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Synthesis and Insect Antifeedant Activity of Some New Chalcones Against *Phenacoccus solanopsis*

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Abstract: Twelve new chalcones were synthesized by Claisen-Schmidt condensation and studied for their insect antifeedant activity against the mealy bug of cotton (*Phenacoccus solanopsis*). All the chalcones have exhibited significant activity.

Key words: Chalcones · Synthesis · Antifeedant activity · *Phenacoccus solanopsis*

INTRODUCTION

There is a need of novel insecticides which are less toxic to humans and more specific to key pests. The pesticides which are presently used in agriculture for control of insects and mealy bugs are highly toxic to human beings. For ecologically sound, equitable and ethical pest management, there is need for control agents that are pest specific, nontoxic to human and less expensive. Amongst various options aqueous extract of neem seeds (kernels of *Azadirachta indica*), *Allium sativum, Lantana camara, Annona squamosa, carica papaya* etc. were highly effective for the control of coffee mealy bugs. The effect of extract of botanicals [1] on mealy bugs is slow than synthetic insecticides, but they are eco-friendly and comparatively non-toxic or less toxic to human beings and easily degradable.

The wide spread flavonoids act as various functional secondary metabolites in plants [2]. Chalcones, flavones, chromones have been reported as insect antifeedant [3-7]. They have been further reported as the constituents for the U.V. defense system against sunlight and also as antioxidants [8].

Considering the reported eco-friendly bio-pesticides properties of flavonoids and are easily degradable in nature, we have synthesized new chalcones and studied insect antifeedant activity.

MATERIALS AND METHODS

Melting points were determined in an open capillary tube and are uncorrected. IR spectra were recorded in Kbr on a Perkin-Elmer spectrometer. 1H NMR spectra were recorded on a Gemini 300-MHz instrument in $CDCl_3$ as solvent and TMS as an internal standard. The mass spectra were recorded on EI-SHIMADZU-GC-MS spectrometer. Elemental analysis was carried out on a Carlo Erba 1108 analyzer. Chalcones were synthesized according to literature [9].The purity of products was checked by thin-layer chromatography (TLC) on silica-gel.

Insect Antifeedant Activity: Mealy bugs of cotton (*Phenacoccus Solanopsis*) are cottony in appearance, small oval, soft-bodied sucking insects. Adult mealy bugs are found on leaves, stems and roots and are covered with white mealy wax, which makes them difficult to eradicate. Mealy bug species attacks on various crops and do the damage up to 70-80%.

They form colonies on stems and leaves developing into dense, waxy, white masses. They suck a large amount of sap from leaves and stems with piercing and sucking type of mouth parts, depriving plants of essential nutrients. The excess sap is excreted as honeydew which attracts ants and develops sooty mould inhibiting the plants ability to manufacture food. Now a days mealy

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Table 1: Insect antifeedant activity of chalcones against mealy bugs (*Phenacoccus solenopsis*)

Compound Used for treatment	Concentra-tion used g/lit.	% Antifeedant Activity Values mean ±S.E. 5			% Mortality Values mean ±S.E. 5		
		12 hr	24 hr	12 hr	24 hr	12 hr	24 hr
3a	0.01	65.00	71.42	80.00	15.00	30.00	50.00
3b	0.01	100	100	100	25.00	40.00	60.00
3c	0.01	100	100	100	10.00	15.00	30.00
3d	0.01	76.92	100	100	35.00	50.00	70.00
3e	0.01	100	100	100	25.00	30.00	40.00
3f	0.01	56.25	57.89	57.89	10.00	15.00	20.00
3g	0.01	68.75	100	100	10.00	20.00	45.00
3h	0.01	30.36	40.15	47.06	00.00	05.00	05.00
3i	0.01	42.87	50.00	75.00	50.00	60.00	80.00
3j	0.01	45.78	62.50	68.42	00.00	05.00	20.00
3k	0.01	100	100	100	00.00	00.00	00.00
3l	0.01	100	100	100	100	100	100
Acetone	____	00.00	00.00	00.00	00.00	00.00	00.00
Fipronil 5% SC (Regent Sc)	0.01	90.00	90.00	90.00	00.00	00.00	00.00

bugs attacks on cotton, coffee, grapes etc. and yield of cotton was reduced up to 30-80%. Eradication of it became problem to botanist, farmers etc.

