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ORIGINAL ARTICLE

Synthesis, spectral studies, antimicrobial and insect antifeedant activities of some substituted styryl 4′-fluorophenyl ketones

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Abstract Good yield of some substituted styryl 4′-fluorophenyl ketones were synthesized by solvent free fly-ash:water catalyzed eco-friendly environmentally benign Aldol reaction. These chalcones were characterized by physical constants, micro analysis and spectral data. Antimicrobial and insect antifeedant activities were measured in all chalcones. The group frequencies of all chalcones like carbonyl stretches *ν*CO, C–F and the deformation modes of vinyl part of CH– *out of plane*, *in-plane*, CH=CH *out of plane* and >C=C< *out of plane* (cm^{-1}), the vinyl hydrogen and carbons *δ*(ppm) of H_α, H_β, C_α, C_β and CO were assigned and these frequencies were correlated with various kinds of substituent constants. From the results of statistical analysis the influence of electronic effects of substituents on the spectral data of carbonyl group, vinyl proton and carbons of the ketones have been explained.

1. Introduction

Green chemistry provides good eco-friendly methods for the synthesis of organic compounds without solvent. This method involving the aqueous phase reaction is of very interesting due to operative simplicity, work up easier, good yield, non-hazardousness and is safer for environment. Chemists and environmental scientists reported various solvent methods for organic synthesis. The use of bases for synthesis of chalcones with solvent or without solvent in chalcone chemistry is important (Thirunarayanan et al., 2010; Guthrie and Wang, 1991; Chaloner et al., 1991; Schmid and Whitesides, 1991; Straub, 1995). Literature survey reveals that there is less number of work reported for 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 (Waldemar et al., 2000; Babua and Perumal, 1997), carbonates (Zhang et al., 2003), chiral boronate ester (Richard et al., 2006), phosphate (Pore et al., 2007), organolithium (Daskiewicz et al., 1999), sodium hydroxide (Fringueli et al., 2002), silica-sulphuric acid (Thirunarayanan, 2007a,b; Thirunarayanan and Vanangamudi, 2006a, 2007), alumina

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(Esmaeili et al., 2005), organic ionic liquids (Ranu and Jana, 2005, 2006; Ranu et al., 2003; Ranu and Banerjee, 2005) metal-nanoparticles (Raveendran et al., 2003) and potassium hydroxide-ethanol (Straub, 1995). Kalluriya and Ray (2003) synthesized more than 60% yield of sydenone chalcones using grinding of aqueous sodium hydroxide-heterogeneous reaction medium with aldehydes. Basaif et al. (2005) reported more than 60% yield of some heteroaryl chalcones obtained by the solvent free reaction with aldehydes in cooling condition in presence of surfactants. Venkat Reddy et al. (2000) reported more than 70% yield of chalcones synthesized using zinc chloride in microwave techniques. Thirunarayanan (2008a) reported aqueous potassium hydroxide used as a reagent for synthesis of some aryl chalcones by grinding aryl aldehydes and ketones. Gopalakrishnan et al. (2006, 2007) have reported that fly-ash is one of the good green catalyst for organic synthesis and they synthesized some heterocyclic compounds by solvent free fly-ash catalyzed reaction. The authors wish to report an efficient and selective method for condensation of 4-fluorophenyl methyl ketone with various *m*- and *p*-substituted benzaldehydes under solvent free conditions in presence of fly-ash:water catalyst to yield the respective *E-2-propen-1-ones* and to study the antibacterial, antifungal, insect antifeedant activities and the quantitative structure property relationship from the group frequency. In this method during the reaction of 4-fluoroacetophenone and aldehydes, they decomposed slowly, forming the products in good yield. 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 (Lévai, 2004). The basic skeleton of chalcones is widely figured in natural products and are known to have multipronged activity (Thirunarayanan, 2003, 2008a; Thirunarayanan et al., 2010). Many of the chalcones are used as agrochemicals and drugs (Mirinda et al., 2000; Monostory et al., 2003; Nowakowska, 2007; Majinda et al., 2001; Sitaram Kumar et al., 2007).

2. Experimental

2.1. Materials and methods

All chemicals used were purchased from Sigma–Aldrich and E-Merck chemical company. Fly-ash is collected from Thermal Power Plant-II, Neyveli Lignite Corporation, Neyveli, Tamil Nadu, India. 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. The NMR spectra are recorded in INSTRUM AV300 spectrometer operating at 300 MHz for ^{1}H spectra and 75.46 MHz for ^{13}C spectra in $CDCl_3$ solvent using TMS as internal standard. Electron impact (EI) (70 eV) and chemical ionization mode FAB^{+} mass spectra were recorded with a JEOL JMS600H spectrometer. Microanalyses of all chalcones were performed in Elementar Model Vario EL III Analyzer.

2.2. Synthesis of substituted styryl 4-fluorophenyl ketones (Thirunarayanan, 2009, 2010)

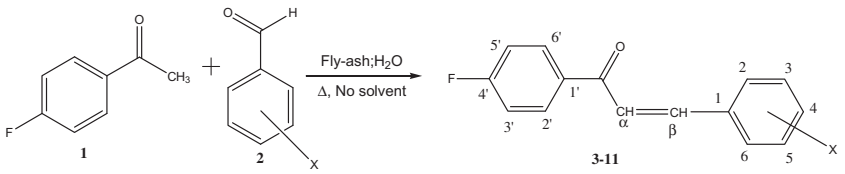
Appropriate mixture of 4-fluoroacetophenone (0.01 mol) and *m*- and *p*- substituted benzaldehydes (0.01 mol), fly-ash (1 g) and 15 ml of water were refluxed for 4 h (Scheme 1). The completion of reaction was confirmed by TLC. The reaction mixture was transferred into a 100 ml corning glass beaker and extracted with 10 ml of dichloromethane. After evaporation of solvent the pure product were obtained more than 65% by recrystallization with ethanol–dioxane mixture and dried in vacuum desiccator. The purity of known compounds was compared with authentic samples of physical constants and spectral data. The characterization data of all chalcones are presented in Table 1 and the spectral data are shown in Tables 2–4.

