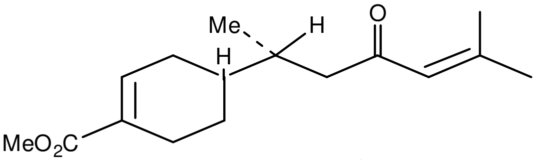
JH-III

(1.3)

The hefty numeral of synthetic acyclic juvenoids have been described in the literature in current history which have revealed substantial JH activity[19].The cyclic juvenoids are those in which acyclic or aromatic ring is connected with side chain. Juvabione (1.4) and dehydrojuvabione (1.5) were probably the first cyclic juvenoids inaccessible from balsamea fir, Abies balsam[20]and from Slovak fir[21]. Together these revealed a high specific JH activity against hemipterans of the family *Pyrrocoridae*.

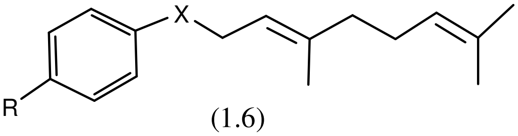


(1.4)



(1.5)

A lot of effort has also been mentioned in compounds of the kind (1.6) in which terpene moiety connected to aromatic ring through hetero atoms like O, N and/or S[22-23].



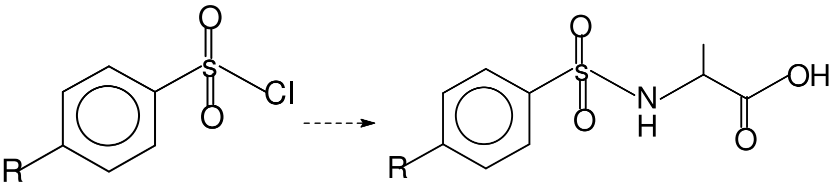
(1.6)

X= O, N, S

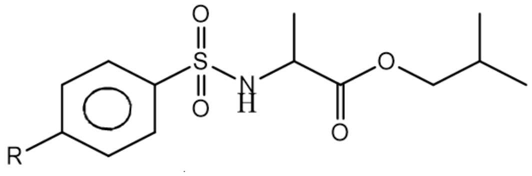
Chemosterilization of insects appears to be one of the capable approaches of insect management. Sulphonamide feature has been pronounced to be accountable for chemosterilizing activity of some compounds[24-25]. Some of phosphorus amides have also been testified to exhibit insect chemo sterilant activity[26]. Huge number of amended JHA prepared by us in our research laboratory having hetero atoms introduced such as ether function, amide group, hydroxamate, carbamate group or peptide feature unveiled favorable Juvenile Hormone/ chemosterilizing activity[27-28]. Some of Juvenile Hormone Mimics designed in our research laboratory encompassing sulphonamide feature, hetero atom N, O or S and certain other hetero cyclic rings have revealed promising Juvenile Hormone activity/ chemosterilizing activity against potato tuber moth[29-33] Phthorimaea operculella. and they have not revealed any quantifiable ecological effluence.

Hereunder, we account for the synthetic study of a few Juvenile Hormone-like substances encompassing sulphonamide moiety, aromatic benzene ring and certain other atoms like O / N Scheme-1. The compound p-Chloro-N-(1, 5-dimethyl-2-oxa-3-oxo-hexanyl) benzenesulphonamide,1.9b exhibited high JH/ chemosterilizing activity against potato tuber moth, Phthorimaea operculella.

Scheme-1



1.7 1.8



1.9

Reagents: i: $NH_2CH(CH_3)$ CO COOH; ii: $CH_3CH(CH_3)$ CH_2OH
Series: a: R=CH_3, b: R=Cl

TECHNICAL EXPERIMENTAL PROCEDURE

Below mentioned melting and boiling points are recorded in H_2SO_4 bath and uncorrected. The infra-red spectrum is taken in KBr pellets or nujol mull on Hitachi 270/50 Spectrophotometer (ν_{max} in cm^{-1}), PMR spectrum in deuterated chloroform or carbon tetra chloride or trichloro acetic acid diluted with carbon tetra chloride on Brucker AC 300 F NMR at 60 MHz (chemical shifts expressed in δ, ppm) by taking tetramethyl silane as core internal standard and Mass spectrum on Varian Mat CH-7 Mass Spectrophotometer (values expressed in m/z).