Procedure: Antifeedant activity was studied according to procedure described in the literature [10].Fresh cotton leaves were collected from field and washed with water and cleaned then they were plugged with cotton. 1ml.spray solution was prepared in different 1ml. plastic capsules by dissolving compounds in acetone. The solution of each compound was sprayed on leafs and dried under ceiling fan for 10 to15 min. for evaporating acetone. 10 fresh mealy bugs were released on each leaf for direct contact with the help of brush. Each treatment including control was replicated for five times. Insects under experiments were examined for mortality after 12, 24. and 36 hr of treatment. The insecticide *Fipronil 5% SC* was used as a standard check. Moribund insects were however considered as dead. Values are given in Table 1.

General Procedure for Synthesis of Chalcone: A solution of acetophenone (0.02 mol) and aldehyde (0.02 mol) were dissolved in ethanol (15 ml), under stirring and aqueous KOH (50%, 12 ml) was added drop wise. The reaction mixture was stirred at room temperature and kept overnight in a bulb oven at 55-60°C. After 14-16 hr, the reaction mixture was diluted with H_2O and acidified with HCl (10%). The separated solid was filtered and crystallized from glacial acetic acid afforded crystalline chalcones.

Structures of chalcones were confirmed by positive Wilson test [11], red colouration with Conc.H_2SO_4, elemental analysis and spectral data.

1-(3-Bromo-5-chloro-2-hydroxy-phenyl)-3-naphthalen-1-yl-propenone (3a): Pale Yellow crystals; Yield 87%; mp 140°C; IR (KBr): 1633, 1600, 1562 cm^{-1}. ^1H NMR (DMSO-d_6): δ7.6 (1H, d *J*=16 Hz, H_α), δ7.94 (1H, d *J*=16 Hz H_β), δ7.53- δ8.23 (m, 9H, Ar-H), δ13.7 (s, 1H, Ar-OH D_2O exchangeable) MS (m/z):388.5(M^+). Anald. Calcd. For $C_{19}H_{12}BrClO_2$: C, 58.83, H, 3.09, X, 29.80 Found C, 58.78, H, 3.04, X, 30.84.

1-(5-Chloro-2-hydroxy-3-iodo-4-methyl-phenyl)-3-naphthalen-1-yl-propenone (3b): Yellow crystals; Yield 80%; mp 144°C; IR (KBr): 1635, 1610, 1595 cm^{-1}. ^1H NMR ($CDCl_3$-DMSO-d_6): δ2.32 (s, 1H, CH_3) δ7.54 (1H, d *J*=16 Hz, H_α), δ7.88 (1H, d *J*=16 Hz H_β), δ7.2-δ8.12 (m, 8H, Ar-H), δ13.15 (s, 1H, Ar-OH D_2O exchangeable) MS (m/z): 448.5(M^+). Anald. Calcd. For $C_{20}H_{14}ClIO_2$: C, 53.51, H, 3.12, X, 36.23 Found C, 53.54, H, 3.15, X, 36.28.

1-(3-Bromo-5-chloro-2-hydroxy-4-methyl-phenyl)-3-naphthalen-1-yl-propenone (3c): Yellow crystals; Yield 78%; mp 174°C; IR (KBr): 1636, 1610, 1595 cm^{-1}. ^1H NMR (DMSO-d_6): δ2.34 (s, 1H, CH_3), δ7.34 (1H, d *J*=16 Hz, H_α), δ7.93 (1H, d *J*=16 Hz H_β), δ7.25-δ8.12 (m, 8H, Ar-H), δ12.85 (s, 1H, Ar-OH D_2O exchangeable) MS(m/z): 401.5(M^+). Anald. Calcd. For $C_{20}H_{14}BrClO_2$: C, 59.77, H, 3.48, X, 28.76 Found C, 59.75, H, 3.51, X, 28.72.

1-(5-Chloro-2-hydroxy-3-iodo-phenyl)-3-naphthalen-1-yl-propenone (3d): Yellow crystals; Yield 84%; mp 146°C; IR (KBr): 1630, 1605, 1580 cm^{-1}. ^1H NMR (DMSO-d_6): δ7.52 (1H, d J=16 Hz, H_α), δ7.93 (1H, d J=16 Hz H_β), δ7.32-δ7.98 (m, 9H, Ar-H), δ11.85 (s, 1H, Ar-OH D_2O exchangeable) MS (m/z): 434.5(M^+). Anald. Calcd. For $C_{19}H_{12}ClIO_2$: C, 52.47, H, 2.76, X, 37.39 Found C, 52.52, H, 3.70, X, 36.35.