3. Results and discussion

Various *m*- and *p*-substituted benzaldehydes containing either electron-releasing or withdrawing groups, 4-fluorophenyl methyl ketone, and fly-ash:water were taken in a round bottomed flask and subjected to aldol condensation by refluxation. During the heating the reactants yield the product by decomposition of reactants. The completion of reaction was monitored by TLC. The driving force of the reaction is the heat of formation while the refluxing reactants and fly-ash during which they decompose slowly into the respective *E*-2-propen-1-ones. The yield of the product is more than 65%. The advantages of this method include mild reaction condition, good yield, slow decomposition of the reactants, environmentally benign reaction, eco-friendly nature since no huge hazardous catalyst or solvent is required.

3.1. Spectral study

Spectroscopic technique is a versatile tool for providing information about the structural diagnosis of most of the organic substrates. It also finds its frequent use in the conformational analysis and in understanding the influence of electronic and conformational effects on chemical shifts and coupling constants. ^{1}H and ^{13}C NMR techniques have been extensively applied in deriving stereo chemical information about a wide variety of systems. Vicinal coupling values have been used in conformational analysis as it can give clue about the orientation of the substituent. Quantitative structure activity relationship study and quantitative property relationships study deal the prediction of ground state molecular equilibration (Wang et al., 2005; Mulliken, 1939) of organic substrates such as *s-cis* and *s-trans* isomers α,β-unsaturated ketones (Thirunarayanan et al., 2007) from spectral data. Their use in structure parameter correlations has become popular for studying biological activities (Rajabi et al., 2005), normal co-ordinate (Sharma et al., 2002; Krishnakumar and Ramasamy, 2002) analysis and transition states of reaction mechanisms (Dass, 2001). Infrared spectroscopy is a powerful tool technique for the qualitative and quantitative study of natural and synthetic molecules (Griffiths and Chalmers, 2002). In the importance of material sciences, IR spectroscopy can provide the information about the nature, concentration and structure of samples at the molecular levels (Pellerin and Pelletier, 2005). Numerous works have been devoted to the reactivity of α,β-unsaturated carbonyl compounds particularly, the theoretical aspects of substituent effects were studied on long range interactions in the β-sheet structure (Horváth et al., 2005) of oligopeptides. QSAR study of substituted benzo[α] phenazines (Chen et al., 2005) cancer agents, Diels–Alder reactions (Dumont and Chaquin, 2006), density functional



Entry	3	4	5	6	7	8	9	10	11
X	H	*p*-Br	*m*-Cl	*p*-Cl	*p*-N(CH$_3$)$_2$	*p*-OCH$_3$	*p*-CH$_3$	*o*-NO$_2$	*m*-NO$_2$

Scheme 1 Fly-ash:water catalyzed aldol reaction between 4-fluoroacetophenone and various substituted benzaldehydes.

theory (Senthilkumar et al., 2006), gas phase reactivity of alkyl allyl sulfides (Izadar and Gholami, 2006), rotational barriers in selenomides (Kaur et al., 2006). Moraleda et al. (2006) has been studied the quantitative structural relationships in α,β-unsaturated carbonyl compounds between the half wave reduction potential, the frontier orbital energy and the Hammett σ_p values. Dhami and Stothers (1963a,b) have extensively studied the ^{1}H NMR spectra of a large number of methylketones and styrenes with a view to establish the validity of the additivity of substituent effect in aromatic shielding first observed by Lauterber (1961). Savin et al. (1975) studied the NMR data of unsaturated ketones of the type RC_6H_4–CH═CH–$COMe_3$ and sought Hammett correlations for the ethylenic protons. Solcaniova and Toma (1980) have measured ^{1}H and ^{13}C NMR spectra of substituted styrenes, styryl phenyls and they obtained good Hammett correlations for the olefinic protons and carbons. Now a day's scientists (Sung and Ananthakrishna Nadar, 2000; Thirunarayanan and Ananthakrishna Nadar, 2006a,b; Shanthi and Kabilan, 2007) have paid more interest to correlate the group frequencies of spectral data with Hammett substituent constants to explain the substituent effects of organic compounds. Recently Thirunarayanan (2008b) investigated elaborately the single and multi-substituent effects on alpha and beta hydrogen and carbons of some naphthyl chalcones. Within the above view there is no information available for the study of structure parameter correlation with the help of infrared and NMR spectral data in literature in the past with substituted styryl 4′-fluorophenyl ketones. Hence the authors have obtained the above ketones by fly-ash:water catalyzed crossed Aldol reaction between 4-fluorophenyl methyl ketone and various *m*- and *p*-substituted benzaldehydes and characterized by physical constants, microanalyses and spectral data. In the present study of this section the author evaluates the substituent effects of assigned group frequencies of all chalcones like carbonyl stretches *v*CO, C–F and the deformation modes of vinyl part CH *out of plane*, *in-plane*, CH═CH and >C═C< *out of planes* (cm^{-1}), the vinyl hydrogen and carbons δ(ppm) of H_α, H_β, C_α, C_β, CO are assigned and these frequencies are correlated with various kinds of substituent constants.

