

Synthesis And Herbicidal Activity Of (E)- 4-Oxo-4-Phenyl-2-Butenoate Derivatives Against Phalaris Minor: Structure Activity Relationships

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Abstract: Analogues of (E)- 4-oxo-4-phenyl-2-butenates, structurally related to phenolics and cinnamates, the allelochemicals of wheat and *Oxalis pes-caprae* L. respectively, have been synthesized and evaluated for their seed germination inhibition activity against *Phalaris minor*, a problematic weed of wheat.

Substituted (E)-4-oxo-4-phenyl-2-butenates were found to exhibit good activity at the tested concentrations 20,40,60,80 and 100 mg litre⁻¹. The activity was compared with standard herbicide, pendimethalin. It was observed that with the increase in concentration of the test solution, the activity also increased. The electron withdrawing groups at benzene rings contribute to increase the activity while electron donating groups decrease the activity significantly.

The compounds are good seed germination inhibitors of *Phalaris minor* under laboratory conditions. The results suggest that the chemical class of substituted 4-oxo-4-phenyl-2-butenates may be developed as potential herbicides to manage *Phalaris minor*. However further experiments are required to ascertain the efficacy of compounds at field level.

Keywords: Allelopathy, (E)-4-oxo-4-phenyl-2-butenates, *Phalaris minor*, herbicidal activity, herbicide, structure and activity relationships

I. INTRODUCTION

Little seed canary grass, *Phalaris minor* is one of the most problematic weeds of wheat. The weed has developed resistance to isoproturon which is one of the effective herbicides to control it (1,2). The case of *P. minor* is not in isolation. Excessive and indiscriminate use of herbicides has resulted in the occurrence of herbicide resistant weeds. An International survey conducted has estimated 194 weed species (114 dicots and 80 monocots) to have acquired resistance against important herbicides (3). Therefore, there is always a necessity to develop efficient herbicides with novel structures and modes of action to overcome the problem of the

resistance of weeds to herbicides. Furthermore, now-a-days in view of environmental concerns like non-biodegradability of pesticides, persistence of pesticides in soil and water for long duration and pesticide residue problem in crops and vegetables, there has been a paradigm shift in the pesticide development strategies. Recently allelopathy has been accepted as one of the best strategies for the development of pesticides. Allelochemicals present in plants have ecological implications as bio-communicators in nature. They are potential source of models of new structural types of herbicides that can be helpful in controlling the herbicide resistant weeds. (4,5)

Three major groups of the allelochemicals identified in wheat are phenolic acids, especially cinnamic acids (6,7) hydroxamic acids (8-11) and short chain fatty acids (12,13). The two hydroxamic acids found in wheat, 2,4-dihydroxy-7-methoxy-1,4-benzoxazin-3-one(DIMOBA) and 2,4-dihydroxy-1,4-benzoxazin-3-one(DIBOA) have been studied extensively for their herbicidal activity by synthesizing their synthetic analogues (14-18) whereas derivatives of cinnamic acids were studied first time by our group by synthesizing a large number of analogues to evaluate their herbicidal potential (19).

Also, in the search of new phytotoxic natural compounds, the chemical investigations carried out by Greca, *et. al.* (20) on the plant *Oxalis pes-caprae* L. (Oxalidaceae) have revealed the presence of (*E*)-3- methoxyphenyl-4-hydroxy cinnamate, a cinnamic acid ester in the plant ,exhibiting potential allelopathic activity.

In the present study, substituted (*E*)-4-oxo-4-phenyl-2-butenates have been synthesized and investigated for their herbicidal activity keeping in view their structural similarity to cinnamic acid esters. Scaffolds of (*E*)-4-oxo-4-phenyl-2-butenates have been designed by structural modification (Figure 1) of cinnamic acid esters scaffold by inserting one additional carbonyl (C=O) group in basic structure of cinnamic acid ester.

