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Isolation, identification, synthesis, and bioefficacy of female *Diacrisia obliqua* (Arctiidae) sex pheromone blend. An Indian agricultural pest*

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Abstract: *Diacrisia obliqua* is a polyphagous pest especially on oil seed crops. Adult female sex pheromone blend consists of five pheromone components, which include (3Z,6Z)-*cis*-9,10-epoxyl,3,6-henicosatriene and (3Z,6Z)-*cis*-9,10-epoxy3,6-henicosadiene. Synthesis of these enantiomers was achieved through alkylative epoxide rearrangement and stereoselective Wittig olefination reactions as key steps. Bioefficacy experiments both at laboratory and minifield were very positive.

INTRODUCTION

The emerging alternative agriculture and worldwide shift toward integrated pest management (IPM) are bringing semiochemicals or behavior-modifying chemicals (BMC) [l], in particular, sex pheromones, to the forefront of pest control. Semiochemicals are those compounds released or emitted by plants and animals for specific communication purpose; if the communication is between the same species, it is called a pheromone and if it is between different species, it is called a kairamone. Pheromones are being looked to with great expectation as being ecologically friendly, chemically safe, and efficient tools of insect pest control.

In general, sex pheromones are volatile chemical scents secreted by female insects containing aspecific blend of different chemical substances, to attract their male counterparts for mating. The methods using pheromones for pest control, therefore, depend on utilizing the normal behavioral response of an insect to a synthetic pheromone source/blend and destroying it subsequently. As sex pheromones elicit behavioral responses from their conspecific counterparts at very low doses, low application rates can be used to influence the natural communication between insects in all pheromone-mediated control techniques. Sex pheromones can be utilized as [2] monitoring, mass trapping, and mating disruption agents.

Diacrisia obliqua (Bihar hairy caterpillar) is a polyphagous pest. It has been recorded feeding on as many as 33 host plants including oil seed crops. Among oil seed crops, the important ones are groundnut, sesamum, linseed, safflower, castor, sunflower, cotton, maize, jower, etc. This pest has been recorded in India as well as in other Asian countries such as Bornea, China, and Japan. The pest makes its first appearance from its winter hibernation in March. Their caterpillars feed gregariously and voraciously on a variety of food plants. Having destroyed one field, they move in swarms to another field. There are 6 generations of this pest in a year. As the pest passes the first generation mostly on weeds, it should be destroyed in the weed itself before the pest multiplies and migrates to the cultivated crops. Application of pheromone system will help in forecasting its attack and intensity.

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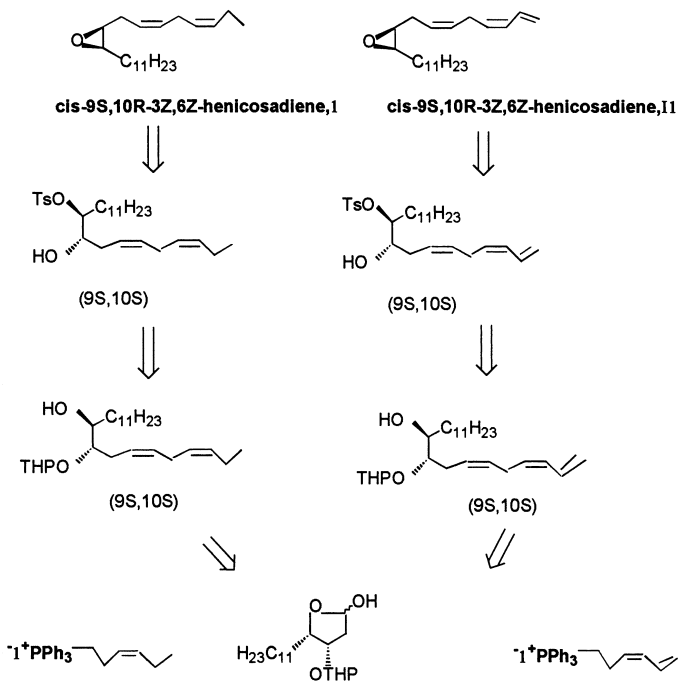
ISOLATION AND IDENTIFICATION OF FEMALE *DIACRISIA OBLIQUA* SEX PHEROMONE BLEND [3]

