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Synthesis and Bioevaluation of 3-(substitutedphenyl)-1-(4-hydroxyphenyl)-2-propen-1-ones and their Carbamate Derivatives against Root - Knot Nematode (*Meloidogyne javanica*)

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ABSTRACT

Synthesis of 3-(4-chloro/methyl/nitro/methoxy/3,4,5-trimethoxy/2,4-dichloro/ 4-bromo/ 3, 4-dimethoxy/ 2, 4-dimethoxy/ 3-bromo/ 2-chloro/ 2-methoxy phenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (14-25) has been carried out from substituted benzaldehyde (1-12) and 4-hydroxy acetophenone (13). The condensation of synthesized 2-propen-1-ones (14-25) with phenyl isocyanate (26) gave 4-[3-(4-chloro/ methyl/nitro/methoxy/3, 4, 5-trimethoxy/2, 4-dichloro/4-bromo/3, 4-dimethoxy/2, 4-dimethoxy/3-bromo phenyl) prop-2-enoyl] phenyl phenylcarbamate (27-36). The synthesized compounds were characterized on the basis of analytical and spectral data. All the compounds were evaluated for their nematicidal activity *in- vitro* against second stage juveniles (J_2) of root - knot nematode (*Meloidogyne javanica*). Incorporation of carbamoyloxy moiety in 2-propen-1-ones enhanced the activity. Irrespective of the concentration, compounds 3-(4-methoxyphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (17) and 4-[3-(4-methoxyphenyl) prop-2-enoyl] phenyl phenyl carbamate (30) have shown maximum nematode mortality i.e. 30% and 51.8%.

Key words: Substituted-2-propen-1-one, Carbamate, Nematicidal activity, Root-knot nematode, *Meloidogyne javanica.*

INTRODUCTION

Plants stunted or diseased by nematode related activity are likely to produce reduced yields and loss in quality and quantity of the produce[1]. Inspite of considerable damage caused by nematodes to various agricultural crops, till today very few nematicides are available for use. Chalcones are natural biocides and are well known intermediates for the synthesis of various organic heterocycles. The presence of a reactive ±, ² unsaturated keto function in chalcones is found to be responsible for their antimicrobial activity[2]. In present study, we have utilized 3-(substituted phenyl)-1-(4-hydroxyphenyl)-2-propen-1-ones as starting material for the synthesis of carbamates. The carbamates are derivatives of carbamic acid, $HOC(O)NH_2$ and are well known class of insecticides. Carbamates were originally extracted from the calabar bean, which grows in west Africa.

Carbamates as a class are not generally persistent in the environment[3]. Carbamates are effective nematicides by virtue of their ability to inhibit acetyl cholinesterase (AchE) in the nervous system and thereby, disrupt nervous transmission at that location[4]. In view of the diverse type of biological activities shown by carbamates, their importance as agrochemicals and as a part of our ongoing new nematicide development programme[5-7], it was thought of interest to synthesize and evaluate nematicidal activity of substituted 4-[3-(substitutedphenyl) prop-2-enoyl]phenyl phenyl carbamates.

EXPERIMENTAL

Materials & Methods

The melting points were determined in open capillaries on a Ganson electrical melting point apparatus and are uncorrected. Homogeneity of the compounds was routinely checked on silica gel-G TLC plates using ethyl acetate: hexane (3:7) as irrigant. IR spectra were recorded on "Perkin Elmer FTIR" spectrophotometer in KBr and frequencies are expressed in cm^{-1}. The NMR spectra were recorded on "Bruker AC-400-F" (400MHz) NMR spectrophotometer in $CDCl_3$ or DMSO-d_6 using tetramethylsilane (TMS) as internal reference. The chemical shift values are expressed in ´ (ppm) units while J values in Hz and are compatible with the assigned structures. The elemental analyses were within ± 0.4 % of that of evaluated values. Only those spectral data have been mentioned which have a direct bearing on the assignment of the structures and are discussed here.

