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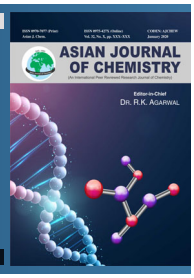

Isolation, Semi-Synthesis and Antifeedant Activity of Constituents from *Derris scandens* Benth.

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This work describes the semi-synthesis of derivatives from derris isoflavone-A (**1**), scandenin (**2**) and 6,8-diprenyl-4′,5,7-trihydroxy isoflavone (**3**) which are major constituents isolated from chloroform extract of *Derris scandens* Benth. All the semi-synthesized derivatives (**4-11**) were characterized by NMR and mass spectroscopic techniques. All these derivatives are evaluated for their antifeedant activity in castor semilooper and tobacco caterpillar using a no-choice laboratory bioassay. The results demonstrated that scandenin (**2**), compounds **5**, **7** and **10** have shown potent insecticidal activity.

Keywords: *Derris scandens* Benth., Scandenin, Antifeedant activity.

INTRODUCTION

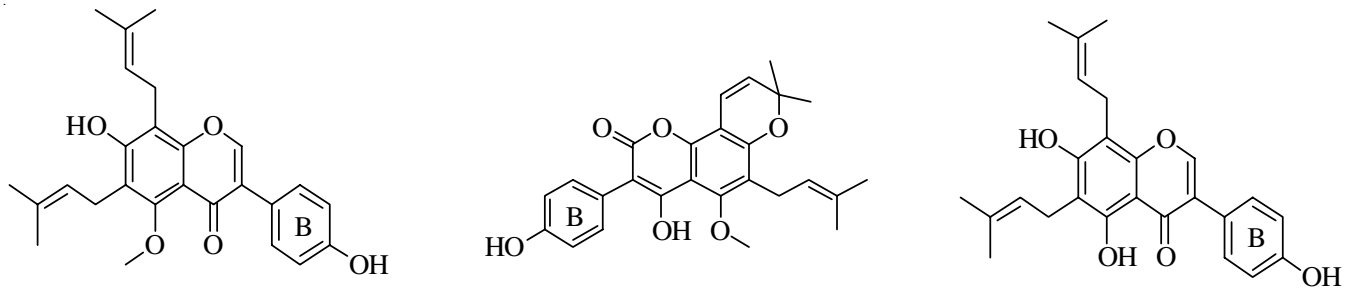
Globally, it is estimated that 10-30% of production losses due to the insect damage and microbial deterioration [1]. *Spodoptera litura* (Fabricius) (Lepidoptera: Noctuidae), known as Asian armyworm is a polyphagous defoliator pest of cosmopolitan distribution having host range of more than 150 species including crops, vegDhaetables, weeds and ornamental plants [2]. In India, it is considered to be one of the significant damages to the present-day agribusiness around the world. While significant investment for the application of synthetic pesticides, global crop losses remain a matter of concern and poses challenges to ensure food security [3]. In this context, plant based insecticides may be potential alternatives as they constitute rich source of bioactive secondary metabolites. Azadirachtin from neem tree is the best example for plant-based insecticides.

Derris scandens Benth (Family: leguminosae), commonly known as "Gonj" is evergreen plant mainly found in sub-himalayan range, south India and Assam. The plant is well known for its insecticidal properties. Rotenone, isolated from derris species is commercially known as insecticidal agent. Its dried stem was used as an expectorant, antitussive, diuretic, antidysenteric agents and for the treatment of muscle aches [4], cough and diarrhea, insecticidal activity [5], antihypertensive, anti-inflammatory [6] and antibacterial [7] activities, respectively. A methanolic extract of the stem was reported for antimicrobial and immune stimulating activities [8]. The previous phytochemical studies indicated the presence of coumarins, isoflavones and isoflavone glycosides from the stem of *D. scandens* [9-18]. As part of our study on the development of plant based insecticidal agents, we have collected stem-bark of *Derris scandens* and conducted detailed phytochemical study of its chemical constituents, which led to the isolation of three major isoflavone constituents (**1**-**3**) (Fig. 1). To further explore their biological activities, few semi-synthetic derivatives were synthesized on these isoflavone constituents and evaluated for their antifeedant activity.