1-(3-Bromo-4-hydroxy-5-methyl-phenyl)-3-naphthalen-1-yl-propenone (3e): Yellow crystals; Yield 88 %; mp 170°C; IR (KBr): 1633, 1602, 1586 cm^{-1}. ^1H NMR (DMSO-d_6): δ7.48 (1H, d J=16 Hz, H_α), δ7.95 (1H, d J=16 Hz H_β), δ7.28-δ8.15 (m, 9H, Ar-H), δ6.78 (s, 1H, Ar-OH D_2O exchangeable) MS (m/z): 367(M^+). Anald. Calcd. For $C_{20}H_{15}BrO_2$: C, 65.39, H, 4.08, X, 21.17 Found C, 65.42, H, 4.11; X, 21.23.

1-(4-Hydroxy-3-iodo-5-methyl-phenyl)-3-naphthalen-1-yl-propenone (3f): Yellow crystals; Yield 81%; mp 178°C; IR (KBr): 1655, 1620, 1605, 1580 cm^{-1}. ^1H NMR (DMSO-d_6): δ2.34 (s, 1H, CH_3), δ7.40 (1H, d J=16 Hz, H_α), δ7.88 (1H, d J=16 Hz H_β), δ7.35-δ8.21 (m, H, Ar-H), δ6.8 (s, 1H, Ar-OH D_2O exchangeable). MS (m/z): 414(M^+). Anald. Calcd. for $C_{20}H_{15}IO_2$: C, 57.97; H, 3.62; X, 30.67 Found C, 57.94; H, 3.64; X, 30.70.

1-(3,5-Dichloro-4-hydroxy-phenyl)-3-naphthalen-1-yl-propenone (3g): Yellow crystals; Yield 84%; mp 196°C; IR (KBr): 1639, 1591 cm^{-1}. ^1H NMR (DMSO-d_6): δ7.56 (1H, d J=16 Hz, H_α), δ7.95 (1H, d J=16 Hz H_β), δ7.46- δ8.62 (m, 9H, Ar-H), δ6.7 (s, 1H, Ar-OH D_2O exchangeable). MS (m/z): 343(M^+). Anald. Calcd. for $C_{19}H_{12}Cl_2O_2$: C, 66.47; H, 3.49; X, 20.69. Found C, 66.42; H, 3.47; X, 20.74.

1-(3,5-Dichloro-2,4-dihydroxy-phenyl)-3-naphthalen-1-yl-propenone (3h): Light Yellow crystals; Yield 90%; mp 218°C; IR (KBr): 1625, 1552 cm^{-1}. ^1H NMR (DMSO-d_6): δ7.53 (1H, d J=16 Hz, H_α), δ7.79 (1H, d J=16 Hz H_β), δ7.9-δ8.4 (m, 8H, Ar-H), δ8.5(s, 1H, Ar-OH/ 4'-OH D_2O exchangeable)) δ13.4 (s, 1H, Ar-OH/ 2'-OH D_2O exchangeable) MS(m/z): 359(M^+). Anald. Calcd. for $C_{19}H_{12}Cl_2O_3$: C, 63.50; H, 3.34; X, 19.77. Found C, 63.54; H, 3.37; X, 19.80.

1-(3-Bromo-5-chloro-2-hydroxy-4-methyl-phenyl)-3-(2-hydroxy-3,5-diiodo-phenyl)-propenone (3i): Yellow crystals;Yield 85%; mp 152°C; IR (KBr): 1634, 1610, 1595 cm^{-1}. ^1H NMR (DMSO-d_6): δ7.46 (1H, d J=16 Hz, H_α), δ7.94 (1H, d J=16 Hz H_β), δ7.38-δ8.81 (m, 3H, Ar-H), δ12.95 (s, 1H, Ar-OH D_2O exchangeable). MS(m/z): 619.5(M^+). Anald. Calcd. for $C_{16}H_{10}BrClI_2O_3$: C, 30.99; H, 1.61; X, 59.64. Found C, 31.03; H, 1.57; X, 59.67.

1-(3-Bromo-5-chloro-2-hydroxy-phenyl)-3-(2-hydroxy-3,5-diiodo-phenyl)-Propenone (3j): Dark Yellow crystals; Yield 84%; mp 218°C; IR (KBr): 1629, 1615, 1590 cm^{-1}. ^1H NMR (DMSO-d_6): δ7.44 (1H, d J=16 Hz, H_α), δ9.05 (1H, d J=16 Hz H_β), δ7.10-δ8.1 (m, 4H, Ar-H), δ13.1 (s, 1H, Ar-OH D_2O exchangeable) MS(m/z): 605.5(M^+). Anald. Calcd. for $C_{15}H_8BrClI_2O_3$: C, 29.72; H, 1.32; X, 61.02. Found C, 29.77; H, 1.29; X, 61.04.

