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(*E*)-N-substitutedbenzylidene-4-methoxyanilines as insect antifeedants

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ABSTRACT

Some substituted aryl Schiff's bases[(*E*)-N-substitutedbenzylidene-4-methoxyanilines] have been prepared and their purities were checked by their physical constants and spectroscopic data reported earlier. The insect antifeedant activities of these Schiff's bases have been studied by leaf-discs bio assay method using 4th instar larvae *Achoea Janata L.*

Keywords: Substituted Schiff's bases; leaf-discs bio assay; Insect antifeedant activity

1. INTRODUCTION

The Schiff's bases are azomethines containing –C=N- moieties in their structure. It is honored by Hugo Schiff, who had synthesized these compounds earlier. Schiff's bases, are condensation products of primary amines with carbonyl compounds either aldehyde or ketones. Schiff's bases are characterized by the –C=N- (*E*-imine) group which finds importance in elucidating the mechanism of transamination and racemization reactions in biological systems [1,2].

Aliphatic Schiff's bases are relatively unstable which readily undergo polymerization while those of aromatic aldehydes having an effective conjugation system are found to be more stable. Schiff bases have been reported to play very important role in many biological and chemical reactions, due to the presence of the *E*-imine linkage. The bi- or tri- dentate Schiff's base ligands were forming complexes with transition metals [3,4]. Schiff's bases, derived from aromatic amines and aromatic aldehydes are reported to be involved in the study of asymmetric catalysis [5], magnetic properties [6], photochromism [7], binding with DNA [8], construction of supra molecular structures [9], the study of activity against Ehrlichascites carcinoma (EAC) [10], the field of dyes and pigments [11], the development of corrosion inhibitors [12], anti-HIV [13] and in the evaluation of physical properties in the crystalline state [14].

Optically active imine derivatives possess multipronged biological activities such as antimicrobial [15], anticancer [16], antiplasmodic- antihypoxic [17], antitubularcular [18], nematicidalinsecticidal [19], anti-inflammatory and lipoxygenase [20].

Recently Suresh et al., Sakthinathan et al., and Mayavel et al., have reported the antimicrobial activities of some *E*-imines [21-23]. Lakshmanan et al have studied the insect antifeedant activities of trifluormethyl imines [24,25]. The halogen substituted epoxides possess insect antifeedant activity and it was studied by Thirunarayanan [26-28].

The insect antifeedant activities of di-imines [29], oxazines [30] and Tröger bases [31]were reported in literature. Recently, Thirunarayanan have evaluated the insect antifeedant activities of some substituted bicycle [2.2.1] heptane-5-ene methanones [32]. Within the above view there is no report available for the insect antifeedant activities of Schiff's bases in literature in the past.

Therefore the authors have taken efforts to study the insect antifeedant activities of some Schiff's bases derived from 4-methoxy aniline and substituted benzaldehydes using 4th instar larvae *Achoea Janata L* by leaf-disc bioassay method.