EXPERIMENTAL

Plant material: Stembark of *Derris Scanden* collected from seshachalam forest at a place of Tirumala in Chittoor district, which is located at Andhra Pradesh in the month of February. Plant was identified by the Prof. K. Madhava Chetty, Department of Botany, Sri Venkateswara University, Tirupati, India. A voucher specimen number 536 for this plant is deposited in the herbarium at Botany department.

Isolation of scandenin and its derivatives: The plant material (5 kg) was shade dried, powdered and extracted with chloroform in a Soxhlet mechanical assembly for 72 h. The



Derris isoflavone (**1**) Scandenin (**2**) 4',5,7-Trihydroxy isoflavone (**3**)

Fig. 1. Isolated compounds from *Derris scandens*

subsequent chloroform extract was concentrated to dryness under plant vacuum at 1 bar, to afford syrupy crude (50 g). The obtained chloroform crude was performed to column chromatography by using 100-200 silica gel mesh (column height and width 150 × 7.5 cm) and using various compositions of pet. ether (100:0) to pet. ether/$CHCl_3$ (10: 90) to get an aggregate number of 20 fractions of 100-250 mL each portion. TLC examinations of obtained fractions by using different mobile phase of petroleum ether/$CHCl_3$, 90:10 and petroleum ether: $CHCl_3$, 0:100) to afford 4 major fractions. Fraction F_1 was further subjected to column chromatography by using hexane:ethyl acetate (90:10) to get the derris isoflavone-A (compound **1**) and scandenin (compound **2**) (1.0 g) were obtained. Fraction F_2 was performed column chromatography with hexane:ethyl acetate (80:20) to get 6,8-diprenyl-4′,5,7-trihydroxy isoflavone (compound **3**).

General procedure for the synthesis of methylation derivatives: Methanol (20 mL) was added to compound **1/2/3** (10 mg, 1.0 mmol) in a two-necked round bottom flask. About 32% sulphuric acid (3.0 mmol) was added slowly for 5 min at 0-5 ºC. After completion of addition, reaction mass was allowed to reflux at ~ 65 ºC and maintained until solid mass completely converted by monitoring *via* TLC [19]. The reaction mass was concentrated under reduced pressure and purified by column chromatography by using hexane:EtOAc (90:10).

General procedure for the synthesis of epoxide: Dichloromethane (20 mL) was added to compound **1/2/3** (10 mg, 1.0 mmol) in a 2 necked round bottom flask. 3-Chloroperbenzoic acid (*m*-CPBA, 1.4 mmol) was charged at 0-5 ºC. Reaction mass was allowed to stand till room temperature attained until solid mass completely converted by monitoring *via* TLC [20]. The reaction mass was washed with a cooled solution of 10% NaOH, followed by saturated brine and dried over Na_2SO_4. The solvent was removed under plant vacuum and the crude epoxide was washed with hexane to get pure compound.

General procedure for the synthesis of allyl formation: Compounds **2/3** (10 mg, 1.0 mmol) was taken into a 20 mL THF solution at 0 °C. Sodium hydride (60% dispersion in mineral oil, 1.2 mmol) was added slowly at 0 °C under nitrogen atmosphere followed by the addition of allyl bromide at 0 ºC. The reaction mixture was stirred until solid mass is completely converted by monitoring *via* TLC and poured into ice water (10 mL) [21]. The aqueous layer is extracted into EtOAc (50 mL). The organic layer was washed with brine (20 mL), dried under Na_2SO_4, filtered and concentrated under reduced pressure. The desired product was obtained by recrystallization from EtOAc/ethanol.

Antifeedant bioassays: Antifeedant activity of the compounds was assessed on a tobacco caterpillar larvae (*S. litura*) and castor semilooper (*A. janata*). The experiments were conducted according to the classical no-choice leaf-disk bioassay as described earlier by Akhtar and Islam [22]; a small circular disk of 5 cm diameter was cut from fresh castor leaves. The leaf discs were treated on their upper surface with individual concentrations of the compounds and one leaf disc each was transferred to petriplate (15 cm diameter) containing moist filter paper. Control leaf discs were treated with the same volume of the solvent. Pre-starved healthy third instar larvae of *A. janata* and *S. litura* were introduced into each petri dish and were allowed to feed on the leaf disc. Progress of the consumption of the leaf area was measured at 6, 12 and 24 h post treatment using AM-300 leaf area meter. The antifeedant index was then calculated as $(C - T)/(C + T) \times 100$, where C is consumption of control discs and T is consumption of treated discs. For each concentration, there were five replicates and each test was repeated three times. The mean of the 15 replicates was taken for each compound and the percentage of antifeedant activity was calculated. Azadirachtin was used as an active control for comparison.

