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Synthesis and insect antifeedant activities of some substituted styryl 3,4-dichlorophenyl ketones

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ABSTRACT

Sixteen substituted styryl 3,4-dichlorophenyl ketones [(2*E*)-1-(3,4-dichlorophenyl)-3-phenyl-2-propen-1-ones] were synthesized using eco-friendly benign stereoselective crossed-aldol reaction. They are characterized by their analytical, infrared, NMR and mass spectral data. The insect antifeedant activities of these chalcones were evaluated using *Caster semilooper* and *Achoea janata* L.

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1. Introduction

Green chemistry provides good eco-friendly methods for synthesis of organic compounds without solvent. Among these methods the aqueous phase reaction is very interesting due to operative simplicity, easy work up, good yield, non-hazardous conditions and being safer for the environment. Chemists and environmental scientists have reported various solvent methods for organic synthesis. The use of bases for synthesis of chalcones with or without solvent is important [1]. A literature survey reveals that there are few papers reporting synthesis of chalcones using bases in aqueous phase aldol condensation reaction between ketones and aldehydes. Various reagents are used for solvent free synthesis like, metals and metal chelates [2], carbonates [3], chiral boronate ester [4], phosphate [5], organolithium [6], sodium hydroxide [7], silica-sulphuric acid [8], alumina [9], organic ionic liquids [10], metal-nanoparticles [11] and potassium hydroxide-ethanol [12]. Kalluriya and Ray [13] synthesized sydenone chalcones with more than 60% yield using grinding of aqueous sodium hydroxide-heterogeneous reaction medium with aldehydes. Hassen and co-workers [14] reported more than 60% yield of some heteroaryl chalcones obtained by the solvent free reaction with aldehydes in 20 °C cooling condition in presence of surfactants. Venkat Reddy et al. [15] reported more than 70% yield of chalcones synthesized using zinc chloride and microwave techniques. Thirunarayanan

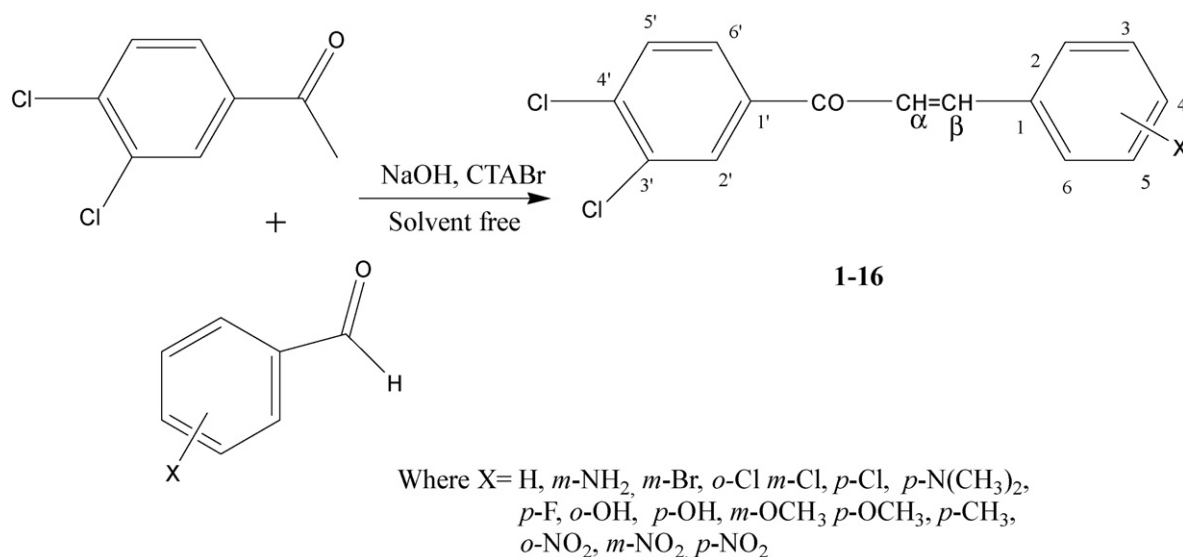
[16] reported aqueous potassium hydroxide used as a reagent for synthesis of some aryl chalcones by grinding aryl aldehydes and ketones. The authors wish to report an efficient and selective method for condensation of 3,4-dichlorophenyl methyl ketones with various *m*- and *p*-substituted benzaldehydes under solvent free conditions by stirring the reactants with sodium hydroxide at room temperature to yield the respective *E*-2-propen-1-ones. Studies of quantitative structure property relationship and insect antifeedant activities are likewise reported. In this method during stirring of 3,4-dichloro acetophenone and aldehydes, they decomposed slowly forming the products in good yield and the reaction time is lower than in the solution phase thermal method. The methylene units of chalcones derived from cyclic or acyclic ketones are found in many naturally occurring compounds and they are useful for the synthesis of pyrimidine derivatives [17]. The basic skeleton of chalcones is widely represented in natural products and are known to have multipronged activity [18]. Many of the chalcones are used as agrochemicals and drugs [19].