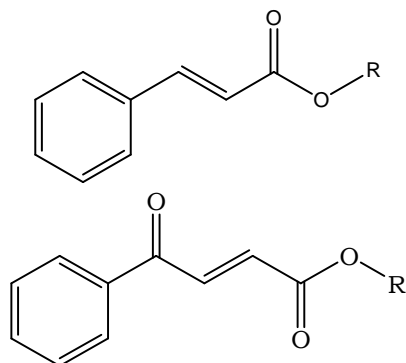


Figure 1: Structure of cinnamic acid ester and (*E*)-4-oxobut-2-enoic ester

Aryl and heteroaryl substituted (*E*)-4-oxobut-2-enoic acid derivatives represent an important class of compounds with diverse pharmacological activities including antiulcer, cytoprotective, kynurenine-3-hydroxylase and human cytomegalovirus protease inhibiting activity (21). Butenoic acid esters are found to exhibit antagonistic activity against phospholipase A2, inhibition activity against snake venom PLA2 and neoplastic He La cells (22). These compounds also exhibit anticancer, antimicrobial, antifungal and antagonistic activity (23). The compounds (*E*)-4-oxobut-2-enoates have not been studied for their herbicidal activity. To the best of our knowledge, we are first to report herbicidal activity of this class of compounds.

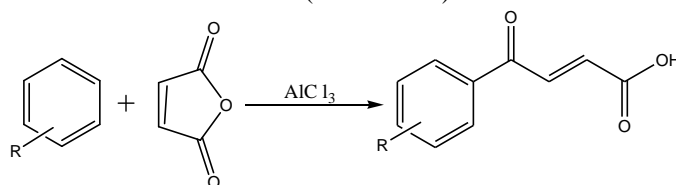
II. MATERIALS AND METHODS

A. GENERAL

Melting points were determined on a Buchi B-540 apparatus and are uncorrected. UV spectra were recorded by

Genesys 10 UV-VIS spectrophotometer. ¹H NMR spectra were recorded on a Bruker Avance 400 NMR spectrophotometer, and IR spectra were recorded on a Bruker IR spectrophotometer. The chemicals benzene, toluene, ethylbenzene, chlorobenzene, bromobenzene, acetophenone, 4-chloroacetophenone, 4-nitroacetophenone, 4-methoxyacetophenone, maleic anhydride were purchased from Hi-Media Ltd.(Bombay, India) .All compounds were of 99.7-99.9 percent purity .Pendimethalin (stomp 30 EC) was obtained from M/S BASF, India. The *Phalaris minor* seeds were obtained from N.E. Borloug Crop Research Centre, G. B. Pant University of Agriculture and Technology, Pantnagar, India.

B. SYNTHESIS OF SUBSTITUTED 4-OXO-4-PHENYL-2-BUTENOIC ACIDS (SCHEME 1)

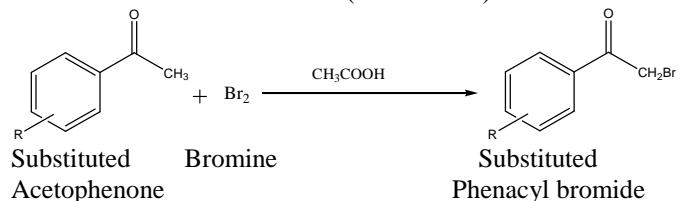


Substituted Benzene + Maleic anhydride → Substituted 4-oxo-4-phenylbut-2-enoic acid

R= H, -CH₃, -C₂H₅Cl, -Br, -CHO, -OH, -OCH₃

The compounds (*E*)-4-oxo-4-phenyl-2-butenic acids were prepared by Friedel-Craft's acylation of substituted benzene with maleic anhydride (24). A 500 ml flask equipped with a magnetic stirring bar, thermometer and condenser was charged with maleic anhydride 24.5g (0.25 mole) and 150 ml of substituted benzene. To the mixture was added in portions, 72g (0.54 mole) of aluminium chloride at room temperature. The mixture was stirred at 80°C for 30 minutes. Then the contents of flask were poured into 300 ml ice water and 75ml concentrated hydrochloric acid was added to the mixture. The solution was extracted with 2X350 ml ethylacetate. The organic layer was dried over 20g of anhydrous magnesium sulphate and filtered. The filtrate was concentrated under reduced pressure to give 4-oxo-4-phenyl-2-butenic acids.