3.1.1. Correlation of IR spectral data

The effect of substituents on the infrared carbonyl frequencies has been reported previously in several studies (Thirunarayanan and Ananthakrishna Nadar, 2006a,b; Jones et al., 1957; Krueger, 1973; Stewart and Yates, 1958, 1960; Thirunarayanan and Vanangamudi, 2006b; Thirunarayanan and Jaishankar, 2003; Iida et al., 2007; Arul Kumaran et al., 2010). The carbonyl group stretching frequency can be assumed to be "mass insensitive". The carbonyl group frequency has been successfully correlated with Hammett σ constants in acetophenones (Brown and Okamoto, 1957), benzophenones (Fuson et al., 1954) and benzoyl chlorides (Flett, 1948).

While seeking Hammett correlation involving group frequencies, the form of the Hammett equation employed is

$$v = \rho\sigma + v_o \tag{1}$$

where v_o is the frequency for the parent member of the series.

The series of ketones chosen in the present study possess α,β-unsaturated carbonyl system. They are expected to exist in *s-cis* and *s-trans* conformations are shown in Fig. 1. The carbonyl stretching frequencies (cm^{-1}) of *s-cis* and *s-trans* isomers of present study are presented in Table 2. The stretching frequencies for carbonyl absorption are assigned based on the assignments made by Hays and Timmons (1968). The lowest carbonyl frequency is observed in both the conformers when strongest electron withdrawing groups are present in phenyl ring while the highest frequency is noted when the strongest electron attracting group present in phenyl ring. The same trend was followed for assigned carbonyl frequencies of *s-cis* and *s-trans* conformers. These frequencies are separately analyzed through various Hammett sigma constants using single and multi-regression analysis. The results of the statistical analysis are presented in Table 5. In all the correlation positive ρ values are obtained. This shows that the normal substituent effects operate in all the compounds. In the case of the *s-cis* conformers the correlation of *v*CO with Hammett σ, σ^+ and σ_I values seems satisfactory when H substituent is excluded. The correlation of σ_R is poor. This is due to the conjugative effect on the carbonyl group from the substituent shown in Fig. 2. The multi-regression analysis (Swain and Lupton, 1968) answers satisfactorily with σ_I and σ_R or *F* and *R* parameters. The correlation equations (2) and (3) are:

$$\begin{aligned} v_{\mathrm{CO}(s\text{-}cis)}\ (\mathrm{cm}^{-1}) &= 1646.272(\pm 7.713) + 37.641(\pm 1.814)\sigma_I \\ &\quad + 14.210(\pm 1.845)\sigma_R \\ &\quad (R = 0.900,\ n = 8,\ P > 90\%) \end{aligned} \tag{2}$$

$$\begin{aligned} v_{\mathrm{CO}(s\text{-}cis)}\ (\mathrm{cm}^{-1}) &= 1637.769(\pm 8.107) + 51.586(\pm 1.723)F \\ &\quad + 18.804(\pm 1.12)R\ \ (R = 0.903, \\ &\quad n = 8,\ P > 90\%) \end{aligned} \tag{3}$$

The correlations observed between *v*CO *s-trans* (cm^{-1}) and Hammett sigma constants are presented in Table 5 and all correlations fail including *F* and *R* parameters. This may mean that the substituents are incapable of predicting substituent ef-

Table 1 Physical constants, microanalysis and mass spectral data of substituted styryl 4′-fluorophenyl ketones.

Entry	X	Mol. formula	Mol. weight	Yield (%)	M.p. (°C)	Found (Calcd.)			Mass *m/z*
						C	H	N	
3	H	$C_{15}H_{11}FO$	226	92	132–133 132[a]	–	–	–	226(M^+), 207, 149, 136, 131, 123, 95, 90, 77, 19
4	*p*-Br	$C_{15}H_{10}BrFO$	305	88	117–118	58.93 (59.05)	3.24 (3.27)	–	305(M^+), 307(M^{2+}), 306, 304, 226, 240, 166, 125, 107, 95
5	*m*-Cl	$C_{15}H_{10}ClFO$	260	90	85–86	69.08 (69.11)	3.76 (3.87)	–	260(M^+), 262(M^{2+}), 241, 165, 149, 137, 136, 124, 111, 95, 29, 19
6	*p*-Cl	$C_{15}H_{10}ClFO$	260	87	125–126	69.06 (69.11)	3.74 (3.87)	–	260(M^+), 262(M^{2+}), 241, 149, 137, 136, 111, 95, 29
7	*p*-$N(CH_3)_2$	$C_{17}H_{16}FNO$	269	89	113–114	75.76 (75.82)	5.92 (5.99)	5.16 (5.20)	269(M^+), 250, 225, 174, 149, 136, 133, 120, 95, 29, 19, 15
8	*p*-OCH_3	$C_{16}H_{13}FO_2$	256	90	97–98 98[b]	–	–	–	256(M^+), 241, 237, 225, 161, 149, 136, 133, 123, 107, 95, 95, 31, 19, 15
9	*p*-CH_3	$C_{16}H_{13}FO$	240	91	123–124	79.93 (79.98)	5.39 (5.45)	–	240(M^+), 225, 221, 145, 140, 136, 95, 91, 29, 19, 15
10	*o*-NO_2	$C_{15}H_{10}FNO_3$	271	86	118–119	66.36 (66.42)	3.66 (3.72)	5.09 (5.16)	271(M^+), 255, 252, 176, 149, 136, 135, 95, 29, 19, 16
11	*p*-NO_2	$C_{15}H_{10}FNO_3$	271	91	92–93	66.39 (66.42)	3.68 (3.72)	5.12 (5.16)	271(M+), 255, 252, 149, 136, 95, 29, 16

[a] Iida et al. (2007).
[b] Harrison et al. (2006).

fects independently on carbonyl frequencies as per the reason stated earlier. It is well known that polar and inductive effects (Thirunarayanan and Ananthakrishna Nadar, 2002) less pronounced considerably with distance. The substituents are separated from the carbonyl group by four or more carbon atoms in the compounds.