2. Experimental

All chemicals used were purchased from Sigma–Aldrich and E-Merck chemical company. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000–400 cm^{−1}) were recorded on AVATAR-300 Fourier transform spectrophotometer. INSTRUM AV300 operating at 500 MHz for ¹H spectra and 125.46 MHz for ¹³C spectra in CDCl₃ solvent using TMS as internal standard. Electron impact (EI) (70 eV) and chemical ion-

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Scheme 1.

Table 1

Physical constants, microanalysis and mass spectral data of substituted styryl 3,4-dichlorophenyl ketones.

Entry	X	Molecular formula	Molecular weight	Time (m)	Yield (%)	M.p. (°C)	Found (Calcd)			Mass <i>m/z</i>
							C	H	N	
1	H	C ₁₅ H ₁₀ Cl ₂ O	276.14	45	91	100–101	64.82 (65.01)	3.59 (3.64)	–	276 (M ⁺), 278, 280, 243, 241, 212, 198, 178, 174, 147, 146, 145, 131, 109, 107, 104, 103, 88, 78, 77, 75, 74, 73, 63, 52,
2	<i>m</i> -NH ₂	C ₁₅ H ₁₁ Cl ₂ NO	291.15	40	86	111–112	61.62 (61.67)	3.94 (3.79)	4.72 (4.79)	291 (M ⁺), 293, 295, 280, 241, 240, 226, 197, 178, 166, 147, 107, 95, 88, 75, 51
3	<i>p</i> -Br	C ₁₅ H ₉ BrCl ₂ O	355.91	50	89	168–169	50.55 (50.60)	2.35 (2.55)	–	356 (M ⁺), 357, 358, 360, 322, 321, 319, 165, 149, 277, 276, 275, 214, 212, 181, 147, 145, 137, 136, 124, 111, 103, 106, 102, 95, 75, 50
4	<i>o</i> -Cl	C ₁₅ H ₉ Cl ₃ O	311.86	45	88	121–122	57.78 (57.82)	2.85 (2.91)	–	311 (M ⁺), 313, 315, 276, 241, 149, 137, 136, 125, 111, 102, 95, 88, 51
5	<i>m</i> -Cl	C ₁₅ H ₉ Cl ₃ O	311.86	50	85	145–146	57.71 (57.82)	2.84 (2.91)	–	311 (M ⁺), 312, 313, 315, 276, 278, 277, 275, 247, 214, 208, 179, 175, 173, 149, 137, 105, 102, 75, 74, 68, 51.
6	<i>p</i> -Cl	C ₁₅ H ₉ Cl ₃ O	311.86	50	90	142–143	57.79 (57.82)	2.88 (2.91)	–	311 (M ⁺), 312, 313, 315, 309, 278, 277, 275, 249, 213, 212, 173, 166, 164, 146, 139, 138, 137, 111, 110, 108, 102, 101, 88, 75, 74, 63, 51.
7	<i>p</i> -N(CH ₃) ₂	C ₁₇ H ₁₅ Cl ₂ NO	321.07	40	88	125–126	63.72 (63.76)	4.68 (4.72)	4.32 (4.37)	321 (M ⁺), 323, 325, 320, 308, 277, 250, 225, 174, 149, 136, 133, 120, 95, 88, 63, 50.
8	<i>p</i> -F	C ₁₅ H ₉ Cl ₂ FO	295.13	55	85	103–105	60.98 (61.04)	2.95 (3.07)	–	295 (M ⁺), 297, 299, 276, 251, 241, 213, 178, 165, 149, 137, 136, 125, 111, 102, 95, 88, 51
9	<i>o</i> -OH	C ₁₅ H ₁₀ Cl ₂ O ₂	293.14	40	88	107–108	61.39 (61.46)	3.38 (3.44)	–	293 (M ⁺), 295, 297, 292, 276, 251, 241, 226, 178, 165, 149, 137, 136, 125, 111, 102, 95, 91, 88, 51.
10	<i>p</i> -OH	C ₁₅ H ₁₀ Cl ₂ O ₂	293.14	35	91	117–118	61.41 (61.46)	3.40 (3.44)	–	293 (M ⁺), 295, 297, 292, 276, 251, 241, 226, 178, 165, 149, 137, 136, 133, 125, 107, 111, 102, 95, 91, 88, 51.
11	<i>m</i> -OCH ₃	C ₁₆ H ₁₂ Cl ₂ O ₂	306.12	45	90	105–106	62.49 (62.56)	3.88 (3.94)	–	306 (M ⁺), 307, 308, 310, 291, 273, 271, 241, 237, 225, 206, 179, 162, 161, 149, 136, 133, 123, 109, 108, 103, 90, 89, 78, 63, 51
12	<i>p</i> -OCH ₃	C ₁₆ H ₁₂ Cl ₂ O ₂	306.12	40	90	152–153	62.54 (62.56)	3.90 (3.94)	–	306 (M ⁺), 307, 308, 310, 291, 273, 271, 237, 225, 206, 179, 162, 149, 136, 133, 123, 109, 108, 89, 78, 63, 51
13	<i>p</i> -CH ₃	C ₁₆ H ₁₂ Cl ₂ O	290.27	35	91	137–138	65.93 (66.00)	4.09 (4.15)	–	290 (M ⁺), 292, 294, 282, 281, 277, 275, 257, 255, 226, 221, 208, 175, 147, 146, 145, 118, 115, 109, 95, 91, 76, 65, 51.
14	<i>o</i> -NO ₂	C ₁₅ H ₉ Cl ₂ NO ₃	321.87	55	86	184–185	66.36 (66.42)	3.65 (3.72)	4.98 (5.16)	321 (M ⁺), 323, 325, 283, 281, 252, 221, 176, 149, 146, 136, 135, 95, 72, 58.
15	<i>m</i> -NO ₂	C ₁₅ H ₉ Cl ₂ NO ₃	321.87	60	88	218–219	65.34 (66.42)	3.69 (3.72)	5.01 (5.16)	321 (M ⁺), 323, 325, 324, 305, 306, 304, 288, 287, 286, 283, 281, 274, 240, 224, 212, 209, 208, 193, 190, 176, 174, 172, 149, 146, 136, 135, 130, 129, 110, 109, 89, 74, 63, 51.
16	<i>p</i> -NO ₂	C ₁₅ H ₉ Cl ₂ NO ₃	321.87	50	91	205–206	66.40 (66.42)	3.66 (3.72)	5.11 (5.16)	321 (M ⁺), 323, 325, 324, 305, 288, 287, 283, 281, 274, 240, 224, 212, 208, 193, 190, 176, 174, 149, 146, 136, 130, 129, 110, 74, 63, 51.