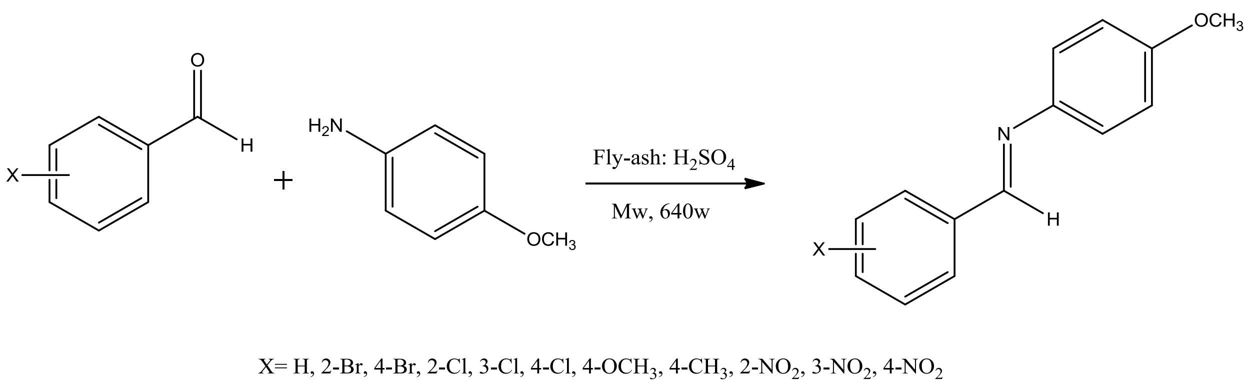
2. EXPERIMENTAL

2. 1. Synthesis of (*E*)-N-substitutedbenzylidene-4-methoxyanilines (Schiff's bases)

The substituted (*E*)-N-substitutedbenzylidene-4-methoxyanilines were synthesized by literature method [21]. An equal molar quantities of aryl amines (2 mmol), substituted benzaldehydes (2 mmol) and fly-ash: H_2SO_4 (0.4 g) have been taken in 50 mL borosil beaker and closed with watch glass.

The was subjected to microwave irradiation for 6-12 min in a microwave oven at 460 W (Scheme 1) (Samsung, Microwave Oven, 160-800 W) and then cooled to room temperature. The reaction mixture was extracted with dichloromethane; evaporation of organic layer gave solid a product. Further the obtained solid was recrystallized with benzene-hexane mixture afforded glittering product.

The insoluble catalyst was recycled by washing with ethyl acetate (8 mL) followed by drying by heating it in an oven at 100 ºC for 1 h and reused for further reaction runs. The physical constants and analytical data are presented in Table 1.



Scheme 1. Synthesis of (*E*)-N-substitutedbenzylidene-4-methoxyanilines (Schiff's bases).

Table 1. The physical constants and analytical data of (*E*)-N-substitutedbenzylidene-4-methoxyanilines (Schiff's bases).

Entry	X	M.F.	M.W.	m.p. (ºC)	Mass (m/z)
1	H	$C_{14}H_{13}NO$	211	51-52 (50-51)[21]	211[M$^+$]
2	2-Br	$C_{14}H_{12}BrNO$	289	59-60(54-56)[21]	282[M$^+$]
3	4-Br	$C_{14}H_{12}BrNO$	289	137-138(138-139)[21]	282[M$^+$]
4	2-Cl	$C_{14}H_{12}ClNO$	246	52-53(51-53)[21]	246[M$^+$]
5	3-Cl	$C_{14}H_{12}ClNO$	246	60-61(59-60)[21]	246[M$^+$]
6	4-Cl	$C_{14}H_{12}ClNO$	246	51-53(81-82)[21]	246[M$^+$]
7	4-OCH_3	$C_{15}H_{15}NO_2$	241	140-141(140)[21]	241[M$^+$]
8	4-CH_3	$C_{15}H_{15}NO$	225	61-62(60-61)[21]	225[M$^+$]
9	2-NO_2	$C_{14}H_{12}NO_3$	256	65-66(64-65)[21]	256[M$^+$]
10	3-NO_2	$C_{14}H_{12}NO_3$	256	60-61(59-60)[21]	256[M$^+$]
11	4-NO_2	$C_{14}H_{12}NO_3$	256	127-128(125-126)[21]	256[M$^+$]

3. RESULTS AND DISCUSSION

3. 1. Insect antifeedant activity

Organic substrates containing carbonyl, unsaturation and halogens, they possess insect antifeedant activity. Therefore, the author wishes to examine the insect antifeedant activity of these substituted Schiff's base derivatives and found to be active as insect antifeedants. This test was performed with a 4th instar larva *Achoea janata* L against castor *semilooper,* were reared as described on the leaves of castor, *Ricinus communis* in the laboratory at the temperature range of 26 °C ±1 °C and a relative humidity of 75-85%. The leaf – disc bioassay method [24-33] was used against the 4th instar larvae to measure the antifeedant activity. The 4th instar larvae were selected for testing because the larvae at this stage feed very voraciously.