A comparison of ρ values for two isomers in relation to a constant reveals that their relative abilities to transmit electronic effects are different. The ratio of ρ *cis*/ρ *trans* is 0.762. This result is in accordance with the hypothesis that, as the two conformers have different approaches of degree of coplanarity and their abilities to transmit electronic effects become different.

The assigned νC–F (cm^{-1}) stretches (Kemp, 1987; Silverstein et al., 1963) are presented in Table 2. These frequencies are correlated with various Hammett substituent constants. The results of statistical analysis are presented in Table 5. The correlation of C–F vibrations with σ, σ^+ and σ_R constants gave satisfactory and good result and that with other constants σ_I, F and R fails. Similarly the multiparameter correlations also fail with the above stretches.

The measured deformation modes of C–H *in-plane* and *out of plane* and CH═CH and >C═C< *out of plane* modes in substituted styryl 4′-fluorophenyl ketones are presented in Table 2. The statistical analysis of all observed deformation modes with various Hammett substituent constants are presented in Table 5. In Table 2, the observed deformation modes predict that the reactions occur normally with substituent constants by the absorption trend. In the styryl moiety, with electron withdrawing groups, absorption is higher and with electron donating groups, absorption is lower. This trend fails in present ketones. Because ketones with nitro-group absorb at some what less values. Therefore the correlation is reduced or reversed. The polar effects, inductive and resonance effects of substituents do not affect the above group absorptions. Therefore these substituents reversed their substituent effect and unable to predict the reactivity on the deformation modes.

The correlations of all deformation modes of styryl 4′-fluorophenyl ketones have been done with all kinds Hammett substituents constants. The results of statistical analysis of these ketones are shown in Table 5. In this series of ketones all correlations are very poor including multi-regression analysis. In this series of ketones some of the correlations produce negative ρ values. This shows that the def. modes of vibrations are unable to predict the reactivity through their substituent effects. This is due to the reversal of substituent effect and the conjugative structure affects the effect of substituents on the absorptions in all ketones shown in Fig. 2. The ratio of ρ between –CH *in-plane def. and* –CH *out of plane def.* is −0.60. This value shows that the correlations of all kinds of –CH absorptions with substituent constants are not obeyed.

3.2. NMR spectral correlation

3.2.1. ^1H NMR spectra

The ^1H NMR spectra of nine chalcones under investigation are recorded in deuterochloroform solutions employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons were assigned. They were calculated as AB or AA′ BB′ systems, respectively. The chemical shifts of H_α are at higher field than those of H_β in this series of ketones. The ethylenic protons give an AB pattern and the β-proton doublet

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

Entry	X	Ar–F	Ar–H	CO (*s-cis*)	CO (*s-trans*)	CH*op* vinyl	CH*ip* vinyl	CH=CH*op* vinyl	Substituent in styryl part
3	H	1098.35	3028.27	1662.88	1608.98	764.86	1153.30	1032.81	–
4	*p*-Br	1094.36	2993.26	1665.36	1619.34	772.98	1153.27	1028.31	–
5	*m*-Cl	1082.64	2923.82	1667.04	1603.99	780.65	1156.87	1020.67	–
6	*p*-Cl	1088.29	3065.51	1661.53	1607.00	784.22	1157.63	1021.08	–
7	*p*-$N(CH_3)_2$	1073.75	2923.82	1662.14	1601.03	732.65	1157.46	1010.70	3332.55 (–$N(CH_3)_2$)
8	*p*-OCH_3	981.06	2988.03	1659.91	1604.54	742.54	1149.49	1021.75	1231.78 (C–O–C)
9	*p*-CH_3	1030.05	3031.04	1659.16	1606.34	739.86	1152.36	1096.61	2852.81 (CH_3)
10	*o*-NO_2	1014.95	3054.93	1667.87	1626.15	750.06	1127.94	1072.50	1510.32 (–NO_2)
11	*m*-NO_2	1004.85	2998.24	1669.83	1625.25	744.92	1159.75	1020.09	1525.25 (–NO_2)

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

Entry	X	4′-F Ph ring (m, 4H)	H_α (d, 1H)	H_β (d, 1H)	Styryl Ph ring (m, 4H)	Substituent in styryl part
3	H	8.022–8.079	7.493 (J = 15.6 Hz)	7.829 (J = 15.6 Hz)	7.125–7.414	–
4	*p*-Br	7.960–8.231	7.563 (J = 16.4 Hz)	7.823 (J = 16.4 Hz)	7.201–7.528	–
5	*m*-Cl	8.025–7.076	7.513 (J = 16.5 Hz)	7.746 (J = 16.5 Hz)	7.138–7.393	–
6	*p*-Cl	8.026–8.072	7.498 (J = 15.6 Hz)	7.780 (J = 15.6 Hz)	7.146–7.258	–
7	*p*-$N(CH_3)_2$	8.032–8.049	7.356 (J = 15.8 Hz)	7.765 (J = 15.8 Hz)	6.867–7.247	2.023 (s, 6H, $N(CH_3)_2$)
8	*p*-OCH_3	8.036–8.054	7.394 (J = 15.3 Hz)	7.801 (J = 15.3 Hz)	7.119–7.246	3.873 (s, 3H, (OCH_3))
9	*p*-CH_3	8.023–8.075	7.490 (J = 15.6 Hz)	7.825 (J = 15.6 Hz)	7.137–7.259	2.390 (s, 3H, (CH_3))
10	*o*-NO_2	8.080–8.164	7.590 (J = 15.7 Hz)	7.731 (J = 15.7 Hz)	7.268–7.318	–
11	*p*-NO_2	8.063–8.500	7.646 (J = 15.9 Hz)	7.853 (J = 15.9 Hz)	7.248–7.617	–

Table 4 ^{13}C NMR spectral data (δ, ppm) of substituted styryl 4′-fluorophenyl ketones.