Female glands extracts were prepared in hexane by dissecting pheromone glands of 1–2-day-old virgin females. As *D. obliqua* belongs to the Arctiidae family, the isolation and identification work for the sex pheromone components was concentrated on the presence of a multicomponent mixture containing C-20 or C-21 diene or triene epoxides [4] (Descoins *et al*., 1988, 91). Using nonpolar (5% CP Sil-5) and polar (5% CP Wax-51) columns on gas chromatography (GC) separation techniques. The bioactive fractions respectively are identified through electroantennograph (EAG) screening. The high-pressure liquid chromatography (HPLC), column 25 cm, i.d. 0.44 mm, Altech Rsil; Uv detection 4 nm was also extensively used in isolating the bioactive fraction through the operation of EAG system. The GC-MS analysis (VG 70/250S instruments fused silica capillary column 50 m × 0.12 mm i.d.; CP Wax-57 CB) was carried out for the bioactive fractions collected both from GC fractionation and HPLC separation and identified the following five components of the female sex pheromone blend:

(Z3,Z6)-*cis*-9,10-epoxy-3,6-heneicosadiene	(Compound I)
(Z3,Z6)-*cis*-9,10-epoxy-1,3,6-heneicosatriene	(Compound II)
(Z9,Z12)-9,12-octadecadienal	(Compound III)
(Z9,Z12,ZI5)-9,12,15-octadecatrienal	(Compound IV)
(Z3,Z6,Z9)-3,6,9-heneicosatriene	(Compound V)

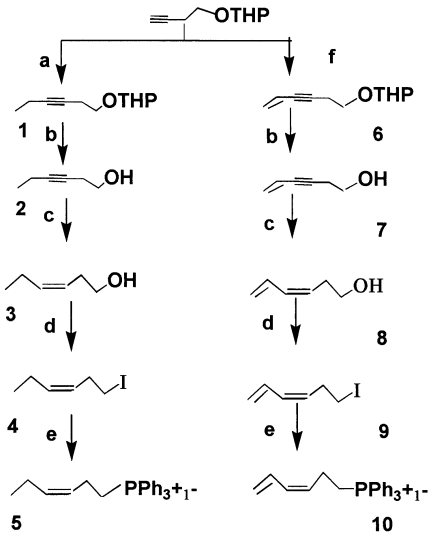
SYNTHESIS OF PHEROMONE COMPONENTS

In the blend, the pheromone components I, II, III, IV, and V are in the ratio 1.0:0.5:1.0:3:0:2.6, respectively. In order to evaluate the active isomers and confirm their configuration, especially compounds I and II, the synthesis of the enantiomers belonging to both the compounds I and II has been taken up [4]. Following the retrosynthetic analysis [5] shown in Scheme 1, the new synthetic routes for both these compounds and their enantiomers are developed.



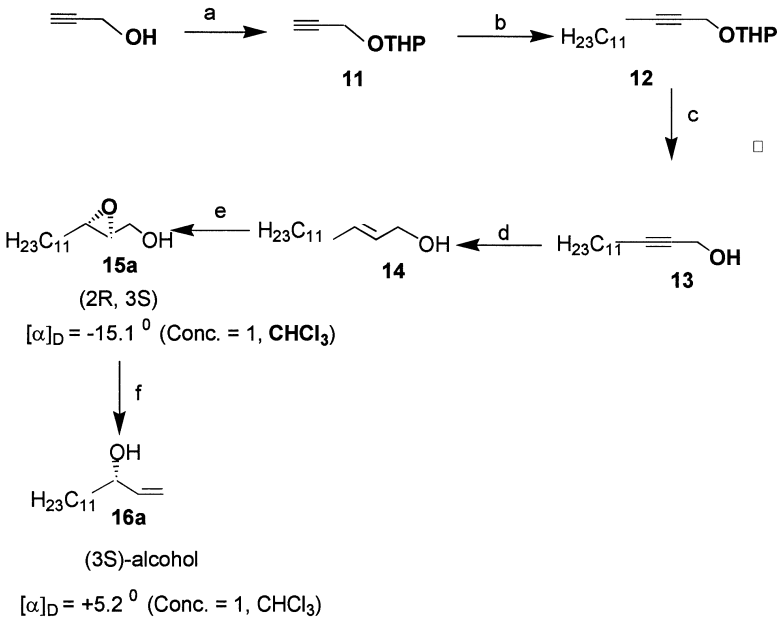
Scheme 1

The required Wittig salts (**5,10**) are prepared by following the routes depicted in Scheme 2.