Chemistry

3-(4-chlorophenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (14)

A solution of 4-chlorobenzaldehyde (2.8gm, 20 mmol) and 4-hydroxyacetophenone (2.72gm, 20 mmol) in ethanol (125 ml) was taken in round bottom flask placed in ice bath and to it added an aqueous sodium hydroxide solution (20ml, 20%) slowly with stirring. It was further stirred for 3h in ice bath. The mixture was then diluted with cold distilled water and neutralized with 2N HCl. The solid that separated out was filtered, washed with cold water and crystallized from ethanol to afford **14**. Yield 4.10g (79.3%), m.p. 213-214°C (Lit. 216°C)[8]. IR (KBr) cm^{-1}:3300 (OH), 1659 (C=O), 750(C-Cl). ^{1}HNMR (DMSO-d_6): 7.19(d, J=8.0Hz, 2H, C_3-H & C_5-H), 7.42(d, J=16.0Hz,1H, COCH=CH), 7.67(d, J=8.0Hz, ´C_3-H & ´C_5-H), 7.69 (d, J= 8.0Hz, 2H, C_2-H & C_6-H), 7.74(d,J=16.0Hz,1H,COCH=CH), 7.95(d, J=8.0Hz,2H, ´C_2-H & ´C_6-H). Analysis found:C, 69.24; H, 4.60; Cl, 13.38%; $C_{15}H_{11}ClO_2$ Required: C, 69.64; H, 4.29; Cl, 13.70 %.

Other compounds 15-25 were prepared similarly from 2-12 and 13.

3-(4-methylphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (15)

Yield 80%, m.p.157-158°C (Lit. 156°C)[8]. IR (KBr) cm^{-1}: 3128(OH), 1671(C=O). ^{1}HNMR ($CDCl_3$):2.38(s, 3H, C_4-CH_3); 7.01(d, J=8.0Hz, 2H, C_3-H & C_5-H); 7.21(d, J=16.0 Hz, 1H, CO-CH=CH); 7.25(d, J=8.0Hz, 2H,C_3'-H & C_5'-H); 7.50 (d, 2H, C_2-H & C_6-H); 7.52 (d, J=16.0 Hz, 1H, CO-CH=CH); 7.69 (d, J=8.0Hz, 2H, C_2'-H & C_6'-H). Analysis found : C, 80.35; H, 5.80%.;$C_{16}H_{14}O_2$ Required : C, 80.65; H, 5.92%.

3-(4-nitrophenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (16)

Yield 71%, m.p. 204-206°C (Lit. 210°C)[8]. IR (KBr) cm^{-1}:3162(OH), 1660(C=O), 1572,1344(C-NO_2). Analysis found: C, 66.92; H, 3.94; N, 5.08%.;$C_{15}H_{11}NO_4$ Required:C, 66.91; H, 4.12; N, 5.20%.

3-(4-methoxyphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (17)

Yield 79%, m.p. 177-179°C (Lit. 179-181°C)[9]. IR (KBr) cm^{-1}: 3126(OH), 1676(C=O), 1250 (C-OCH_3). ^{1}HNMR ($CDCl_3$): 3.82 (s, 3H, C-OCH_3); 6.93 (d, J=16.0Hz, 1H, CO-CH=CH); 7.67 (d, J=16.0 Hz, 1H, CO-CH=CH); 7.54 - 7.59 (m, 6H, Ar-H). Analysis found :C, 75.38; H, 5.32%. ;$C_{16}H_{14}O_3$ Required:C, 75.57; H, 5.55%.

3-(3,4,5-trimethoxyphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (18)

Yield 60%, m.p. 221-223°C (Lit. 222°C)[8]. IR (KBr) cm^{-1}: 3121(OH), 1621(C=O), 1250 (C-OCH_3).^{1}HNMR ($CDCl_3$):3.90 (s, 3H, C-OCH_3); 3.92 (s, 9H, 3 x OCH_3); 6.96 (d, 1H, CO-CH=CH); 7.64 (d, 1H, CO-CH=CH); 6.85 (s, 2H, C_2-H & C_6-H). Analysis found:C, 68.34; H, 5.74%. ;$C_{18}H_{18}O_5$ Required:C, 68.78; H, 5.77%.

3-(2,4-dichlorophenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (19)

Yield 77%, m.p. 157-158°C. IR (KBr) cm^{-1}: 3171(OH), 1651(C=O), 710 (C-Cl). Analysis found :C, 61.18; H, 3.46; Cl, 23.64% ;$C_{15}H_{10}Cl_2O_2$ Required:C, 61.46; H, 3.44; Cl, 24.19%.

3-(4-bromophenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (20)

Yield 51%, m.p. 181-182°C (Lit. 180°C)[8]. IR (KBr) cm^{-1}: 3147(OH), 1670(C=O), 561(C-Br). Analysis found: C, 59.53; H, 3.53; Br, 25.96% ;$C_{15}H_{11}BrO_2$ Required :C, 59.43; H, 3.66; Br, 26.36%.