Specimen under investigation, Potato tuber moths, Phthorimaea operculella (male and female) stayed conserved on renewed potato plants especially leaves in petri dishes with protections and bottles with thin cotton cloth (muslin) protections in testing center beneath normal environmental circumstances of NTP (ambient temperature 15-20^0). They stayed reserved under continuous visual for the egg laying.

Then eggs were taken and four different groups (I, II, III & IV) comprising sixty regulator and the eggs applied with compound at desired concentration were equipped. Likewise, larvae and pupae are found and conserved for application with compound. The compound under investigation was liquified in 50% acetone to achieve concentrations of the liquids having 10, 25 and 50 μg/mL correspondingly. Consequently, in every case the groups were skilled as specified below:

Stage	Normal controls untreated	10 μg/ mL	25 μg/ mL	50 μg/ mL
	I	II	III	IV
Eggs	60	60	60	60
Larvae	30	30	30	30
Pupa male	30	30	30	30
Pupa female	30	30	30	30

Acetone solution (1mL) comprising the compound under investigation was dispensed on the filter paper in separate petri dish and allowed to disappear. Afterwards, the calculated quantity of eggs/larvae/pupae who were applied the concentration of the compound, transported in the disinfect freshly prepared petri dishes.

Synthesis of p-Chloro-N-(1, 5-dimethyl-2-oxa-3-oxo-hexanyl) benzenesulphonamide and related Juvenile Hormone Analogues (JHA):

Toluene-p-sulphonyl alanine 1.8a: Alanine (8.9 g, 0.1mol), toluene-p-sulphonyl chloride (19.05 g, 0.1 mol and NaOH solution (1N, 200 mL) were mixed together and stirred at 65-70^0 for about 2 hours. A transparent liquid solution was achieved. The blend was chilled to 5-10^0 and conc. HCl was added just to make it a bit acidic (pH 6.5) thereby toluene-p-sulphonyl alanine, 1.8a detached out as white shining crystals. It was recrystallized from warm H_2O to afford clean toluene-p-sulphonylalanine 1.8a (15.34 g, 72 %), m.p.127-129^0.

^{1}**H NMR: δ** 7.75 (2H, Ar-H, *ortho* to –SO_2NH-); 7.36 (2H, Ar-H, *meta* to –SO_2NH-); 4.03 (m,1H, -NH-CH-(CH_3)-); 2.36 (s, 3H, Ar-CH$_{3)}$;1.13 (d, 3H, -CH(CH$_{3-}$).

Analysis observed: C, 49.40; H, 5.30; N, 5.70, $C_{13}NO_4S$ requires: C, 49.38; H, 5.34; N, 5.76%.

p-Chlorobenzenesulphonyl alanine 1.8b: The reaction of alanine (8.9 g, 0.1 mol) with p-chlorobenzenesulphonyl chloride (21.1 g, 0.1 mol) as above furnished p-chlorobenzenesulphonyl alanine 1.8b (18.5 g, 70 %), m.p. 160-162^0**.**

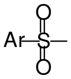
^{1}H NMR: δ 7.82 (2H, Ar-H, *ortho* to $–SO_2NH-$); 7.65 (2H, Ar-H, *meta* to-SO_2NH-); 4.07 (m, 1H, -NH-CH-(CH_3)); 1.15 (d, 3H, -CH (CH_{3-}).

Analysis observed: C, 40.90; H, 3.73; N, 5.30, $C_9H_{10}NO_4SCl$ requires: C, 40.98; H, 3.79; N, 5.32%.