Table 2
Infrared spectral data (ν , cm^{-1}) of substituted styryl 3,4-dichlorophenyl ketones.

Entry	X	CO (<i>s-cis</i>)	CO (<i>s-trans</i>)	CHop vinyl	CHip vinyl	CH=CHop vinyl	>C= op vinyl	Subst. styryl part
1	H	1659.75	1601.25	761.30	1129.93	1026.31	521.50	—
2	<i>m</i> -NH ₂	1665.21	1628.39	753.26	1134.23	1022.45	527.43	3346.58 (–NH ₂)
3	<i>p</i> -Br	1659.29	1600.62	737.31	1127.11	1048.80	567.48	—
4	<i>o</i> -Cl	1662.04	1603.99	735.65	1136.87	1040.67	534.23	—
5	<i>m</i> -Cl	1664.08	1606.23	773.39	1134.17	1049.16	563.74	—
6	<i>p</i> -Cl	1659.46	1599.93	732.69	1128.29	1049.16	567.71	—
7	<i>p</i> -F	1651.65	1549.35	732.69	1128.29	1049.16	567.71	—
8	<i>p</i> -N(CH ₃) ₂	1662.14	1601.03	738.65	1127.46	1044.70	555.84	—
9	<i>o</i> -OH	1664.38	1613.28	748.34	1134.23	1066.37	546.26	3435.86 (–OH)
10	<i>p</i> -OH	1666.38	1609.25	753.48	1142.46	1064.37	536.24	3343.86 (–OH)
11	<i>m</i> -OCH ₃	1646.45	1603.76	724.74	1144.24	1073.69	545.87	1236.17 (C–O–C)
12	<i>p</i> -OCH ₃	1656.48	1593.73	717.72	1134.54	1033.62	515.72	1236.17 (C–O–C)
13	<i>p</i> -CH ₃	1659.71	1598.91	733.50	1123.36	1049.81	524.51	2857.81 (CH ₃)
14	<i>o</i> -NO ₂	1668.28	1607.55	741.98	1150.52	1046.16	583.71	1521.03 (–NO ₂)
15	<i>m</i> -NO ₂	1668.18	1607.38	742.00	1150.28	1046.07	583.66	1515.26 (–NO ₂)
16	<i>p</i> -NO ₂	1687.67	1589.52	772.87	1151.01	1027.28	561.58	1515.26 (–NO ₂)