Entry	X	CO	C_α	C_β	C_1	C_2	C_3	C_4	C_5
3	H	188.73	121.46	144.99	134.68	128.74	130.62	128.44	130.62
4	*p*-Br	188.76	121.54	144.74	134.62	128.53	131.64	122.65	131.64
5	*m*-Cl	188.24	122.46	143.35	136.65	126.57	134.45	127.16	130.71
6	*p*-Cl	188.45	121.85	143.48	133.02	129.24	129.57	134.30	129.57
7	*p*-$N(CH_3)_2$	188.85	119.32	145.30	123.11	127.58	115.46	148.51	115.46
8	*p*-OCH_3	188.80	119.12	144.87	130.24	129.41	114.38	161.70	114.38
9	*p*-CH_3	188.85	120.45	145.11	131.96	128.48	129.69	141.20	129.48
10	*o*-NO_2	188.92	125.03	148.47	130.41	140.43	125.03	129.24	133.55
11	*m*-NO_2	187.89	122.25	141.84	136.45	124.03	148.66	122.23	130.05

		C_6	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	Substituent in styryl part
3	H	128.74	134.47	134.43	115.85	167.23	115.85	134.43	–
4	*p*-Br	128.74	133.68	131.49	116.92	168.93	119.92	131.49	–
5	*m*-Cl	122.71	134.73	131.56	115.75	167.32	115.85	131.56	–
6	*p*-Cl	129.24	136.52	131.18	115.92	167.32	115.92	131.18	–
7	*p*-$N(CH_3)_2$	127.58	134.74	131.00	115.75	167.35	115.75	131.00	45.63 ($N(CH_3)_2$)
8	*p*-OCH_3	129.41	134.71	130.98	115.75	167.09	115.75	130.98	55.37 (OCH_3)
9	*p*-CH_3	128.48	134.67	131.06	115.79	167.17	115.79	131.06	21.51 (CH_3)
10	*o*-NO_2	126.95	133.59	131.37	116.03	168.02	116.03	131.37	–
11	*p*-NO_2	131.28	133.84	131.15	116.08	167.53	116.08	131.15	–

in most cases is well separated from the signals of the aromatic protons. The assigned chemical shifts of the ethylenic protons are presented in Table 3.

In nuclear magnetic resonance spectra, the proton or the ^{13}C chemical shifts (δ) depend on the electronic environment of the nuclei concerned. These shifts can be correlated with reactivity parameters. Thus the Hammett equation may be used in the form as

$$\log \delta = \log \delta_0 + \rho\sigma \quad (4)$$

where δ_0 is the chemical shift in the corresponding parent compound.

The assigned H_α and H_β proton chemical shifts (ppm) are correlated with various Hammett sigma constants. The results of statistical analysis are presented in Table 5. All the attempted correlation involving substituent parameters gave only positive ρ value. This shows that the normal substituent

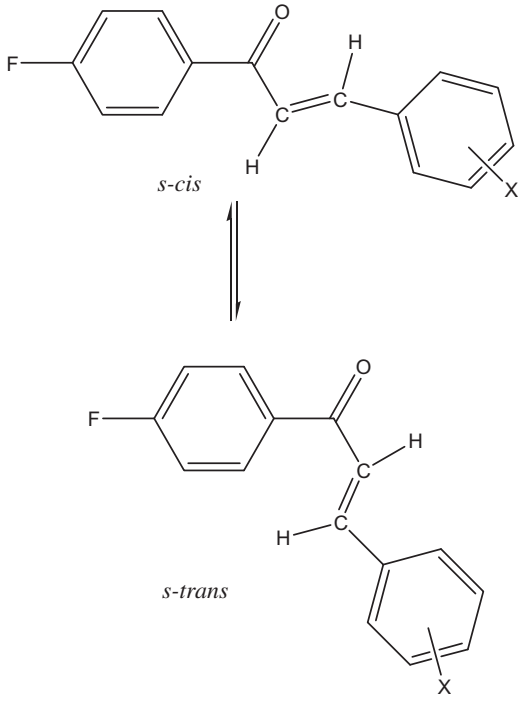


Figure 1 The *s-cis* and *s-trans* conformers of substituted styryl 4′-fluorophenyl ketone.

effect operates in all chalcones. The H_α proton chemical shifts satisfactorily correlate with Hammett substituent constants. The σ_I constants produce the correlation excluding the methoxy substituent in styryl part. The correlations of H_β proton chemical shifts with Hammett σ and σ_I constants are satisfactory excluding nitro substituents in styryl part and with the other constants fail.

From Table 5 the r values show that the substituents predicting the reactivity on H_α and H_β are not equal in all ketones. This is in contrast to the findings of Solcaniova and Toma (1980). In fact the extent of transmission of electrical effect is almost same from the substituents to H_α and H_β in the present investigation. It has been the observation of Solcaniova et al. (1976) that the chemical shifts of the β-protons do not correlate with any type of substituent parameters. But in the present investigation the chemical shifts of both protons correlate satisfactorily with Hammett sigma constants.