3-(3,4-dimethoxyphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (21)

Yield 67%, m.p.121-122°C. IR (KBr) cm^{-1}: 3100(OH), 1690(C=O), 1275 (C-OCH_3). ^{1}HNMR ($CDCl_3$): 3.96 (s, 3H, C-OCH_3); 3.98 (s, 3H, C-OCH_3); 7.40 (d, J=16.0Hz, 1H, CO-CH=CH); 7.86 (d, J=16.0Hz, 1H, CO-CH=CH); 7.90-8.45 (m, 8H, Ar-H). Analysis found: C, 71.96; H, 5.64%. ;$C_{17}H_{16}O_4$ Required :C, 71.82; H, 5.67%.

3-(2,4-dimethoxyphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (22)

Yield 69%, m.p. 123-124°C. IR (KBr) cm^{-1}: 3260(OH), 1680(C=O), 1255, 1250 (C-OCH_3). Analysis found :C, 71.68; H, 5.60%. ;$C_{17}H_{16}O_4$ Required: C, 71.82; H, 5.67%.

3-(3-bromophenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (23)

Yield 60%, m.p. 164-165°C. IR (KBr) cm^{-1}: 3200(OH), 1677(C=O). Analysis found: C, 59.16; H, 3.45; Br, 26.29% ;$C_{15}H_{11}BrO_2$ Required : C, 59.43; H, 3.66; Br, 26.36%.

3-(2-chlorophenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (24)

Yield 74%, m.p. 155-156°C. IR (KBr) cm^{-1}: 3300(OH),1660(C=O), 750(C-Cl) Analysis found:C, 69.69; H, 4.29; Cl, 13.57% ;$C_{15}H_{11}ClO_2$ Required : C, 69.64; H, 4.29; Cl, 13.70%.

3-(2-methoxyphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (25)

Yield 70%, m.p. 164-166°C. IR (KBr) cm^{-1}:1635(C=O), 3270(OH), 1252 (C-OCH_3). Analysis found :C, 75.32; H, 5.56%. ; $C_{16}H_{14}O_3$ Required:C, 75.57; H, 5.55%.

4-[3-(4-chlorophenyl) prop-2-enoyl]phenyl phenylcarbamate (27)

A mixture of 3-(4-chlorophenyl)-1-(4-hydroxyphenyl)-2-propen-1-one **(14,** 1gm, 4 mmol) and phenylisocyanate (**26,** 0.476gm, 4 mmol) in dry benzene (20ml) was refluxed for 12 hours on steam bath. Completion of the reaction was monitored by TLC. It was then concentrated under vacuum, to give solid residue which was crystallized from benzene to afford **27**. Yield 66%, m.p. 191-192°C. IR (KBr) cm^{-1}: 3380 (NH), 1690 (NH-CO), 740 (C-Cl). ^{1}HNMR (DMSO-D_6): 7.01 (d, J=8.0Hz, 2H, C_3-H& C_5-H), 7.36(d, J=16.0Hz, 1H, COCH=CH), 7.38 (d,J=8.0Hz,2H,´C_3-H &´C_5-H), 7.52 (d, J=16.0Hz, 1H,COCH=CH), 7.55(d, J=8.0Hz,2H, C_2-H & C_6-H), 7.66 (d, J=8.0Hz,2H, ´C_2-H & ´C_6-H), 7.66-7.75(m, 5H, Ar-H), 8.50(s, 1H, NH). Analysis found: C, 69.72; H, 4.25; Cl, 9.31; N, 3.64%.; $C_{22}H_{16}ClNO_3$ Required : C, 69.94; H, 4.27; Cl, 9.38; N, 3.71%.

Other compounds 28-36 were prepared similarly from 15-23 and 26.

4-[3-(4-methylphenyl) prop-2-enoyl]phenyl phenylcarbamate (28)

Yield 60%, m.p. 192-194°C. IR (KBr) cm^{-1}: 3370 (NH), 1692 (NH-CO), 1380 (C-CH_3). Analysis found: C, 77.38; H, 5.33; N, 3.89% ; $C_{23}H_{19}NO_3$ Required :C, 77.29; H, 5.36; N, 3.92%.

4-[3-(4-nitrophenyl) prop-2-enoyl]phenyl phenylcarbamate (29)

Yield 68%, m.p. 215-216°C. IR (KBr) cm^{-1}: 3380 (NH), 1695 (NH-CO), 1540, 1370 (C-NO_2). Analysis found: C, 67.95; H, 3.97; N, 7.19% ;$C_{22}H_{16}N_2O_5$ Required: C, 68.04; H, 4.15; N, 7.21%.