ization mode FAB⁺ mass spectra were recorded with a VARIAN 500 spectrometer. Microanalysis of all chalcones was performed in Elementar Model Vario EL III Analyzer.

2.1. General procedure for synthesis of substituted styryl 3,4-dichlorophenyl ketones

Appropriate mixture of 3,4-dichloroacetophenone (100 mmol) and *m*- and *p*-substituted benzaldehydes (100 mmol) and cetyltrimethyl ammonium bromide (CTABr) (15 mmol) were added to an aqueous solution of sodium hydroxide (200 ml 0.5 M). The reaction mixture was vigorously stirred at room temperature (Scheme 1) for the time reported in Table 1. Completion of reaction was confirmed by TLC. The product was filtered and washed with cold water and recrystallized from ethanol, dried well and kept in a desiccator. The analytical and Mass spectral data of all chalcones are presented in Table 1 and the spectral data are shown in Tables 2–4.

3. Results and discussion

Our previous investigations [20–25] deal with to carbon–carbon bond formation and we studied in this article the crossed-aldol condensation of 3,4-dichloroacetophenone and a variety of different substituted aryl aldehydes. This occurs in water at room temperature and in the presence of cetyltrimethylammonium bromide (CTABr) as the proper cationic surfactant for the synthesis of (2E)-

1-(3,4-dichlorophenyl)-3-phenyl-2-propen-1-ones in an excellent yield with high stereoselectivity. Efficient stirring of an equimolar quantity of 3,4-dichloroacetophenone and various substituted aryl aldehydes in aqueous sodium hydroxide solution in presence of cetyltrimethylammonium bromide (CTABr) as surfactant at room temperature, feasible stereoselective crossed-aldol condensation with precipitation of the 3-phenyl-1,3,4-dichlorophenylprop-2-ene-1-ones in high yields with in the short time (*t*) as shown in Table 1. This methodology offers significant advantages over conventional methods such as, (i) safe, clean and simple methodology, (ii) modified stereoselectivity reaction, (iii) improved reaction rates and increased yields through suppression of side reactions. (iv) aqueous alkali metal hydroxides replace alkoxides. (v) reaction was carried out at room temperature and easier- workup and (vi) avoid the expensive and hazard organic solvents.

3.1. Insect antifeedant activity

The multipronged activities present in different chalcones are intended to examine their insect antifeedant activities against cater *semilooper*. The larvae's of *Achoea Janata* L. were reared as described on the leaves of cater *Riclmus Cammunis* in the laboratory at the temperature range of $26 \pm 1^\circ\text{C}$ and a relative humidity of 75–85%. The leaf-disc bioassay method [16] 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.

Table 3
¹H NMR spectral data (δ , ppm) of substituted styryl 3,4-dichlorophenyl ketones.