Application of Swain–Lupton (Swain and Lupton, 1968) treatment to the relative chemical shifts of H_α and H_β with F and R values is successful with either resonance, inductive or F and R parameter generates the multi-regression equations (5)–(8):

$$\delta_{H_\alpha}\ (\text{ppm}) = 7.440(\pm0.043) + 0.195(\pm0.011)\sigma_I + 0.472(\pm0.010)\sigma_R \quad (R = 0.900,\ n = 8,\ P > 90\%) \tag{5}$$

$$\delta_{H_\alpha}\ (\text{ppm}) = 7.518(\pm0.022) + 0.091(\pm0.040)F + 0.207(\pm0.011)R \quad (R = 0.963,\ n = 8,\ P > 95\%) \tag{6}$$

$$\delta_{H_\beta}\ (\text{ppm}) = 7.816(\pm0.024) + 0.073(\pm0.005)\sigma_I + 0.730(\pm0.010)\sigma_R \quad (R = 0.901,\ n = 8,\ P > 90\%) \tag{7}$$

$$\delta_{H_\beta}\ (\text{ppm}) = 7.829(\pm0.033) + 0.816(\pm0.071)F + 0.496(\pm0.043)R \quad (R = 0.900,\ n = 8,\ P > 90\%) \tag{8}$$

3.2.2. ^{13}C NMR spectra

Physical organic chemists and scientists (Annapoorna et al., 2002; Dhami and Stothers, 1963a,b; Thirunarayanan, 2007a,b) have made an extensive study of ^{13}C NMR spectra for a large number of different ketones and styrenes. They found a linear correlation of the chemical shifts of C_β carbons with Hammett σ constants in styrenes. Attempts to correlate the C_α chemical shifts with any kind of σ constants fail in their systems. An attempt is made in the present investigation to determine substituent effects on vinyl C_α, C_β and carbonyl carbon chemical shifts of the 4′-fluorophenyl chalcones to what extent. The ^{13}C chemical shifts of vinyl C_α, C_β and carbonyl carbons of all ketones are given in Table 4.

The chemical shifts (ppm) observed for the carbonyl carbons are correlated with Hammett constants and the results of statistical analysis are presented in Table 5. All correlations gave negative slopes with fair degree of r values. This negative slope shows that the substituent effect reverses on the carbonyl carbon absorptions in all ketones. The correlation of σ, σ^+ and σ_I constants with $\delta_{C=O}$ (ppm) are satisfactory excluding some substituents such as nitro and methoxy groups and when they are included, the correlation fails. Poor correlation was obtained with σ_R constants. This is due to the reason stated earlier that the conjugation exists between the substituent and the carbonyl group shown in Fig. 2.

In view of the inability of some of the σ constants to produce individually satisfactory correlations, it was thought worthwhile to seek multiple correlations involving either σ_I and σ_R constants or Swain–Lupton (Swain and Lupton, 1968) F and R parameters produce Eqs. (9) and (10):

$$\delta_{C=O}\ (\text{ppm}) = 188.834(\pm0.216) + 0.746(\pm0.050)\sigma_I + 0.129(\pm0.060)\sigma_R \quad (R = 0.900,\ n = 8,\ P > 90\%) \tag{9}$$

$$\delta_{C=O}\ (\text{ppm}) = 188.750(\pm0.272) - 0.623(\pm0.058)F + 0.193(\pm0.039)_R \quad (R = 0.900,\ n = 8,\ P > 90\%) \tag{10}$$

The ^{13}C chemical shift (ppm) values of vinyl carbons of all ketones are correlated with various Hammett substituent constants. The results of statistical analysis of substituent effects on carbonyl carbons are shown in Table 5. Satisfactory correlations obtained with C_α carbon chemical shifts and produce positive ρ values with σ and σ^+ constants. This implies that the normal substituent effect operates in all constants with C_α carbons in all ketones. The negative ρ values in σ_I and σ_R constants imply that the substituent effects are reversed in these constants and give poor correlation. This is due to the fact that the resonance and inductive effects are not operating considerably for prediction of reactivity through the conjugative structure of all chalcones in Fig. 2. The Swain–Lupton

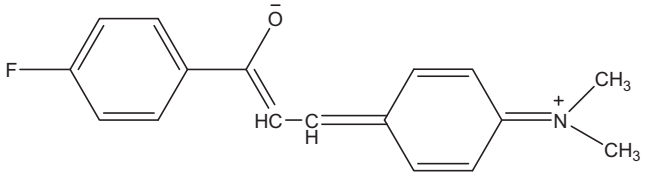


Figure 2 Resonance structure of chalcone.

(Swain and Lupton, 1968) parameters correlation also fails within these carbon chemical shifts. The individual correlations of C_β carbon chemical shifts with Hammett σ, σ^+ and σ_I constants produce satisfactory correlation excluding *p*-CH_3 substituent and fail with σ_R constants. All correlations gave negative ρ values. The negative ρ values imply that the substituent effect is reversed within these constants. The degree of transmission of substituent effect is found to be high in C_α chemical shifts than C_β carbon chemical shifts. Uniformly σ_I and σ_R parameters or F and R values adequately explain substituent effects in all cases as evidenced from the correlation equations (11) and (12) are

$$\delta_{C_\alpha}\ (\text{ppm}) = 144.153(\pm 1.110) - 3.182(\pm 2.650)\sigma_I - 0.288(\pm 2.650)\sigma_R \quad (R = 0.900,\ n = 8,\ P > 90\%) \tag{11}$$

$$\delta_{C_\beta}\ (\text{ppm}) = 143.148(\pm 1.168) - 1.918(\pm 2.438)F - 2.774(\pm 1.708)R \quad (R = 0.918,\ n = 8,\ P > 90\%) \tag{12}$$