N-(1, 5-Dimethyl-2-oxa-3-oxo-hexanyl) toluene-p-sulphonamide1.4a: To the freshly acid chloride of benzenesulphonyl alanine made from benzenesulphonyl alanine (2.33 g, 0.01 mol) was poured an extra quantity of 2-methylpropanol (5 g). The combined blend after constantly rousing at normal temperature for fifteen minutes was gently heated up to 35-40^0 and stirred at this steady temperature for about 3 hours. A transparent mixture solution was found. The surplus 2-methylpropanol was removed to afford a slick compound which solidify on standup. It was recrystallized from petroleum ether (60-80^{0}C) to give N-(1, 5-dimethyl-2-oxa-3-oxo-hexanyl) benzenesulphonamide (1.5 a 2.08 g, 71%), b. p. 213-217^0/ 40 mm, Rf 0.62 (system a).

Analysis observed: C, 56.12; H, 6.92; N, 4.57%, $C_{14}H_{21}NO_4S$ requires: C, 56.19; H, 7.02; N, 4.68%.

^{1}H NMR: δ 7.75 (2H, Ar-H, *ortho* to -SO_2NH-); 7.36 (2H, Ar-H, *meta* to -SO_2NH-); 5.87 (broad, 1H, Ar-SO_2-NH-CH-(CH_3); 4.15 (m,1H, -NH-CH-(CH_3); 3.72 (d, 2H, -O-CH_2 –CH-); 2.36 (s, 3H, Ar-CH_3); 1.51-1.94 (m, 1H, -CH_2 –CH-(CH_3)$_2$); 1.20 (d, 3H, -CH(CH_{3-}); 0.90 (d, 6H, -CH-(CH_3)$_2$.

IR: ν_{max} cm^{-1} 3280 (broad due to >N—H); 1760 -C=O; 1370 and 1165 due to  $Ar-\overset{O}{\underset{O}{S}}-$ group).

Mass: m/z $[M]^{\cdot +}$299; 198; 155; 101; 91(*base peak*); 77; 73; 57; 43.

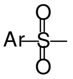
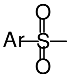
p-Chloro-N-(1, 5-dimethyl-2-oxa-3-oxo-hexanyl) benzenesulphonamide 1.5b:

The reaction of acid chloride of p-chlorobenzenesulphonyl alanine freshly prepared from p-chlorobenzenesulphonyl alanine (2.82g, 0.01 mol) with an excess of 2-methylpropanol (5 g) as above furnished p-chloro-N-(1, 5-dimethyl-2-oxa-3-oxo-hexanyl) benzenesulphonamide 1.9b, (1.98 g; 62%), b. p. 222-226^0/ 40 mm, Rf 0.58 (system a).

Anal. Found: C, 48.79; H, 5.60; 4.32%, $C_{13}H_{28}NO_4SCl$ requires: C, 48.82; H, 5.63; N, 4.38%.

The characterization data of the compounds 1.9a & 1.9b synthesized above is given in Table 1.