Toxicity bioassays: Toxicity of the compounds was determined by topical application of the test compounds to fourth instar larvae as previously described [23]. Each compound (4 mg) was applied directly to the dorsum of the larva in a 1 mL drop of acetone using a micro applicator. The controls were treated similarly with the solvent. The treated and control larvae were fed with fresh castor leaves. Mortality was determined daily until 3 days after treatment. Larvae that lost elasticity and showed no responses when their tails were pinched with forceps were regarded as dead. There were 10 replicates for each experiment, leading to 30 replicates with each concentration of compounds. The mean of 30 replicates was taken and the percentage of mortality with standard error was calculated.

The NMR spectra were recorded on a Bruker 400 MHz spectrometer for proton and 100 MHz for ^{13}C, respectively, using TMS as internal standard. The chemical shifts are expressed as δ values in parts per million (ppm) and the coupling constants (*J*) are given in hertz (Hz). Mass spectra were perfor-

med on Agilent Technologies 6510 Q-TOF Mass spectrometer. The chromatography was executed with silica gel (100-200 mesh, Qing-dao Marine Chemical, Inc., Qingdao, China) using mixtures of ethyl acetate and hexane as eluents. Reactions, which required the use of anhydrous, inert atmosphere techniques, were carried out under nitrogen atmosphere. Commercially available reagents, solvents and starting materials were used without further purification. Analytical TLC was performed on recoated Merck plates (60 F254, 0.2 mm) with the solvent system EtOAc/hexane and compounds were viewed under a UV lamp and sprayed with 10% H_2SO_4, followed by heating.

Spectral data

5,7-Dimethoxy-3-(4-methoxyphenyl)-6,8-*bis*(3-methylbut-2-en-1-yl)-4*H*-chromen-4-one (4): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (1H, s) 7.48 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.22 (brs, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 3.53 (d, *J* = 6.5 Hz, 2H), 3.44 (d, *J* = 6.5 Hz, 2H), 1.83 (s, 3H), 1.80 (s, 3H), 1.71 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 161.0, 159.5, 157.0, 155.2, 150.6, 132.3, 131.5, 130.2, 126.8, 125.4, 124.3, 123.3,122.0, 119.7, 113.9, 62.2, 61.9, 55.3, 31.9, 29.6, 25.6, 23.3, 22.6, 17.9. HRESI-MS: $C_{28}H_{33}O_5$, calculated mass 449.2328 $[M+H]^+$ obtained mass 449.2357.

6,8-*bis*((3,3-Dimethyloxiran-2-yl)methyl)-7-hydroxy-3-(4-hydroxyphenyl)-5-methoxy-4*H*- chromen-4-one (5): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (1H, s), 7.32 (d, *J* = 9.1 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H), 3.16 (dd, *J* = 4.8, 13.7 Hz, 2H), 3.03 (m, 2H), 2.95 (dd, *J* = 4.7, 14.9 Hz, 1H), 1.56 (s, 6H), 1.48 (s, 6H). HRESI-MS: $C_{26}H_{29}O_7$, calculated mass 453.1913 $[M+H]^+$ observed mass 453.1894.

4,5-Dimethoxy-3-(4-methoxyphenyl)-8,8-dimethyl-6-(3-methylbut-2-en-1-yl)-2*H*,8*H*-pyrano[2,3-f]chromen-one (6): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.85, 2H), 6.96 (d, *J* = 9.9, 2H) 6.65 (d, *J* = 8.85, 1H), 5.71 (d, *J* = 9.9 Hz, 1H), 5.27 (m, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.54 (s, 3H), 3.49 (d, *J* = 7.4 Hz 2H), 1.85 (s, 3H), 1.67 (s, 3H), 1.47 (s, 6H). HRESI-MS: $C_{28}H_{31}O_6$, calculated mass 463.2920 $[M+H]^+$ observed mass 463.2154.