Entry	X	3,4-Dichloro phenyl ring		H ₆ (d, 1H)	vinyl H _α (d, 1H)	vinyl H _β (d, 1H)	Styryl Ph ring (m, 4H)	Substituent in styryl part
		H ₂ (s, 1H)	H ₅ (d, 1H)					
1	H	7.978	7.421 (<i>J</i> = 2.12 Hz)	7.628 (<i>J</i> = 2.12 Hz)	7.536 (<i>J</i> = 15.2 Hz)	7.795 (<i>J</i> = 15.2 Hz)	7.298–7.372	—
2	<i>m</i> -NH ₂	7.794	7.381 (<i>J</i> = 3.3 Hz)	7.573 (<i>J</i> = 3.3 Hz)	7.356 (<i>J</i> = 16.3 Hz)	7.732 (<i>J</i> = 16.3 Hz)	6.561–6.973	3.721 (s, 2H, –NH ₂)
3	<i>p</i> -Br	7.893	7.284 (<i>J</i> = 3.2 Hz)	7.601 (<i>J</i> = 3.2 Hz)	7.526 (<i>J</i> = 15.6 Hz)	7.762 (<i>J</i> = 15.6 Hz)	7.012–7.421	—
4	<i>o</i> -Cl	8.075	7.432 (<i>J</i> = 2.5 Hz)	7.691 (<i>J</i> = 2.5 Hz)	7.323 (<i>J</i> = 18.5 Hz)	8.233 (<i>J</i> = 18.5 Hz)	7.255–7.302	—
5	<i>m</i> -Cl	8.095	7.509 (<i>J</i> = 1.5 Hz)	7.598 (<i>J</i> = 1.5 Hz)	7.435 (<i>J</i> = 17.0 Hz)	7.751 (<i>J</i> = 17.0 Hz)	7.350–7.420	—
6	<i>p</i> -Cl	8.079	7.391 (<i>J</i> = 2.3 Hz)	7.828 (<i>J</i> = 2.3 Hz)	7.410 (<i>J</i> = 15.5 Hz)	7.771 (<i>J</i> = 15.5 Hz)	7.562–7.855	—
7	<i>p</i> -N(CH ₃) ₂	7.913	7.726 (<i>J</i> = 4.6 Hz)	7.835 (<i>J</i> = 4.6 Hz)	7.491 (<i>J</i> = 17.7 Hz)	7.813 (<i>J</i> = 17.7 Hz)	6.651–7.321	2.647 (s, 6H, N(CH ₃) ₂)
8	<i>p</i> -F	8.032	7.558 (<i>J</i> = 3.2 Hz)	7.601 (<i>J</i> = 3.2 Hz)	7.532 (<i>J</i> = 16.3 Hz)	7.872 (<i>J</i> = 16.3 Hz)	6.813–7.113	—
9	<i>o</i> -OH	7.812	7.441 (<i>J</i> = 5.3 Hz)	7.653 (<i>J</i> = 5.3 Hz)	7.362 (<i>J</i> = 18.4 Hz)	8.215 (<i>J</i> = 18.4 Hz)	6.671–7.238	—
10	<i>p</i> -OH	7.981	7.514 (<i>J</i> = 4.7 Hz)	7.765 (<i>J</i> = 4.7 Hz)	7.714 (<i>J</i> = 17.8 Hz)	7.788 (<i>J</i> = 17.8 Hz)	6.652–7.182	—
11	<i>m</i> -OCH ₃	7.813	7.174 (<i>J</i> = 4.7 Hz)	7.563 (<i>J</i> = 4.7 Hz)	7.321 (<i>J</i> = 17.8 Hz)	7.715 (<i>J</i> = 17.8 Hz)	6.710–7.154	3.934 (s, 3H, –OCH ₃)
12	<i>p</i> -OCH ₃	8.086	7.828 (<i>J</i> = 2.5 Hz)	7.845 (<i>J</i> = 2.5 Hz)	7.319 (<i>J</i> = 16.0 Hz)	7.808 (<i>J</i> = 16.0 Hz)	7.564–7.619	3.934 (s, 3H, –OCH ₃)
13	<i>p</i> -CH ₃	8.071	7.527 (<i>J</i> = 2.0 Hz)	7.551 (<i>J</i> = 2.0 Hz)	7.389 (<i>J</i> = 15.5 Hz)	7.804 (<i>J</i> = 15.5 Hz)	7.217–7.257	2.392 (s, 3H, (CH ₃))
14	<i>o</i> -NO ₂	8.531	8.284 (<i>J</i> = 1.8 Hz)	7.763 (<i>J</i> = 1.8 Hz)	7.756 (<i>J</i> = 15.5 Hz)	7.915 (<i>J</i> = 15.5 Hz)	7.622–7.702	—
15	<i>m</i> -NO ₂	8.185	7.423 (<i>J</i> = 4.2 Hz)	7.878 (<i>J</i> = 4.2 Hz)	7.263 (<i>J</i> = 16.0 Hz)	8.169 (<i>J</i> = 16.0 Hz)	7.575–8.123	—
16	<i>p</i> -NO ₂	7.843	7.543 (<i>J</i> = 3.0 Hz)	7.769 (<i>J</i> = 3.0 Hz)	7.561 (<i>J</i> = 16.25 Hz)	7.807 (<i>J</i> = 16.25 Hz)	7.265–7.563	—