1-(3-Bromo-5-chloro-2-hydroxy-phenyl)-3-(3,4,5-trimethoxy-phenyl)-propenone (3k): Yellow crystals; Yield 86%; mp 164°C, IR (Kbr): 1625, 1625, 1605, 1585 cm^{-1}. ^1H NMR (DMSO-d_6): δ7.58 (1H, d J=16 Hz, H_α), δ7.94 (1H, d J=16 Hz H_β), δ7.25-δ8.25 (m, 4H, Ar-H), δ12.62 (s, 1H, Ar-OH D_2O exchangeable), MS (m/z): 427.5(M^+). Anald. Calcd. for $C_{18}H_{16}BrClO_5$: C, 50.52; H, 3.74; X, 27.01. Found C, 50.55; H, 3.71; X, 26.97.

1-(3-Bromo-5-chloro-2-hydroxy-4-methyl-phenyl)-3-(3,4,5-trimethoxy-phenyl)-Propenone (3l): Pale Yellow crystals; Yield 87%; mp 180°C, IR (KBr):1637, 1560 cm^{-1}. ^1H NMR (DMSO-d_6): δ2.54(s,3H, CH_3), δ3.73(s, 3H, OCH_3), δ3.87 (s, 6H, 2×OCH_3), δ7.85 (1H, d J=16 Hz, H_α), δ7.98 (1H, d J=16 Hz, H_β), δ7.3(s, 2H,2',6'Ar-H), δ8.5 (s,1H,6Ar-H), δ13.8 (m, 1H, Ar-OH D_2O exchangeable)) MS (m/z): 441.5(M^+). Anald. Calcd. for $C_{19}H_{18}BrClO_5$: C, 51.64, H, 4.07, X, 26.16 Found C, 51.62; H, 4.03; X, 26.20.

RESULT AND DISCUSSION

We have synthesized and evaluated twelve new chalcones (Schme), out of that eight chalcones (3a-h) contain naphthalene moiety, two chalcones contains (3i-j) 2-hydroxy-3,5-diiodophenyl moiety and remaining two chalcones (3k-l) contains 3,4,5-trimethoxy moiety as B ring. In this study, the values allowed to us conclude that chalcones (3k,3l) having methoxy groups at position 3,4,5 in ring B showed better antifeedant activity than standard. Chalcones 3b, 3c and 3e containing methyl group in ring A and naphthalene moiety as a ring B also increases the antifeedant activity. While rest of chalcones gave moderate activity than Fipronil.

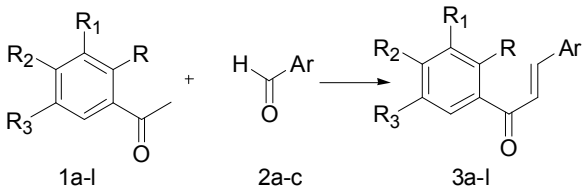
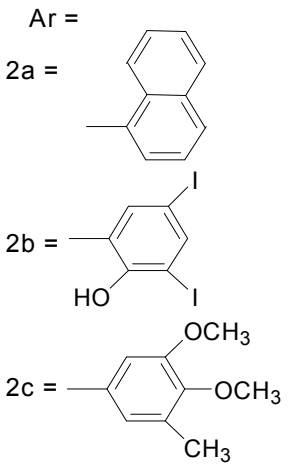


Table 1: Insect antifeedant activity of chalcones against mealy bugs (*Phenacoccus solenopsis*)

Entry	R	R_1	R_2	R_3	Ar
1a, 3a	OH	Br	H	Cl	2a
1b, 3b	OH	I	CH_3	Cl	2a
1c, 3c	OH	Br	CH_3	Cl	2a
1d, 3d	OH	I	H	Cl	2a
1e, 3e	H	CH_3	OH	Br	2a
1f, 3f	H	CH_3	OH	I	2a
1g, 3g	H	Cl	OH	Cl	2a
1h, 3h	OH	Cl	OH	Cl	2a
1i, 3i	OH	Br	CH_3	Cl	2b
1j, 3j	OH	Br	H	Cl	2b
1k, 3k	OH	Br	H	Cl	2c
1l, 3l	OH	Br	CH_3	Cl	2c



Scheme 1:

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