6-((3,3-Dimethyloxiran-2-yl)methyl)-4-hydroxy-5-methoxy-3-(4-methoxyphenyl)-8,8-dimethyl-3,4-dihydro-2*H*,8*H*-pyrano[2,3-f]chromen-2-one (7): ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (1H, s) 7.42 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 10.07 Hz, 1H), 5.77 (d, *J* = 10.07 Hz, 1H), 3.98 (s, 3H), 3.06 (dd, *J* = 5.95 Hz, 1H), 2.97 (t, *J* = 5.95, 1H), 2.85 (dd, *J* = 5.95 Hz, 1H),1.55 (s, 3H), 1.50 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 162.709, 160.658, 155.495, 155.033, 151.748, 150.664, 131.782, 131.306, 122.688, 115.099, 110.767, 110.506, 103.884, 101.604, 77.665, 64.399, 63.063, 59.908, 28.097, 27.772, 24.702, 22.139, 19.143. HRESI-MS: $C_{26}H_{27}O_7$, calculated mass 451.1756 $[M+H]^+$ observed mass 451.1766.

4-(Allyloxy)-3-(4-(allyloxy)phenyl)-5-methoxy-8,8-dimethyl-6-(3-methylbut-2-en-1-yl)-2*H*,8*H*-pyrano[2,3-f]chromen-2-one (8): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 10.07 Hz, 1H), 6.05-5.99 (1H, m), 5.71 (d, *J* = 10.07 Hz, 1H), 5.54 (d, *J* =17.2 Hz, 1H), 5.27 (d, *J* = 10.5, 14.3 Hz, 2H), 5.14 (d, *J* = 16.3 Hz, 1H), 5.10 (m, 2H), 5.04 (m, 3H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.47 (d, *J* = 5.3 Hz, 2H), 3.78 (s, 3H), 3.53 (q, *J* = 6.7, 15.8 Hz, 1H), 3.17 (q, *J* = 1.2, 12.2 Hz, 1H), 1.76 (s, 3H), 1.65 (s, 3H), 1.41 (s, 6H). ^{13}C NMR (100MHz, $CDCl_3$): δ 161.4, 159.9, 158.2, 150.4, 149.6, 144.5, 144.4,142.4, 136.4, 133.2, 131.9, 130.3, 128.7, 127.3, 124.6, 121.5, 117.6, 114.7, 112.8, 112.2, 107.2, 62.0, 29.7, 28.1, 25.8, 21.8, 17.9. HRESI-MS: $C_{32}H_{35}O_6$, calculated mass 515.2433 $[M+H]^+$ observed mass 515.2311.

5,7-Dimethoxy-3-(4-methoxyphenyl)-6,8-*bis*(3-methylbut-2-en-1-yl)-4*H*-chromen-4-one (9): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.48 (d, *J* = 8.85, 2H) 6.96 (d, *J* = 8.85, 2H), 5.21 (m, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 3.53 (d, *J* = 7.4 Hz, 2H), 3.44 (d, *J* = 7.4 Hz, 2H), 1.83 (s, 3H), 1.80 (s, 3H), 1.71 (s, 3H), 1.68 (s, 3H). HRESI-MS: $C_{28}H_{33}O_5$ calculated mass 449.2250$[M+H]^+$ observed mass 449.2274.

6,8-*Bis*((3,3-dimethyloxiran-2-yl)methyl)-5,7-dihydroxy-3-(4-hydroxyphenyl)-4*H*-chromen-4-one (10): ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.17 (s, 1H), 7.83 (s, 1H), 7.49 (d, *J* = 8.30 Hz, 2H), 6.96 (d, *J* = 8.30 Hz, 2H), 5.97 (s, 1H), 3.12-2.87 (m, 6H), 1.50 (s, 3H), 1.48 (s, 6H), 1.33 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 175.47, 159.40, 155.13, 153.52, 131.94, 130.48, 130.27, 125.18, 124.37, 121.52, 116.49, 113.85, 113.29, 112.94, 67.36, 62.66, 55.27, 31.89, 29.67, 25.57, 22.69, 21.77, 17.89. HRESI-MS: $C_{25}H_{27}O_7$ calculated mass 439.1756 $[M+H]^+$ observed mass 439.1564.