3.3. Microbial activities

Chalcones possess a wide range of biological activities such as antibacterial (Sivakumar et al., 2007), antifungal (Lahtcher et al., 2008), antiviral (Trivedi et al., 2007), antifeedant (Thirunarayanan, 2008a; Thirunarayanan et al., 2010) anticancer (Modzelewska et al., 2006), antimalarial (Dominguez et al., 2005), anti-tuberculosis (Lin et al., 2002), antiAIDS (Deng et al., 2007) and antioxidant (Werber et al., 2005) activities. These multipronged activities present in different chalcones are intended to examine their above activities against respec-

Table 5 Results of statistical analysis of group frequencies of substituted styryl 4′-fluorophenyl ketones with Hammett substituent constants σ, σ^+, σ_I, and σ_R.

Frequency	Constants	*r*	ρ	*I*	*s*	*n*	Correlated derivatives
ν_{C-F} (cm^{-1})	σ	0.910	3.840	1016.57	0.15	8	*p*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ^+	0.992	6.245	1021.65	0.11	8	*p*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_I	0.683	3.867	1048.41	0.12	9	H, *p*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_R	0.900	6.434	1628.73	1.60	8	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
$\nu_{CO(s\text{-}cis)}$ (cm^{-1})	σ	0.900	8.940	1657.70	0.15	7	*m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ^+	0.900	12.465	1659.04	0.16	7	*m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_I	0.900	32.817	1648.41	0.12	7	*m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_R	0.713	14.444	1658.73	1.60	8	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
$\nu_{CO(s\text{-}trans)}$ (cm^{-1})	σ	0.769	11.723	1607.37	5.41	9	H, *m*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ^+	0.684	6.456	1609.46	6.13	9	H, *m*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_I	0.817	16.462	1603.60	6.71	9	H, *m*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_R	0.846	10.887	1609.29	7.17	9	H, *m*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
δ_{H_α} (ppm)	σ	0.930	0.171	7.479	0.03	8	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ^+	0.936	0.106	7.511	0.03	8	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_I	0.900	0.211	7.433	0.71	8	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_R	0.983	0.113	7.505	0.09	7	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-CH_3, *o*-NO_2, *m*-NO_2
δ_{H_β} (ppm)	σ	0.900	0.692	7.792	0.35	7	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *m*-NO_2
	σ^+	0.673	0.015	7.701	0.46	9	H, *m*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_I	0.910	0.458	7.805	0.31	7	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2
	σ_R	0.726	0.490	7.790	0.48	9	H, *m*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
δ_{CO} (ppm)	σ	0.903	−0.381	188.64	0.33	7	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *m*-NO_2
	σ^+	0.900	−0.230	188.57	0.33	6	H, *m*-Cl, *p*-Cl, *p*-OCH_3, *p*-CH_3, *m*-NO_2
	σ_I	0.902	−0.700	188.81	0.32	7	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *m*-NO_2
	σ_R	0.781	−0.132	188.58	1.43	9	H, *p*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
δ_{C_α} (ppm)	σ	0.905	0.053	120.37	0.23	8	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ^+	0.900	0.400	120.42	0.23	9	H, *p*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_I	0.805	−0.736	120.61	0.71	9	H, *p*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
	σ_R	0.175	−1.330	120.32	1.25	8	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2
δ_{C_β} (ppm)	σ	0.911	−2.589	143.47	1.40	7	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *o*-NO_2, *m*-NO_2
	σ^+	0.906	−1.540	143.00	1.45	7	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *o*-NO_2, *m*-NO_2
	σ_I	0.900	−3.280	144.19	1.73	7	H, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *o*-NO_2, *m*-NO_2
	σ_R	0.613	−0.878	143.36	2.35	9	H, *p*-Br, *m*-Cl, *p*-Cl, *p*-N(CH_3)$_2$, *p*-OCH_3, *p*-CH_3, *o*-NO_2, *m*-NO_2

r = Correlation coefficient; ρ = slope; *I* = intercept; *s* = standard deviation; *n* = number of substituents.

Table 6 Antibacterial activity of substituted styryl 4′-fluorophenyl ketones.

Entry	X	*E. coli*	*S. aureus*	*Pseudomonas*	*Klebsiella*	*P. vulgaris*	*Entrococcus faecalis*
3	H	±	+	±	±	±	—
4	*p*-Br	+ +	+ +	+	+ +	+	+ +
5	*m*-Cl	+	+	+	+	+	—
6	*p*-Cl	+	+	+	+	+	—
7	*p*-$N(CH_3)_2$	+ +	+ +	+ +	+	+	—
8	*p*-OCH_3	+	+	+	+	+	+ +
9	*p*-CH_3	±	+	±	±	±	—
10	*o*-NO_2	+	+	+	+	+	—
11	*p*-NO_2	+	+	+	+	+	—

Disc size: 6.35 mm; duration: 24–45 h; standard: ampicillin (30–33 mm) and streptomycin (20–25 mm); control: methanol; —: no activities; ±: active (8–12 mm); +: moderately active (13–19 mm); + +: active (20–24 mm).

Table 7 Antifungal activities of substituted styryl 4′-fluorophenyl ketones.