4-[3-(4-methoxyphenyl) prop-2-enoyl]phenyl phenylcarbamate (30)

Yield 70%, m.p. 147-148°C. IR (KBr) cm^{-1}:3400 (NH), 1680 (NH-CO), 1250 (CO-CH_3). Analysis found: C, 73.61; H, 5.17; N, 3.29%. ;$C_{23}H_{19}NO_4$ Required: C, 73.98; H, 5.13; N, 3.75%.

4-[3-(3,4,5-trimethoxyphenyl)prop-2-enoyl] phenyl phenylcarbamate (31)

Yield 66%, m.p. 149-150°C. IR (KBr) cm^{-1}: 3365 (NH), 1690 (NH-CO), 1200 (C-OCH_3).

^{1}HNMR (DMSO-D_6): 3.86 (s, 9H, 3xOCH_3); 6.97 (d,J=16.0Hz,1H, COCH=CH), 7.64 (d,J=16.0Hz, 1H, COCH=CH), 7.78-8.30 (m, 9H, Ar-H), 8.50(s, 1H, NH). Analysis found: C, 69.69; H, 5.37; N, 3.17%. ;$C_{25}H_{23}NO_6$ Required: C, 69.27; H, 5.35; N, 3.23%.

4-[3-(2,4-dichlorophenyl)prop-2-enoyl]phenyl phenylcarbamate (32)

Yield 72%, m.p. 225-226°C. IR (KBr) cm^{-1}: 3380 (NH), 1680 (NH-CO), 760 (C-Cl). Analysis found: C, 63.86; H, 3.64; Cl, 17.22; N, 3.29%. ;$C_{22}H_{15}Cl_2NO_3$ Required: C, 64.09; H, 3.67; Cl, 17.20; N, 3.40%.

4-[3-(4-bromophenyl) prop-2-enoyl]phenyl phenylcarbamate (33)

Yield 58%, m.p. 196-198°C. IR(KBr) cm^{-1}:3390 (NH), 1675 (NH-CO), 540,520 (C-Br). Analysis found: C, 62.76; H, 3.84; Br, 18.73; N, 3.19%. ;$C_{22}H_{16}BrNO_3$ Required:C, 62.57; H, 3.82; Br, 18.92; N, 3.32%.

4-[3-(3,4-dimethoxyphenyl) prop-2-enoyl]phenyl phenylcarbamate (34)

Yield 65%, m.p. 198-199°C. IR (KBr) cm^{-1}: 3400 (NH), 1695 (NH-CO), 1255 (C-OCH_3). ^{1}HNMR (DMSO-D_6): 3.76 (s, 3H, OCH_3); 3.80 (s, 3H, OCH_3); 6.95(d, J=16.0Hz, 1H, COCH=CH), 7.62(d, J=16.0Hz, 1H, COCH=CH), 7.79-8.30 (m, 10H, Ar-H), 8.45(s, 1H, NH). Analysis found :C, 71.23; H, 5.24; N, 3.26%. ;$C_{24}H_{21}NO_5$ Required: C, 71.45; H, 5.25; N, 3.47%.

4-[3-(2,4-dimethoxyphenyl) prop-2-enoyl]phenyl phenylcarbamate (35)

Yield 62%, m.p. 220-221°C. IR (KBr) cm^{-1}: 3380 (NH), 1690 (NH-CO), 1250 (C-OCH_3). Analysis found : C, 71.39; H, 5.22; N, 3.21% ;$C_{24}H_{21}NO_5$ Required : C, 71.45; H, 5.25; N, 3.47%.

4-[3-(3-bromophenyl) prop-2-enoyl]phenyl phenylcarbamate (36)

Yield 56%, m.p. 223-225°C. IR (KBr) cm^{-1}:3388 (NH), 1670 (NH-CO), 540 (C-Br). Analysis found: C, 62.76; H, 3.84; Br, 18.73; N, 3.19%.;$C_{22}H_{16}BrNO_3$. Required:C, 62.57; H, 3.82; Br, 18.92; N, 3.32%.