C. SYNTHESIS OF SUBSTITUTED PHENACYLBROMIDES (SCHEME 2)

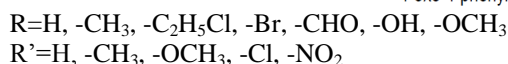
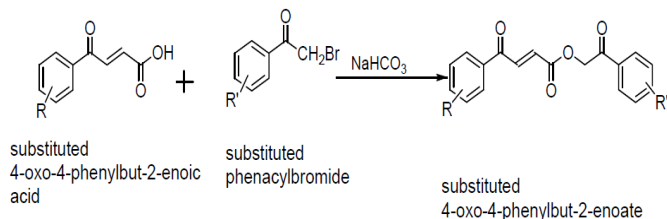


R=H, -CH₃, -OCH₃, -Cl, -NO₂

Phenacylbromides were prepared by bromination of substituted acetophenones (25).To a round bottom flask, solution of 0.025 mole of substituted acetophenone in 10 ml of glacial acetic acid was introduced. To this 4g (1.25ml, 0.025mole) of bromine was added from a dropping funnel. The mixture was stirred vigorously during the addition at the temperature below 20°C. Phenacylbromide commences to separate as needles after about half of the bromine has been

introduced. After the addition of bromine, the mixture was cooled in ice water. Crude product was filtered and washed with 50% alcohol until colorless product obtained. Crude product was obtained by crystallization from ethyl alcohol.

D. SYNTHESIS OF 4-OXO-4-PHENYL-2-BUTENOATES (SCHEME 3)



Esters have been prepared by using substituted acids prepared in Scheme-1 and substituted phenacylbromides prepared in Scheme-2 (26). To a round bottom flask, substituted 4-oxo-4-phenylbut-2-enoic acid (1.25 mmole) and substituted phenacyl bromide (1.375 mmole) were added. To the mixture 3.7ml DMF and a 0.10g (1.25 mmole) of sodium bicarbonate were added. The reaction mixture was heated on water bath at 80°C and cooled to room temperature. Then it was extracted with ethyl acetate. The organic layer was separated and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure. Crude product was crystallized from ethyl alcohol.

E. BIOLOGICAL EVALUATION

The method applied is same as described by us earlier (19). Stock solution of 100 mg l⁻¹ of each synthesized compound was prepared by dissolving the compound in minimum amount of DMSO and then making up with distilled water. One drop of surfactant Tween-20 solution (3 ml/lit) was also added to the test solution prior to making up the volume. Stock solution of standard pendimethalin was also prepared in the same way taking into account the presence of 30 percent active ingredient in it. Test solutions of 80, 60, 40 and 20 mg l⁻¹ were prepared by serial dilution of stock solution. Seeds of *P. minor* were surface sterilized with distilled water followed by 95% ethanol for 20 sec and finally with distilled water. Twenty seeds were taken in each Petri dish. Seed germination paper was placed in the Petri dishes to which 7 mL of test solution was poured. A mixture of distilled water/ DMSO / Tween-20 (97: 2.5: 0.5) was taken as the control. All treatments were taken in triplicate. Petri dishes containing *P. minor* seeds were put at 19±2°C in incubation with 12 hr photoperiod and 12 hr dark period. The germination process was observed, numbers of seeds germinated in each Petri dish were counted.

F. STATISTICAL ANALYSIS

The percent seed germination inhibition values were determined and were subjected to analysis of variance (ANOVA). Critical differences (CDs) were calculated at 5 percent probability. IC₅₀ values were calculated by interpolation from linear regression analysis.

III. RESULTS

Symptomology of seedlings: Germination of seeds in control started at 4th day and completed within 6 days while in treated seeds germination delayed by one to two days. The shoot lengths of treated seedlings were 20-30 percent shorter and root lengths were 20-25 percent shorter than control. The colour of seedlings in control was dark green while in treated seedlings the colour was yellowish. After 15 days treated seedlings dried while in control the seedlings were green and healthy. After 15 days experiment was stopped.

Total 18 compounds of (*E*)- 4-oxo-4-phenyl-2-butenate derivatives were synthesized (Figures 3). The set of 18 compounds was subjected to ANOVA using the seed germination inhibition data. IC₅₀ values and Critical Differences (CDs) between compounds including standard pendimethalin and between different concentrations of individual compound are presented in Table 1.

The basic structure of compounds is made up of two moieties, consisting of two benzene rings, ring A and ring B. Benzene ring A is of acid moiety and B that of alcohol moiety. Henceforth, in the discussion ring A and ring B will be stated as 'benzene ring of acid moiety' and 'benzene ring of alcohol moiety' respectively. Different structures have been obtained by varying the substituents R and R' on two benzene rings.

In all, the six substituents (three electron releasing -CH₃, -C₂H₅, and -OCH₃ and three electron withdrawing -Cl, -Br and -NO₂) and two sites (benzene ring of acid moiety and benzene ring of alcohol moiety) for substitution have been used to obtain eighteen analogues.