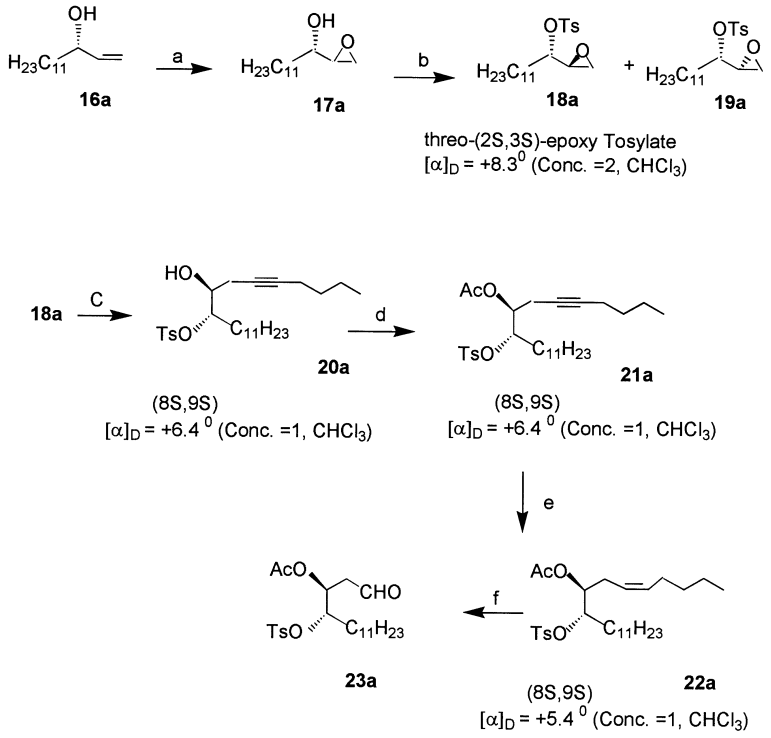


Scheme 2 Reagents: a) C_2H_5Br, Li-Liq. NH_3, THF; b) MeOH, p-TSA; c) Lindlar-H_2; d) TPP, I_2, imidazole, benzene, r.t.; e) TPP, benzene, reflux; f) vinyl magnesium bromide, Pd^0 CuI, THF-TEA.

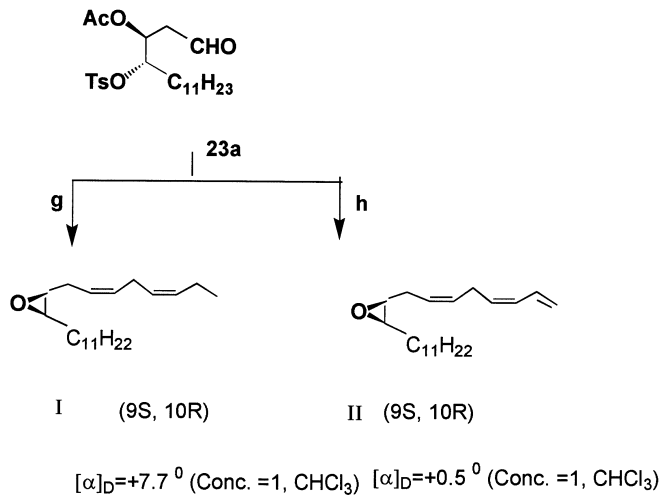
Synthesis of the target molecules (i.e., compounds I and II, along with their possible enantiomers) is achieved through the routes described in Schemes 3–7.



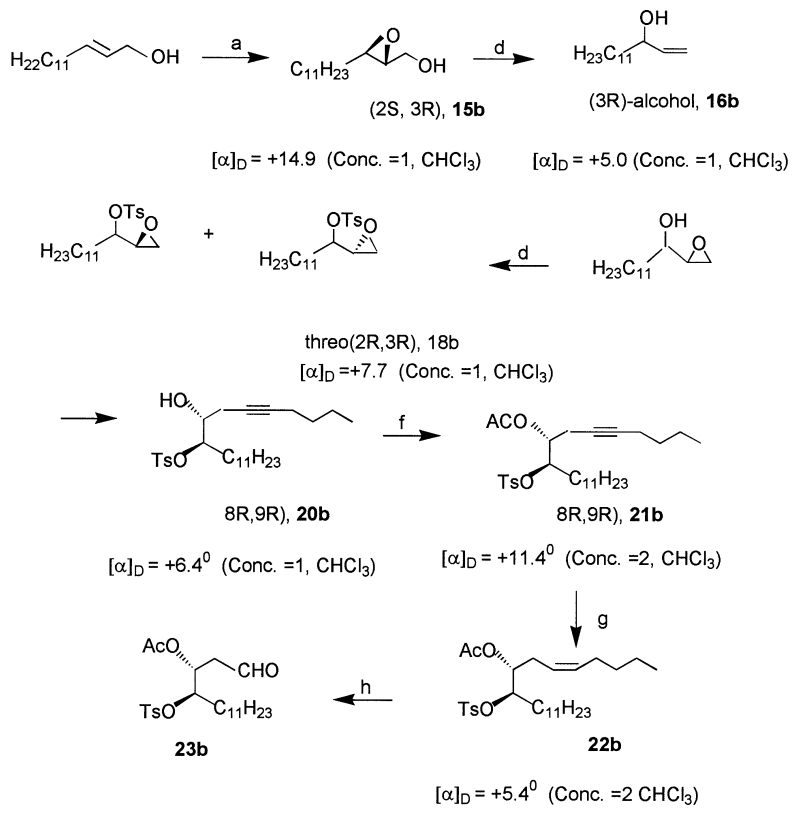
Scheme 3 Reagents: a) DHP, p-TSA, DCM; b) $C_{11}H_{23}Br$, Li-Liq. NH_3-THF; c) MeOH-p-TSA; d) LAH, THF, reflux; e) (+)-DIPT, TIP, TBHP, 4A molecular sieves, DCM, –25 ºC; f) Cp_2TiCl_2, Zn, $ZnCl_2$.