Entry	X	Disc diffusion technique (250 μg/ml)	Drug dilution method (50 μg/ml)	
		Candida albicans	*Penicillin*	*Aspergillus niger*
3	H	—	—	—
4	*p*-Br	+ +	+ +	+ +
5	*m*-Cl	—	±	+
6	*p*-Cl	±	—	—
7	*p*-$N(CH_3)_2$	±	+ +	+ +
8	*p*-OCH_3	+ +	+ +	+
9	*p*-CH_3	+	+	—
10	*o*-NO_2	—	—	—
11	*p*-NO_2	—	—	—

Standard: griseofulvin and gentamycin; duration: 72 h; control: methanol; medium: potato dextrose agar; + +: no fungal colony; +: one fungal colony; ±: two–three fungal colonies; —: heavy fungal colony.

Table 8 Antifeedant activity of substituted styryl 4′-fluorophenyl ketones.

Entry	X	4–6 pm	6–8 pm	8–10 pm	10–12 pm	12–6 am	6–8 am	8 am–12 Nn	12 Nn–2 pm	2–4 pm	Total leaf disc consumed in 24 h
3	H	1	1	0.5	0.5	0.5	1	1	1	1	8
4	*p*-Br	0.5	0.25	0.25	0.5	0.5	0.5	1	1	0.5	0.5
5	*m*-Cl	0.5	0.5	0.25	1	0.5	0.5	0.25	0.25	0.25	0.4
6	*p*-Cl	0.25	0.25	0.25	0	0	0.25	0	0	0	0.1
7	*p*-$N(CH_3)_2$	1	2	2	1	0	0	1	1	1	9
8	*p*-OCH_3	1	0.5	0.5	1	1	0	1	1	1	9
9	*p*-CH_3	0.5	0.5	0.5	2	2	1	1	1	1	9
10	*o*-NO_2	2	3	3	1	1	1	0.5	1	0	12
11	*p*-NO_2	1	2	2	2	1	0.5	0.5	1	0	10

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

tive microbes-bacteria's, fungi and insect antifeedant activities against caster *semilooper*.

3.3.1. Antibacterial activity

The antibacterial activities of all prepared chalcones were evaluated against two gram positive pathogenic strains *Staphylococcus aureus*, *Entrocccus faecalis* while *Escherichia coli*, *Klebsiella* species, *Psuedomonas* and *Proteus vulgaris* were the gram negative strains. The disc diffusion technique was followed using the Kirby–Bauer (Bauer et al., 1996) method, at a concentration of 250 μg/ml with ampicillin and streptomycin taken as the standard drugs. The measured antibacterial activities of all chalcones are presented in Table 6. Against *E. coli*, two compounds **4** and **7** show maximum zone inhibition with greater than 20 mm while **3**, **5**, **6**, **8**, **9**, **10** and **11**. The chalcones **4** and **7** were active against *Staphylococcus*, showing maximum inhibition. The other chalcones show less effectiveness against *S. aureus*. Three chalcone derivatives **3**, **7** and **8** are more active against *Pseudomona* at greater than 20 mm zone inhibition and the other derivatives inhibit the growth of bacterial between 12 and 19 mm zone inhibitions. The chalcones **4**, **7** and **8** are effective against *Klebsiella* in 20–24 mm zone inhibition while the other ketones show a moderate activity. The chalcones **3**, **4**, **7** and **9** are active when they are screened against *P. vulgaris*

Table 9 Antifeedant activity of compound **6** (2*E*)-1-(4′-fluorophenyl)-3-(-*p*-chlorophenyl)-2-propen-1-one at four 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 am–6 am	6–8 am	8 am–12 Nn	12 Nn–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

and the other compounds are less effective. The chalcones **4** and **8** shows moderate activities against *E. faecalis* when then are screened with 13–19 mm zone inhibition.

3.3.2. Antifungal activity

Measurement of antifungal activities of all chalcones were done using *Candida albicans* as the fungal strain and the disc diffusion technique was followed for the antifungal activity while the two other stains *Penicillium* species and *Aspergillus niger*, the dilution method was adopted. The drugs dilution was 50 μg/ml. *Grisseofulvin* is taken as the standard drug. The observed antifungal activities of all chalcones are presented in Table 7. The antifungal activities of all chalcones against *C. albicans*, the two compounds **4** and **8** are effective at 20 mm as the zone inhibition with 250 μg/disc while chalcones **7** and **8** are active at 13–19 mm zone inhibition and the ketones **3** and **5** are the least active in 8–12 mm zone inhibitions. Against *Penicillum* species, compound **4** is visible while development of the fungal colony and 2–3 colonies was recorded for the compounds **8**. The chalcones inhibition against *A. niger* was less in two compounds **4** and **7** being highly active followed by **8**. Presence of a methoxy, methyl, dimethyl and bromo substituents are responsible for antimicrobial activities of chalcones.

3.3.3. Insect antifeedant activity

The multipronged activities present in different chalcones are intended to examine their insect antifeedant activities against caster *semilooper*. The larvae's of *Achoea janata* L. were reared as described on the leaves of caster *Riclmus cammunls* in the laboratory at the temperature range of 26 ± 1 °C and a relative humidity of 75–85%. The leaf-disc bioassay method (Thirunarayanan, 2008a) 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.

3.3.3.1. Measurement of insect antifeedant activity of chalcones. Leaf discs of a diameter of 1.85 cm were punched from caster 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 rest, 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 consumptions was measured by Dethlers (Dethler, 1947) method. The observed antifeedant activity of chalcones was presented in Table 8.

The results of the antifeedant activity of 2-propen-1-ones presented in Table 8 reveal that the compounds **4**–**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**, **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, and the activity also decreased. It is observed from the results in Table 9 and that the ketone **6** *(2E)-1-(4′-fluorephenyl)-3-(3-chlorophenyl)-2-propen-1-one* shows an appreciable antifeedant activity at 200 ppm concentration.

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