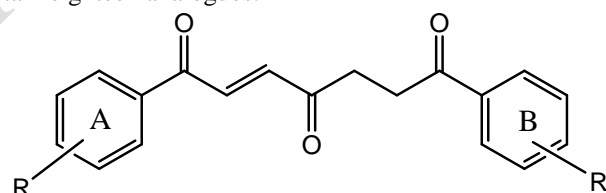
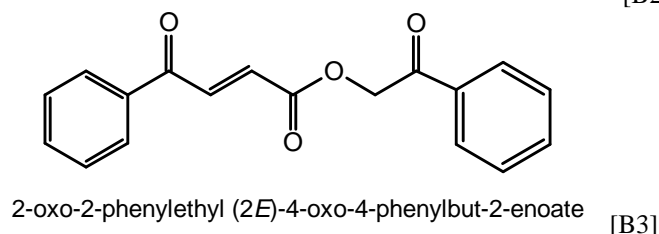
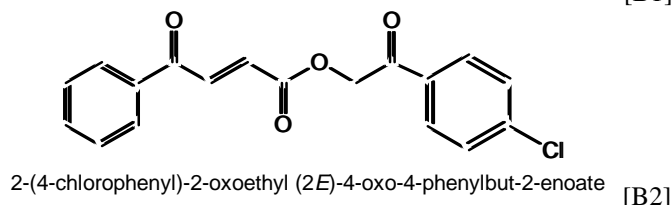
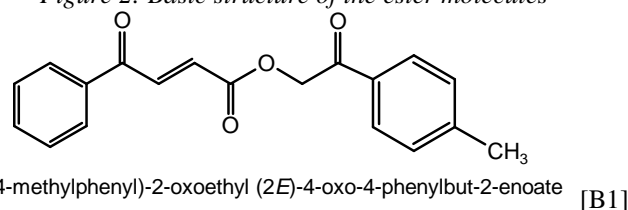