Table 1- Characterization data of the compounds 1.9a &1.9b

Comp-ound No.	$^@$B.p. ^{0}C	Rf *'a'	^{1}H NMR (δ values)	IR (ν_{max} cm^{-1})	Mass (m/z)
1.9a	210-213/ 40mm	0.76	7.75 (2H, Ar-H, *ortho* to $–SO_2NH-$); 7.36 (2H, Ar-H, *meta* to $–SO_2NH-$); 5.87 (broad, 1H, Ar-SO_2-NH-); 4.15 (m,1H, -NH-CH-(CH_3); 3.72 (d, 2H, -O-CH_2 –CH-); 2.36 (s, 3H, Ar-CH_3); 1.5-1.94 (m, 1H, -CH_2 –CH-(CH_3)$_2$; 1.20 (d, 3H, -CH(CH_3)-CO-); 0.90 (d, 6H, -CH-(CH_3)$_2$.	3280 (broad due to >N—H); 1760 –C=O; 1370 and 1165 due to  $Ar-\overset{O}{\underset{O}{S}}-$ group).	$[M]^{\cdot +}$299; 198; 155; 101; 91(*base peak*); 77; 73; 57; 43.
1.9b	217-220/ 40mm	0.68`	7.82 (2H, Ar-H, *ortho* to $–SO_2NH-$); 7.65 (2H, Ar-H, *meta* to $–SO_2NH-$); 5.88 (broad, 1H, Ar-SO_2-NH-); 4.17 (m,1H, -NH-CH-(CH_3); 3.73 (d, 2H, -O-CH_2 –CH-); 1.5-1.94 (m, 1H, -CH_2 –CH-(CH_3)$_2$S; 1.20 (d, 3H, -CH(CH_3)-CO-); 0.90 (d, 6H, -CH-(CH_3)$_2$.	3280 (broad due to >N—H); 1760 –C=O; 1370 and 1165 due to  $Ar-\overset{O}{\underset{O}{S}}-$ group).	$^{\#}[M]^{\cdot +}$319; 233;189; 180; 126(*base peak*); 101; 73; 57.

*Solvent system for TLC: **a** Benzene: Ethyl acetate 9:1; **b** Ether: Pet ether: Ethyl acetate 5:5:2.

In the mass spectrum of the compounds **1.9b** containing chlorine atom, additional $[M^+ +2]$ peaks at m/z 321, 235, 191, 182 and at 128were also observed due to the presence of ^{37}Cl isotope.

$^@$The temperature is recorded in degree Celsius, i.e., ^{0}C

BIOLOGICAL EVALUATION

Preliminary investigation for biological testing of compound p-chloro-N-(1, 5-dimethyl-2-oxa-3-oxo-hexanyl) benzenesulphonamide (1.9b) for Juvenile Hormone /chemo sterilizing activity revealed an optimistic Juvenile Hormone /chemo sterilizing activity. Eggs tested/treated with at a quantum frequency dose of 25 µg/ mL and 50 µg/ mL provided adults having below established normal ovarioles having had an irregular extension of wings which were usually petite besides frizzy. Historical appearance indicated that compound under investigation (1.9b) possesses a discrete chemo sterilizing impact in the ovaries of Phthorimaea operculella at a quantity amount of 25 µg/ mL and 50 µg/ mL. The impairment to the ovaries seemed to be so critical that not a solitary regular oocyte possibly be observed even in some of the segments. Though, at a smaller quantity of dose rate of 10 µg/mL, the compound under investigation (1.9b) was virtually sedentary. Since, there was no mortality and nearly 100% eggs sustained viable, the compound does not appear to have any insecticidal action.

ADVANTAGES

The foremost advantage of juvenoids over insecticides depends on its very little or virtually zero harmfulness. JH and their degradation products are not injurious to warm-blooded faunae; the ecological contamination will be insignificant in their use. Moreover, juvenoids performance is selectively on certain classes of insect pests which may permit to apply careful regulator with least trouble of normal zoocenosis, including standard growth of the pest’s expected opponent such as parasites and predators. Additional benefit is the extremely high biological activity of certain juvenoids which make it conceivable to practice significantly lesser quantities of the active compounds and to diminish the probabilities of environmental contamination.

CONCLUSION

The grouping of present-day synthetic strategies and biotic and physiological experimental procedures have led to the synthesis of pesticides/ insecticides having an improved eco-friendly outline through diverse mechanism of accomplishment besides having abridged hazard to alive beings. In the prevailing situation, substances like insect growth regulators or Juvenile Hormone Analogues (JHA) showing an extraordinary activity may have a promising future ahead in their application.

ACKNOWLEDGEMENT

Author (**VPP**) thanks UGC New Delhi for PDF and Research Project.

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