Table 4¹³C NMR spectral data (δ , ppm) of substituted styryl 3,4-dichlorophenyl ketones.

Entry	X	CO	C α	C β	C $_1$	C $_2$	C $_3$	C $_4$	C $_5$
1	H	187.87	120.83	146.03	136.28	127.16	128.64	128.43	128.64
2	<i>m</i> -NH $_2$	180.10	121.40	144.91	137.32	111.08	149.30	114.72	130.20
3	<i>p</i> -Br	181.30	122.28	144.40	133.56	128.21	132.71	122.48	132.71
4	<i>o</i> -Cl	187.85	123.55	141.73	133.34	131.59	128.82	129.66	127.11
5	<i>m</i> -Cl	187.53	122.02	144.24	136.29	126.97	135.09	128.03	130.30
6	<i>p</i> -Cl	187.63	121.23	144.19	133.36	127.48	129.35	133.38	129.35
7	<i>p</i> -N(CH $_3$) $_2$	181.33	122.82	147.32	123.17	127.57	115.28	148.91	115.28
8	<i>p</i> -F	190.23	122.65	145.83	130.73	127.33	116.72	163.54	116.72
9	<i>o</i> -OH	188.79	121.33	146.52	116.78	159.83	115.23	130.40	120.14
10	<i>p</i> -OH	188.32	121.48	146.27	127.67	127.08	114.58	158.87	114.58
11	<i>m</i> -OCH $_3$	188.80	122.14	145.52	135.24	111.29	163.14	114.61	130.38
12	<i>p</i> -OCH $_3$	187.96	118.53	145.93	127.44	127.23	114.46	162.05	114.46
13	<i>p</i> -CH $_3$	187.99	119.85	146.16	131.76	128.76	129.80	137.93	129.80
14	<i>o</i> -NO $_2$	188.87	122.48	142.83	130.17	149.71	120.71	127.87	134.46
15	<i>m</i> -NO $_2$	187.89	122.25	141.84	136.45	124.03	148.66	122.23	130.05
16	<i>p</i> -NO $_2$	190.87	122.34	144.52	142.25	127.34	120.74	150.05	120.74

Entry	X	C $_6$	C $_1'$	C $_2'$	C $_3'$	C $_4'$	C $_5'$	C $_6'$	Substituent in styryl part
1	H	127.16	137.30	130.99	133.28	137.74	130.99	129.36	–
2	<i>m</i> -NH $_2$	117.25	137.90	130.50	130.91	140.92	121.89	129.02	–
3	<i>p</i> -Br	128.21	138.92	132.71	133.92	139.92	132.71	128.21	–
4	<i>o</i> -Cl	127.84	137.45	132.38	133.57	139.28	130.78	129.66	–
5	<i>m</i> -Cl	124.56	137.43	130.79	133.41	137.69	130.83	130.77	–
6	<i>p</i> -Cl	127.48	137.49	130.49	132.95	137.56	130.84	129.75	–
7	<i>p</i> -N(CH $_3$) $_2$	127.57	136.93	131.54	133.01	138.92	130.82	130.31	46.63 (N(CH $_3$) $_2$)
8	<i>p</i> -F	127.33	136.27	131.07	133.27	140.11	131.32	130.32	–
9	<i>o</i> -OH	127.78	137.67	130.01	133.36	140.92	130.81	130.01	–
10	<i>p</i> -OH	127.08	136.94	130.92	133.38	140.29	132.74	130.11	–
11	<i>m</i> -OCH $_3$	119.87	137.57	131.36	133.72	139.35	130.25	129.28	56.39 (OCH $_3$)
12	<i>p</i> -OCH $_3$	127.43	137.02	130.68	133.20	138.11	130.64	130.38	55.45 (OCH $_3$)
13	<i>p</i> -CH $_3$	128.76	137.16	131.76	133.24	141.66	130.48	130.42	21.59 (CH $_3$)
14	<i>o</i> -NO $_2$	127.56	136.92	131.95	133.60	139.54	130.95	128.15	–
15	<i>m</i> -NO $_2$	131.92	138.21	131.92	133.83	140.32	130.92	130.11	–
16	<i>p</i> -NO $_2$	127.34	137.75	132.36	133.28	138.97	130.74	130.33	–