Figure 2: Basic structure of the ester molecules



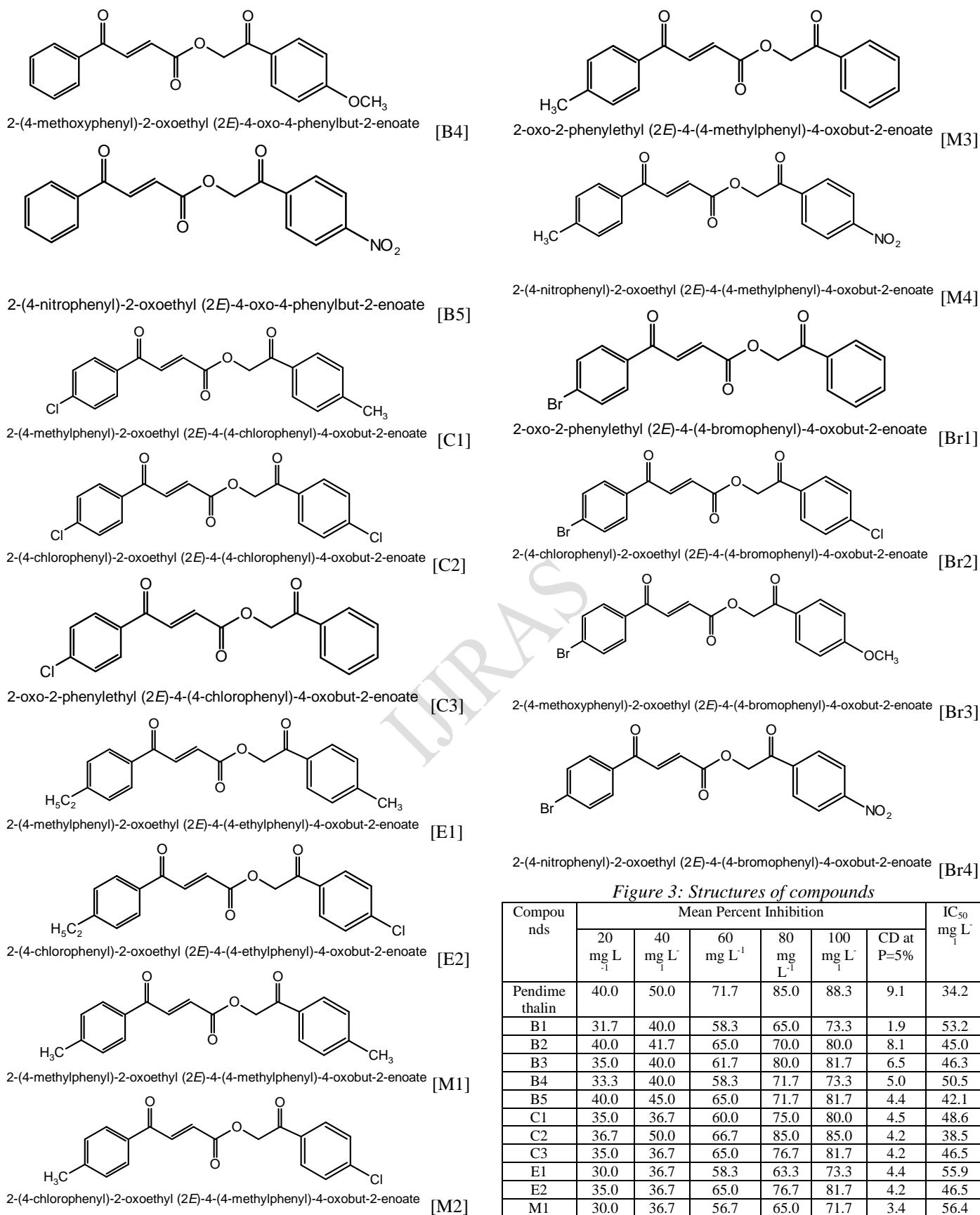


Figure 3: Structures of compounds

| Compounds | Mean Percent Inhibition | | | | | | IC ₅₀ mg L ⁻¹ |
|-------------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------|---------------|--|
| | 20 mg L ⁻¹ | 40 mg L ⁻¹ | 60 mg L ⁻¹ | 80 mg L ⁻¹ | 100 mg L ⁻¹ | CD at P=5% | |
| Pendime thalin | 40.0 | 50.0 | 71.7 | 85.0 | 88.3 | 9.1 | 34.2 |
| B1 | 31.7 | 40.0 | 58.3 | 65.0 | 73.3 | 1.9 | 53.2 |
| B2 | 40.0 | 41.7 | 65.0 | 70.0 | 80.0 | 8.1 | 45.0 |
| B3 | 35.0 | 40.0 | 61.7 | 80.0 | 81.7 | 6.5 | 46.3 |
| B4 | 33.3 | 40.0 | 58.3 | 71.7 | 73.3 | 5.0 | 50.5 |
| B5 | 40.0 | 45.0 | 65.0 | 71.7 | 81.7 | 4.4 | 42.1 |
| C1 | 35.0 | 36.7 | 60.0 | 75.0 | 80.0 | 4.5 | 48.6 |
| C2 | 36.7 | 50.0 | 66.7 | 85.0 | 85.0 | 4.2 | 38.5 |
| C3 | 35.0 | 36.7 | 65.0 | 76.7 | 81.7 | 4.2 | 46.5 |
| E1 | 30.0 | 36.7 | 58.3 | 63.3 | 73.3 | 4.4 | 55.9 |
| E2 | 35.0 | 36.7 | 65.0 | 76.7 | 81.7 | 4.2 | 46.5 |
| M1 | 30.0 | 36.7 | 56.7 | 65.0 | 71.7 | 3.4 | 56.4 |
| M2 | 35.0 | 36.7 | 63.3 | 76.7 | 81.7 | 4.4 | 47.0 |
| M3 | 30.0 | 40.0 | 60.0 | 65.0 | 73.3 | 2.4 | 53.4 |
| M4 | 35.0 | 36.7 | 65.0 | 78.3 | 81.7 | 3.4 | 46.1 |
| Br1 | 40.0 | 46.7 | 66.7 | 70.0 | 81.7 | 4.2 | 39.4 |
| Br2 | 41.7 | 46.7 | 66.7 | 70.0 | 80.0 | 0.2 | 38.9 |

| | | | | | | | |
|----------|------|------|------|------|------|-----|------|
| Br3 | 36.7 | 38.3 | 63.3 | 78.3 | 81.7 | 5.2 | 45.1 |
| Br4 | 41.7 | 46.7 | 65.0 | 71.7 | 80.0 | 2.4 | 38.9 |
| CD at 5% | 4.3 | 5.0 | 4.4 | 5.3 | 4.7 | | |

Table 1: Mean Percent Seed Germination Inhibition Values

IV. DISCUSSION

Perusal of Table-1 clearly reveals that all compounds exhibit significant increase in mean percent inhibition with increase in concentration.