3. 2. Measurement of insect antifeedant activity of (*E*)-N-substitutedbenzylidene-4-methoxyanilines (Schiff's bases).

About 1.85 cm diameter of castor leaf discs were punched and intact with the petioles. The prepared (*E*)-N-substitutedbenzylidene-4-methoxyanilines were dissolved in acetone at a concentration of 200 ppm dipped for 5 minutes. The leaf discs were air-dried and placed in one liter beaker containing little water in order to facilitate translocation of water. Therefore, the fresh leaf discs were performed throughout the duration of the test. The 4th instar larvae of the test insect, which had been preserved on the leaf discs of all *E*-imines and allowed to feed on them for 24 h.

The areas of the leaf discs consumed were measured by leaf-disc bio assay method [24-33]. The observed antifeedant activity of substituted *E*-imine derivatives was presented in Table 2.

Table 2. The insect antifeedant activities of (*E*)-N-substitutedbenzylidene-4-methoxyanilines (Schiff's bases).

Entry	R	4-6 pm	6-8 pm	8-10 pm	10 pm - 12 am	12-6 am	6-8 am	8 am - 12 Nn	12 Nn - 2 pm	2-4 pm	Total leaf disc consumed by 24h
1	H	1	0.5	1	0.5	0.5	1	1	1	1	7
2	2-Br	0.5	0.5	1	1	1	0	0	0	0	4
3	4-Br	0.5	0	0	0.5	0.5	0.5	0.5	1	1	4
4	2-Cl	1	0	0.5	0	0	0	1	1	1	4.5
5	3-Cl	0.5	0.5	0.5	0.5	0	0	0.5	0.5	0.5	4
6	4-Cl	0.25	1	0.25	0.25	0.25	0	0	1	0.5	3.5
7	4-OCH_3	1	1	0	1	1	1	1	1	1	8
8	4-CH_3	1	0.5	1	1	1	0.5	1	0.5	0.5	7
9	2-NO_2	2	1	0	1	1	1	0	1	1	8
10	3-NO_2	1	1	1	1	0.5	0.5	0.5	0.5	1	7
11	4-NO_2	1	0	1	1	1	1	0	1	1	7

Number of leaf discs consumed by the insect (values are mean + SE of five).

Table 3. Antifeedant activity of compound **6** (*E*)-4-chlorobenzylidene-4-methoxyaniline showed an appreciable antifeedant activity at 3 different concentrations.

ppm	4-6 pm	6-8 pm	8-10 pm	10 pm - 12 am	12-6 am	6-8 am	8 am - 12 Nn	12 Nn - 2 pm	2-4 pm	Total leaf disc consumed by 24h
50	0.5	0.25	0.25	0	0	0	0	0	0	1
100	0.25	0.25	0.25	0	0	0	0	0	0	0.75
150	0.25	0	0.25	0	0	0	0	0	0	0.5

Number of leaf discs consumed by the insect (values are mean + SE of five).

The results of the antifeedant activity of (*E*)-N-substitutedbenzylidene-4-methoxyanilines (Schiff's bases) are presented in Table **2** reveals that compounds **2-6** were found to reflect satisfactory antifeedant. This test is performed with the insects which ate only two-leaf disc soaked under the solution of this compound. Compound **5** showed enough antifeedant activity but lesser than **6**. Further compound **6** was subjected to measure the antifeedant activity at different 50, 100, 150 ppm concentrations and the observation reveals that as the concentrations decreased, the activity also decreased. It is observed from the results in Table 3 and that the **6** 4-chloro substituted 4-methoxy Schiff's base showed an appreciable antifeedant activity at 150 ppm concentration.

4. CONCLUSIONS

A series of (*E*)-N-substitutedbenzylidene-4-methoxyanilines (Schiff's bases) have been synthesized and examined their purities with their physical constants and spectroscopic data reported in earlier. The insect antifeedant activities of these Schiff's bases have been evaluated using leaf-disc bioassay method. The Schiff's base **6** (*E*)-4-chlorobenzylidene-4-methoxyaniline Schiff's base showed an appreciable antifeedant activity.

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