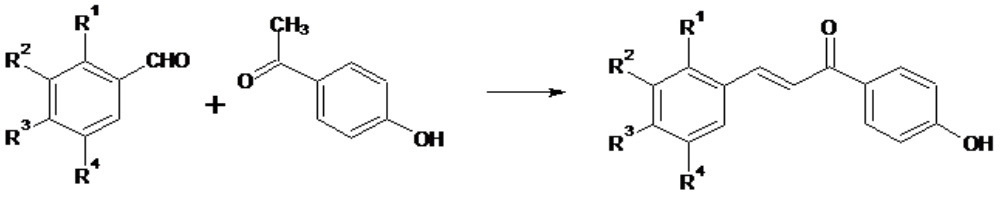
Nematicidal Bioevaluation

The plant parasitic nematode *Meloidogyne javanica* (Treub) Chitwood was used as test organism. Stock solutions of 2000mg L^{-1} of all the compounds were prepared by dispersing these in acetone. Nematicidal activity was evaluated against second stage juveniles (J_2) of *M. javanica*. A suspension of juveniles (1 ml) was poured into 5cm Petri-dishes. Measured quantities of stock solution were added to these Petri-dishes to make final concentrations of 1000, 500, 250 and 125 ppm. Acetone with water was used as control. No nematode mortality was recorded in these controls, and is therefore not included in the table. Each treatment was replicated three times. These Petri-dishes were kept in a BOD incubator at 28±1°C. Observations were recorded after 24h and 48h by counting live (active) and dead (inactive) J_2s under a stereoscopic binocular microscope and the per cent mortality was counted[10]. The revival of immobilized nematodes was examined by randomly transferring ten J_2s to water for 24 h. None of those immobilized J_2s revived. The experimental data was statistically analyzed using two factorial completely randomized design; the compounds and the concentrations constituting the two factors.

RESULTS AND DISCUSSION

The condensation of 4-chloro/methyl/nitro/ methoxy/3,4,5-trimethoxy/2,4-dochloro/4-bromo/3,4-dimethoxy/2,4-dimethoxy/3-bromo/2-chloro/2-methoxy benzaldehyde (1-12) with 4-hydroxy acetophenone (13) in using 20% ethanolic sodium hydroxide after stirring gave the corresponding 3-(4-chloro/ methyl/ nitro/ methoxy/ 3,4,5-trimethoxy/ 2,4-dichloro/ 4-bromo/3,4-dimethoxy/2,4-dimethoxy/3-bromo phenyl)-1-(4-hydroxy phenyl)-2-prop-1-one (14-25). Thus, a total of twelve different chalcones were synthesized. The different benzaldehyde derivatives used in this reaction are listed in Scheme (Scheme-I).

The ^{1}HNMR spectra of 14-25 were in accordance with the proposed structures. The substituted-2-propen-1-ones were found to possess E-configuration, which is confirmed on the basis of their ^{1}H NMR spectra. The diagnostic olefinic protons (-CO-CH=CH-) attached to carbonyl functionality appeared as clean doublets at around 7.42 and 7.67 δ (each with J= 16.0 Hz), situated at α and β respectively and this confirms the condensation of the reactants. Methyl, methoxy and trimethoxy

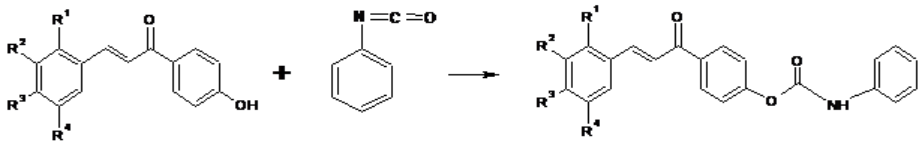


1-12 13 14-25

Reagents and reaction conditions
NaOH (20%), Ethanol, Stirring

Compd.	R^1	R^2	R^3	R^4
1, 14	H	H	Cl	H
2, 15	H	H	CH_3	H
3, 16	H	H	NO_2	H
4, 17	H	H	OCH_3	H
5, 18	H	OCH_3	OCH_3	OCH_3
6, 19	Cl	H	Cl	H
7, 20	H	H	Br	H
8, 21	H	OCH_3	OCH_3	H
9, 22	OCH_3	H	OCH_3	H
10, 23	H	Br	H	H
11, 24	H	Cl	H	H
12, 25	H	OCH_3	H	H

Scheme 1: Synthesis of 3-(substitutedphenyl)-1-(4-hydroxyphenyl)-2-propen-1-ones



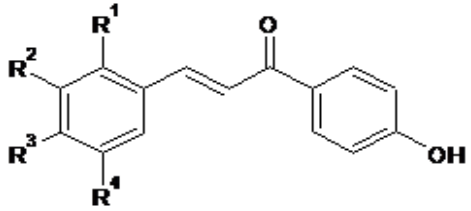
14-23 26 27-36

Reagents and reaction conditions:
Benzene, Δ

Compd.	R^1	R^2	R^3	R^4
27	H	H	Cl	H
28	H	H	CH_3	H
29	H	H	NO_2	H
30	H	H	OCH_3	H
31	H	OCH_3	OCH_3	OCH_3
32	Cl	H	Cl	H
33	H	H	Br	H
34	H	OCH_3	OCH_3	H
35	OCH_3	H	OCH_3	H
36	H	Br	H	H