At 20 mg L⁻¹ concentration, compounds (Br2) and (Br4) exhibit highest mean percent inhibition (41.7). Inhibition values of compounds (B2), (B5) and (Br1) including pendimethalin (standard) are at par with those of (Br2) and (Br4). The compounds exhibiting inhibition at par with pendimethalin have either two electron withdrawing groups (in case of Br2 and Br4) or one electron withdrawing group (in case of B2, B5 and Br1). Other compounds exhibit significantly lower activity than Br2 and Br4. All the compounds, exhibiting significantly lower activity, except C2, either have one electron donating group, two electron donating groups, one electron donating and one electron withdrawing group or no substituent group at benzene rings.

At 40 mg L⁻¹ concentration, compounds (C2) and pendimethalin exhibit highest inhibition. Inhibition exhibited by compounds due (B5), (Br1), (Br2), and (Br4) is at par with that of pendimethalin. Other compounds exhibit significantly lower activity than pendimethalin. Again with two exceptions B2 and C3, compounds exhibiting significantly lower activity have electron donating groups attached to benzene rings.

At 60 mg L⁻¹ concentration, pendimethalin exhibits highest inhibition. Activity exhibited by all other compounds is significantly lower than pendimethalin.

At 80 mg L⁻¹ concentration, highest activity is exhibited by the compound C2 and pendimethalin. The compound C2 has two electron withdrawing groups attached to two benzene rings.

At 100 mg L⁻¹ concentration, highest activity is exhibited by pendimethalin. The compound C2 with two electron withdrawing groups exhibited activity at par with pendimethalin.

IC₅₀ values are also in agreement with above concluded SAR. Perusal of IC₅₀ values clearly indicates that the compounds with two electron withdrawing groups fall in lowest range (38.5-38.9) of IC₅₀ values, compounds with two electron donating groups fall in highest range (55.9-56.4) of IC₅₀ values while compounds with one electron withdrawing group or one electron donating group and those with one electron withdrawing group and one electron donating group fall in middle range (45.1-53.4). Only exception is compound Br1 which has only one electron withdrawing group but exhibits activity comparable to those with two electron withdrawing groups.

In our previous investigations carried out on cinnamic acid amide derivatives for seed germination inhibition activity, we established structural activity relationships and concluded that activity is effected by electronic effects also, as electron withdrawing group on benzene ring of acid moiety and electron donating group on benzene ring of amine moiety were

found to increase the activity (19). Here we find that electron withdrawing groups tend to increase activity whether attached to benzene ring of acid moiety (ring A) or alcohol moiety (ring B) (Fig 2). Omokawa *et al.* (27) also studied the effects of substituents on benzene ring of α -phenylsulphonylpropanamide in which they found electron withdrawing groups to increase the activity remarkably.

It is clearly established that electron withdrawing groups significantly increase the activity while electron donating groups decrease it significantly. The compounds 2-(4-chlorophenyl)-2-oxoethyl(2E)-4-(4-chlorophenyl)-4-oxobut-2-enoate, 2-oxo-2-phenylethyl(2E)-4-(4-bromophenyl)-4-oxobut-2-enoate, 2-(4-chlorophenyl)-2-oxoethyl(2E)-4-(4-bromophenyl)-4-oxobut-2-enoate and 2-(4-nitrophenyl)-2-oxoethyl(2E)-4-(4-bromophenyl)-4-oxobut-2-enoate were found to exhibit seed germination inhibition activity comparable with standard pendimethalin.

V. CONCLUSION

Application of synthetic herbicides to control weeds in major agricultural crops is standard farming practice. There has always been demand for novel, environmental benign and potential herbicides. A new and rational alternative to synthetic herbicides is to screen compounds that are structurally analogous to the secondary metabolites in plants exhibiting allelochemical effects. Keeping this in view, analogues of naturally occurring allelochemicals have been synthesized and screened for seed germination inhibition activity. The investigation is a significant contribution to the field of crop protection and chemical ecology as it will add a new class of simple compounds to herbicides.