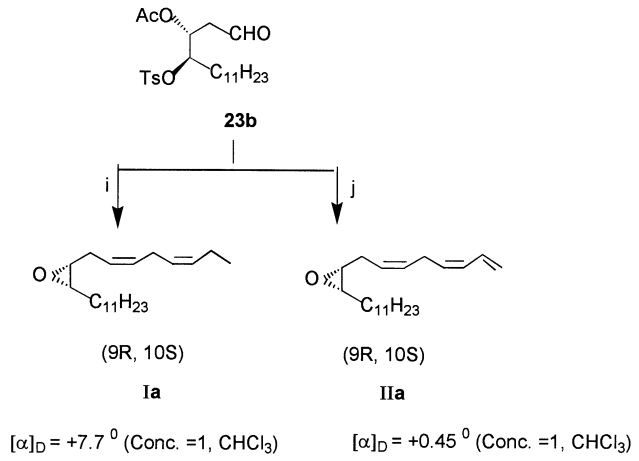
Scheme 4



Scheme 5 Reagents: a) m-CPBA, DCM; b) TsCl, TEA-DCM, 0 ºC; c) 1-hexyne, BuLi, BF_3–Et_2O; d) Ac_2O, Pyridine, DMAP, DCM; e) Lindlar catalyst-H_2; f) ozonolysis; g) *cis*-3-hexenyl triphenyl phosphonium iodide, $NaN(Me_3Si)_2$THF, –78 ºC; h) *cis*-3-hexadienyl triphenyl phosphonium iodide, $NaN(Me_3Si)_2$, THF, –78 ºC.



Scheme 6



Scheme 7 Reagents: a) (–)-DIPT, TIP, TBHP, 4A^{o} molecular sieves, DCM, –25 ºC; b) Cp_2TiCl_2, Zn, $ZnCl_2$; c) m-CPBA, DCM; d) TsCl, TEA, DCM, 0 ºC; e) 1-Hexyne, BuLi, BF_3–Et_2O, THF, –78 ˚C; f) Ac_2O, pyridine, DMAP; g) Lindlar catalyst-H_2; h) ozonolysis; i) *cis*-3-hexenyl triphenyl phosphonium iodide, $NaN(SiMe_3)_2$, THF, –78 ºC; j) *cis*-hexadienyl triphenyl phosphonium iodide, $NaN(SiMe_3)_2$, THF, –78 ˚C.

BIOASSAY AND FIELD EXPERIMENTS

These are carried out with wind tunnel in the laboratory and in 1 ha of sunflower field. The preliminary results are encouraging.

Wind tunnel

The experiments were carried out in a wind tunnel made of a plexiglass cylinder having a length of 150 cm and diameter of 55 cm. The air velocity is kept at 0.5 m/s. The tests were carried out in the middle of the scotophase using calling virgin females (1–2 days old), and the synthetic pheromone blend having the ratio I:II:III:IV:V = 1.0:0.5:1.0:3.0:2.6. The virgin females attracted 70–80% of the males released, whereas the blend attracted 50–60%.

Field trial

The pheromone-monitoring technique was attempted to evaluate the synthesized pheromone blend for its bioefficacy in 1 ha of sunflower crop. Six funnel-and-sleeve traps were used for trapping the insect. The pheromone blend having the synthetic compounds at the ratio of I:II:III:IV:V = 1.0:0.5:1.0:3.0:2.6 is tested. Commercially available rubber septa were used as lures after pretreatment. Each lure is loaded with 3 mg of the above blend. The traps were placed for nearly 45 days in the field. On an average, 5 insects per trap per day were trapped from the 10^{th} to the 40^{th} day.

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