Scheme 2: Synthesis of 4-[3-(substitutedphenyl)prop-2-enoyl]phenyl phenyl carbamates

Table 1: Nematicidal Activity of 3-(substitutedphenyl)-1-(4-hydroxyphenyl)-2-propen-1-ones (14-23) against *Meloidogyne javanica* after 24 h

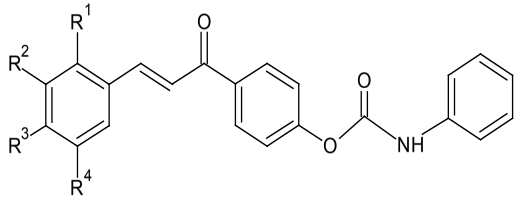
Compound No.	Chalcones (1,3-diaryl-2-propen-1-ones)				Mean of three replicates % J_2 mortality after 24 h				
									
	R^1	R^2	R^3	R^4	1000 ppm	500 ppm	250 ppm	125 ppm	Mean (compd.)
14	H	H	Cl	H	26.5 (30.9)	20.1 (26.6)	10.8 (19.2)	0.0 (0.0)	14.4 (19.2)
15	H	H	CH_3	H	38.0 (38.0)	26.5 (30.8)	18.8 (25.7)	11.9 (20.0)	23.8 (28.6)
16	H	H	NO_2	H	24.1 (29.3)	20.0 (26.6)	13.3 (21.1)	7.4 (15.3)	16.2 (23.1)
17	H	H	OCH_3	H	48.5 (44.1)	34.5 (35.9)	26.7 (31.0)	10.8 (19.2)	30.1 (32.5)
18	H	OCH_3	OCH_3	OCH_3	33.3 (35.2)	30.0 (33.2)	11.8 (20.1)	0.0 (0.0)	18.8 (22.1)
19	Cl	H	Cl	H	27.2 (31.2)	21.9 (27.9)	17.4 (24.4)	8.7 (17.0)	18.8 (25.1)
20	H	H	Br	H	30.2 (33.3)	26.9 (31.1)	20.7 (27.1)	20.0 (26.6)	24.5 (29.5)
21	H	OCH_3	OCH_3	H	38.7 (38.4)	29.4 (32.8)	20.0 (26.6)	10.0 (18.4)	24.5 (29.1)
22	OCH_3	H	OCH_3	H	39.3 (38.8)	29.4 (32.8)	17.4 (24.4)	10.0 (15.0)	24.1 (27.7)
23	H	Br	H	H	33.8 (35.5)	30.0 (33.2)	17.4 (24.4)	12.3 (20.4)	23.4 (28.4)
			Mean (Conc.)		34.0 (35.5)	26.9 (31.1)	17.4 (24.4)	9.1 (15.2)	

C.D (5%): Compound= (2.88); Concentration= (1.82); Compound x Concentration = (5.76)

Figures in parentheses are angular transformed values

Table 2: Nematicidal Activity of 4-[3-(substitutedphenyl)prop-2-enoyl]phenyl phenyl carbamates (27-36) against Meloidogyne javanica after 24 h

Compound No. **4-[3-(substitutedphenyl)prop-2-enoyl] phenyl phenyl carbamate**



Mean of three replicates

	R^1	R^2	R^3	R^4	1000 ppm	500 ppm	250 ppm	125 ppm	Mean (compd.)
27	H	H	Cl	H	47.7 (43.6)	35.9 (36.8)	26.9 (31.1)	19.8 (26.0)	32.6 (34.4)
28	H	H	CH_3	H	52.3 (46.3)	44.0 (41.5)	35.9 (36.8)	26.9 (31.1)	39.8 (38.9)
29	H	H	NO_2	H	42.0 (40.4)	30.9 (33.7)	24.1 (29.3)	20.0 (26.6)	29.3 (32.5)
30	H	H	OCH_3	H	72.7 (58.5)	64.5 (53.4)	45.7 (42.5)	24.4 (29.5)	51.8 (46.0)
31	H	OCH_3	OCH_3	OCH_3	55.3 (48.0)	39.4 (38.9)	22.4 (28.2)	21.5 (27.3)	34.7 (35.6)
32	Cl	H	Cl	H	63.7 (52.9)	52.3 (46.3)	30.0 (33.2)	23.2 (28.7)	42.3 (40.3)
33	H	H	Br	H	60.0 (50.7)	48.5 (44.1)	31.7 (34.2)	17.5 (24.4)	39.4 (38.4)
34	H	OCH_3	OCH_3	H	55.3 (48.0)	48.5 (44.1)	29.1 (32.6)	27.4 (31.5)	40.1 (39.1)
35	OCH_3	H	OCH_3	H	50.0 (45.0)	30.0 (33.2)	20.8 (27.1)	10.0 (12.3)	27.7 (29.4)
36	H	Br	H	H	52.3 (46.3)	43.3 (41.1)	29.6 (32.9)	14.1 (21.7)	34.8 (35.5)
			Mean (Conc.)		55.1 (48.0)	43.7 (41.3)	29.6 (32.8)	20.5 (25.9)	