3.2. Measurement of insect antifeedant activity of chalcones

Leaf discs of a diameter of 1.85 cm were punched from castor leaves with the petioles intact. All ketones were dissolved in acetone at a concentration of 200 ppm dipped for 5 min. The leaf discs were air-dried and placed in 1 l beaker containing little water in order to facilitate translocation of water. Therefore the leaf discs remain fresh throughout the duration of the test, 4th instar larvae of the test insect, which had been preserved on the leaf discs of all chalcones and allowed to feed on them for 24 h. The area of the leaf disc consumed were measured by Dethler's [26] method. The observed antifeedant activity of chalcones was presented in Table 5.

The results of the antifeedant activity of substituted styryl 3,4-dichlorophenyl ketones presented in Table 5 reveal that the compounds **3–6** are found to reflect remarkable antifeedant among all other chalcones. This test is performed with the insects' which ate only two-leaf disc soaked under the solution of this compound. Compounds **4** and **5** also show 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 6 that the ketone **6** (*2E*)-1-(3,4-dichlorophenyl)-3-(4-chlorophenyl)-2-propen-1-one shows an appreciable antifeedant activity at 200 ppm concentration.

Table 5

Antifeedant activity of substituted styryl 3,4-dichlorophenyl ketones. Number of leaf discs consumed by the insect (Values are mean + SE of five).

Entry	X	4–6 pm	6–8 pm	8–10 pm	10–12 pm	12–6 am	6–8 am	8 am–12 Noon	12 Noon–2 pm	2–4 pm	Total leaf disc consumed in 24 h
1	H	1	1	0.5	0.5	0.5	1	1	1	1	8
2	<i>m</i> -NH $_2$	1	1	1	0.5	1	0.5	1	1	1	8
3	<i>p</i> -Br	0.5	0.25	0.25	0.5	0.5	0.5	1	1	0.5	1.5
4	<i>o</i> -Cl	0.5	0.25	0.25	0.5	0.5	0.25	0.25	0.25	0.25	2.5
5	<i>m</i> -Cl	0	0.25	0.25	1	0.5	0.5	0.25	0	0	1.5
6	<i>p</i> -Cl	0.25	0.5	0.25	0	0	0.25	0	0	0	0.5
7	<i>p</i> -N(CH $_3$) $_2$	1	2	2	1	0	0	1	1	1	9
8	<i>p</i> -F	1	2	2	1	0	0	1	1	1	9
9	<i>o</i> -OH	1	1	.05	0.5	1	0.5	1	1	1	7.5
10	<i>p</i> -OH	1	2	2	1	0	0	1	1	1	9
11	<i>m</i> -OCH $_3$	0.5	2	0.25	1	0.5	0.5	0.25	0	0	5
12	<i>p</i> -OCH $_3$	1	0.5	0.5	1	1	0	1	1	1	9
13	<i>p</i> -CH $_3$	0.5	0.5	0.5	2	2	1	1	1	1	9
14	<i>o</i> -NO $_2$	2	3	3	1	1	1	0.5	1	0	12
15	<i>m</i> -NO $_2$	2	3	3	1	1	1	0.5	1	0	12
16	<i>p</i> -NO $_2$	1	2	2	2	1	0.5	0.5	1	0	10

Table 6
Antifeedant activity of compound 6 (2E)-1-(3,4-dichlorophenyl)-3-(4-chlorophenyl)-2-propen-1-one at 4 different concentrations -number of leaf discs consumed by the insect (Values are mean + SE of five).

ppm	4–6 pm	6–8 pm	8–10 pm	10–12 pm	12–6 am	6–8 am	8 am–12 Noon	12 Noon–2 pm	2–4 pm	Total leaf disc consumed in 24 h
50	0.5	0.5	0	0	0	0	0	0	0	0.1
100	0	0.25	0.25	0	0	0	0	0	0	0.05
150	0	0	0	0	0	0	0	0	0	0

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