SPECTRAL ANALYTICAL DATA

- ✓ 2-(4-chlorophenyl)-2-oxoethyl-(2E)-4-oxo-4-phenylbut-2-enoate (B2): λ_{max} (nm)/DCM, 248. IR ν_{max} (cm⁻¹, KBr): 3073.6, 2942.2, 1725.2, 1702.9, 1662.8, 1624.7, 1176.9. ¹H NMR (400 MHz, CDCl₃): 7.04 (1H, d, J=15.8, -CH=CH-), 8.02 (1H, d, -CH=CH-), 5.46 (2H, s, CH₂), 7.48-8.04 (m, benzene ring).
- ✓ 2-(4-nitrophenyl)-2-oxoethyl-(2E)-4-oxo-4-phenylbut-2-enoate (B5): λ_{max} (nm)/DCM, 240. IR ν_{max} (cm⁻¹, KBr): 3079.0, 2938.2, 1734.7, 1707.6, 1671.4, 1614.4, 1166.1. ¹H NMR (400 MHz, CDCl₃): 7.04 (1H, d, J=15.7, -CH=CH-), 8.04 (1H, d, -CH=CH-), 5.53(2H, s, CH₂), 7.51-8.78 (m, benzene ring).
- ✓ 2-(4-methylphenyl)-2-oxoethyl -(2E)-4-(4-chlorophenyl)-4-oxobut-2-enoate (C1): λ_{max} (nm)/DCM, 250. IR ν_{max} (cm⁻¹, KBr): 3076.5, 2928.1, 1727.3, 1696.7, 1666.8, 1625.7, 1171.5. ¹H NMR (400 MHz, CDCl₃): 7.05 (1H, d, J=15.9, -CH=CH-), 7.97 (1H, d, -CH=CH-), 2.43 (3H, s, CH₃), 5.49 (2H, s, CH₂), 7.26-7.99 (m, benzene ring).
- ✓ 2-oxo-2-phenylethyl-(2E)-4-(4-chlorophenyl)-4-oxobut-2-enoate (C3): λ_{max} (nm)/DCM, 244. ¹H NMR (400 MHz, CDCl₃): 7.05 (1H, d, J=15.8, -CH=CH-), 7.97 (1H, d, -CH=CH-), 5.41 (2H, s, CH₂), 7.49-7.97 (m, benzene ring).

- ✓ 2-(4-methylphenyl)-2-oxoethyl (2E)-4-(4-methylphenyl)-4-oxobut-2-enoate (M1): λ_{\max} (nm)/DCM, 254. $^1\text{H NMR}$ (400 MHz, CDCl_3): 7.02 (1H, d, $J=15.9$, $-\text{CH}=\text{CH}-$), 8.02 (1H, d, $-\text{CH}=\text{CH}-$), 2.44 (3H, s, CH_3), 5.46 (2H, s, CH_2), 7.30-7.93 (m, benzene ring).
- ✓ 2-(4-chlorophenyl)-2-oxoethyl-(2E)-4-(4-methylphenyl)-4-oxobut-2-enoate (M2): λ_{\max} (nm)/DCM, 258. IR ν_{\max} (cm^{-1} , KBr): 3068.2, 2941.9, 1729.0, 1705.7, 1661.6, 1621.5, 1171.5. $^1\text{H NMR}$ (400 MHz, CDCl_3): 7.02 (1H, d, $J=15.7$, $-\text{CH}=\text{CH}-$), 8.02 (1H, d, $-\text{CH}=\text{CH}-$), 2.44 (3H, s, CH_3), 5.46 (2H, s, CH_2), 7.30-7.93 (m, benzene ring).
- ✓ 2-(4-chlorophenyl)-2-oxoethyl-(2E)-4-(4-bromophenyl)-4-oxobut-2-enoate (Br2): λ_{\max} (nm)/DCM, 260. $^1\text{H NMR}$ (400 MHz, CDCl_3): 7.04 (1H, d, $J=15.9$, $-\text{CH}=\text{CH}-$), 7.96 (1H, d, $-\text{CH}=\text{CH}-$), 5.47 (2H, s, CH_2), 3.89, 6.99-8.15 (m, benzene ring).
- ✓ 2-(4-methylphenyl)-2-oxoethyl -(2E)-4-(4-ethylphenyl)-4-oxobut-2-enoate (E1): λ_{\max} (nm)/DCM, 256. $^1\text{H NMR}$ (400 MHz, CDCl_3): 7.03 (1H, d, $J=15.8$, $-\text{CH}=\text{CH}-$), 8.02 (1H, d, $-\text{CH}=\text{CH}-$), 5.48 (2H, s, CH_2), 2.73(2H, q), 1.27(3H, t), 7.29-7.96 (m, benzene ring).
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