C.D (5%): Compound= (3.25); Concentration= (2.05); Compound x Concentration = (6.50)

Figures in parentheses are angular transformed values

moieties could be picked up at around 2.38 δ, 3.83 δ and 3.91 δ as singlets, each integrating three and nine protons. The A_2B_2 pattern of aromatic protons in the NMR spectra of compounds possessing para methyl phenyl moiety, could be picked up as ortho coupled doublets at about 7.01 δ (ortho to methyl) and 7.50 δ (ortho to -CH=CH- group), each integrating for two protons with J=8.0Hz. Similar pattern was also observed in para chloro or bromo moieties, 7.70 δ due deshielding effect of carbonyl functionalities.

In the ^{1}HNMR spectrum of 3-(4-chlorophenyl)-1-(4-hydroxyphenyl)-2-propen-1-one **(14)**, a doublet at 7.19 ´ integrating for two protons (J=8.0Hz) was observed, which confirm the two aromatic protons of C_3 and C_5 positions (ortho to chloro) respectively. The two diagnostic doublets (J=16.0 Hz) could be assigned at 7.42 ´ and 7.74 ´ respectively for -CO-CH=CH- protons (± and ² to keto) was indication of two olefinic protons. A doublet integrating for two protons with J=8.0Hz was observed at 7.67 ´ for C_3‘ & C_5‘ respectively while C_2 and C_6 protons were picked up as doublet at 7.69 δ (J=8.0Hz). A methoxy group was observed as singlet at 3.83 δ and all other protons at their usual positions in 3-(4-methoxyphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one **(17)** supported the assigned structure. Appearance of peaks near 1680 cm^{-1} and 3300 cm^{-1} for C=O stretching and OH functionality, in the IR spectra of the above compounds further corroborated their structures.

In the next step of synthesis, condensation of compounds 3-(4-chloro/ methyl/ nitro/ methoxy/ 3,4,5-trimethoxy/ 2,4-dichloro/ 4-bromo/3,4-dimethoxy/2,4-dimethoxy/3-bromo phenyl)-1-(4-hydroxy phenyl)-2-prop-1-one (**14**-**25)** with phenylisocyanate **(26)** in equimolar ratio in dry benzene by refluxing on steam bath for 12 h, afforded their corresponding 4[3-(4-chloro/methyl/nitro/methoxy/3,4,5-trimethoxy/2,4-dichloro/4-bromo/3,4-dimethoxy/2,4-dimethoxy/3-bromo phenyl) prop-2-enoyl] phenyl phenylcarbamate (**27**-36) in good yields.(Scheme-II)

Thus, a total of ten different 4-[3-(substitutedphenyl)prop-2-enoyl]phenyl phenyl carbamates were synthesized. The different 3-(substitutedphenyl)-1-(4-hydroxyphenyl)-2-propen-1-ones used in this reaction are listed in scheme-II.

In the ^{1}HNMR spectrum of 4-[3-(4-chlorophenyl) prop-2-enoyl] phenyl phenyl carbamate (**27**), two aromatic protons at positions 3 and 5 appeared at 7.01 δ (J=8.0Hz) as doublet. Another two doublets at 7.38 ´ and 7.55 ´ integrating for two protons each were assigned to protons at positions C_3‘ and C_5‘ or C_2 and C_6 respectively. The downfield shift of C_2‘ and C_6‘ protons ortho to carbonyl functionalities appeared at 7.66 δ. The remaining aromatic protons appeared as multiplet at 7.66 δ to 7.55 δ. The broad singlet at 8.50 δ was assigned to NH proton of carbamoyloxy moiety. The formation of carbamates of the above compounds follows from the mode of synthesis and were supported by the appearance of a band around 3340 cm^{-1} for NH functionality and around 1670 and 1690 cm^{-1} for carbonyl and carbamoyloxy (C=O) functionalities respectively. Thus, structures of all these compounds were fully supported by their NMR and IR spectra.

Nematicidal Bioevaluation

The mortality of *M. javanica* J_2s after 24h by various 3-(substitutedphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one has been given in table 1. Overall moderate activity was shown by 3-(4-chloro/ methyl/ nitro/methoxy/3, 4, 5-trimethoxy/2, 4-dichloro/4-bromo/3, 4-dimethoxy/2, 4-dimethoxy/3-bromo phenyl)-1-(4-hydroxyphenyl)-2-propen-1-one**(14-23)** compounds. The perusal of the activity data revealed that interaction of compounds and concentrations was statistically significant. Irrespective of the concentration, compound 3-(4-methoxyphenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (**17**) have shown maximum nematode mortality i.e. 30% and it is highest activity of this series. This was followed by compounds **15**, **20**, **21**, **22** and **23**, which resulted in the range of 29.5-27.7% and were found statistically at par. Compounds **16**, **18** and **19** were relatively less active. The compound 3-(4-chlorophenyl)-1-(4-hydroxyphenyl)-2-propen-1-one **(14)** was found least active.

In general, nematoxicity increased with time. Among these compounds no significant difference was recorded after 48h. Compound **17**, **22** and **21** exhibited highest toxicity at 1000ppm and compound **14**, **18, 16** and **19** showed least

toxicity at 125 ppm and were statistically at par. Replacement of chloro with bromine, methyl and methoxy at position-3 increased the nematicidal activity. Presence of dimethoxy groups also showed appreciable activity. Unexpectedly, nematicidal activity decreased by increasing number of methoxy groups as in case of compound 3-(3,4,5-trimethoxy phenyl)-1-(4-hydroxyphenyl)-2-propen-1-one (**18**). Irrespective of compounds, 1000ppm concentration proved to be most toxic to nematodes and 125 ppm concentration was found least effective. However, all the concentrations were significantly different from one another.

In this series, compounds 4-[3-(substitutedphenyl)prop-2-enoyl]phenyl phenyl carbamates (**27**-**36**) were synthesized from 3-(substitutedphenyl)-1-(4-hydroxyphenyl)-2-propen-1-ones (**14**-**23**) and selected for nematicidal activity *in vitro*. There was an overall increase in the nematicidal activity as compared to starting material 3-(substitutedphenyl)-1-(4-hydroxyphenyl)-2-propen-1-ones (**14**-**23**). Due to incorporation of carbamoyloxy moiety in 2-propen-1-ones enhanced the activity but not up to the desired value. Table-2, shows the data on the mortality of *M. javanica* J_2s after 24h by various 4-[3-(substitutedphenyl)-prop-2-enoyl]phenyl phenyl carbamate (**27**-**36**). The perusal of the activity data revealed that interaction of compounds and concentrations was statistically significant. Irrespective of the concentration, in this series compound 4-[3-(4-methoxyphenyl) prop-2-enoyl] phenyl phenyl carbamate (**30**) have shown maximum nematode mortality i.e. 51.8% and it was comparatively highest. This was followed by compounds **28**, **32**, **33**, and **34**, which resulted in a range of 42.2-39.1% and were statistically at par. Compounds **27**, **29**, **31** and **36** were relatively less active. The compound 4-[3-(2,4-dimethoxyphenyl) prop-2-enoyl]phenyl phenylcarbamate (**35**) was least active and significantly, low toxicity of 35% was shown by this compound.

Among these compounds nematicidal activity increased after 48h. Compound 4-[3-(4-methoxyphenyl) prop-2-enoyl]phenyl phenylcarbamate (**30**) and 4-[3-(2,4-dichlorophenyl) prop-2-enoyl]phenyl phenylcarbamate (**32**) showed highest toxicity 72% at 1000ppm and were at par with 500 ppm concentration, followed by compounds **28**, **29**, **31**, **33**, **34**, **35** and **36** which showed moderate toxicity and were statistically at par. Further introduction of carbamoyloxy moiety in these compounds resulted in higher nematicidal activity. Replacement of chloro with bromine, methyl and methoxy at position-3 increased the nematicidal activity. Compound containing chloro moiety at para-position was found least effective while dichloro moiety significantly increased the nematicidal activity. Irrespective of compounds, concentration 1000 ppm proved to be most toxic to nematode. However, all the concentrations were significantly different from one another.

Observations on nematode mortality were also recorded after 48h; however since there was no significant increase in mortality, the data is not reproduced in table.

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