7-(Allyloxy)-5-hydroxy-3-(4-hydroxyphenyl)-6,8-*bis*(3-methylbut-2-en-1-yl)-4*H*-chromen-4-one (11): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.46 (d, *J* = 8.85, 2H) 6.97 (d, *J* = 8.85, 2H), 6.75 (d, *J* = 10.07 Hz, 1H), 6.196 (m, 1H), 6.08 (m, 1H), 5.70 (d, *J* = 10.07 Hz, 1H), 5.42 (d, *J* = 1.5, 17.2 Hz, 1H), 5.34 (d, *J* = 1.5, 17.2 Hz, 1H), 5.28 (d, *J* = 1.5Hz, 1H), 5.22 (d, *J* = 1.5Hz, 2H), 4.57 (d, *J* = 5.3 Hz, 2H), 4.50 (d, *J* = 5.3 Hz, 2H), 3.46 (d, *J* = 7.4 Hz, 2H), 3.44 (d, *J* = 7.4 Hz, 2H), 1.83 (s, 3H), 1.70 (s, 3H), 1.56(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 158.9, 156.6, 153.9,152.6, 152.4, 140.7, 138.7, 136.0,134.8, 133.8, 130.9, 130.2, 128.0, 125.6, 124.3, 123.8,123.0, 121.9, 114.9, 105.4, 62.0, 29.6, 28.2, 26.3, 25.7, 21.2, 17.8. HRESI-MS: $C_{31}H_{35}O_5$ calculated mass 487.2484 $[M+H]^+$ observed mass 487.2454.

RESULTS AND DISCUSSION

The chloroform extract was chromatographed on silica gel and resultant fractions were subjected to series of chromatographic separations to afford three major compounds. The structures of these compounds were elucidated based on their spectroscopic data and further comparison with literature, they were characterized as derris isoflavone-A (**1**), scandenin (**2**) and 6,8-diprenyl-4',5,7-trihydroxy isoflavone (**3**) (Fig. 1). All the isolated compounds were tested for their antifeedant activities aganist *Spodoptera litura* using no-choice laboratory assay were shown in Table-1.

It is well-known fact that structural modification of an active molecule is a tool to obtain a more efficacious than its natural counterpart. Today, majority of commercially available

TABLE-1
ANTIFEEDANT ACTIVITY OF SYNTHESIZED COMPOUNDS

Compounds	µg/cm^2% Mortality LC$_{50}$(95%FL[a])µg/insect	
	Achea janata	*Spodoptera litura*
1	62.4 ± 1.2	65.1 ± 1.3
2	93.2 ± 0.8	93.6 ± 0.5
3	75.2 ± 0.9	74.8 ± 0.6
4	26.9 ± 4.8	25.6 ± 2.2
5	85.2 ± 3.7	85.8 ± 1.8
6	19.1 ± 3.3	26.6 ± 3.1
7	81.1 ± 5.1	81.4 ± 3.2
8	16.6 ± 0.5	17.5 ± 2.3
9	9.4 ± 0.6	7.3 ± 0.7
10	82.5 ± 1.3	89.5 ± 2.7
11	75.9 ± 1.8	81.3 ± 2.9
Azadirachtin[b]	100 ± 0.00	100 ± 0.00

[a]Values are mean ± SE; [b]Azadirachtin at a dose of 1.5 µg/cm^2

TABLE-2
TOPICAL BIOASSAY ACTIVITY OF SYNTHESIZED COMPOUNDS

Compounds	µg/cm^2% Mortality LC$_{50}$(95%FL[a])µg/insect	
	Achea janata	*Spodoptera litura*
1	57.3 ± 3.2	66.2 ± 1.1
2	77.6 ± 1.1	75.9 ± 1.4
3	74.5 ± 2.6	76.7 ± 5.0
4	22.4 ± 3.3	24.5 ± 2.6
5	87.4 ± 4.2	79.5 ± 1.3
6	15.7 ± 0.6	20.8 ± 4.4
7	78.5 ± 1.1	79.3 ± 0.5
8	18.9 ± 1.3	19.3 ± 0.6
9	7.8 ± 0.9	6.8 ± 0.6
10	79.4 ± 1.2	85.7 ± 1.3
11	78.3 ± 1.2	80.2 ± 1.3
Azadirachtin[b]	100 ± 0.00	100 ± 0.00

[a]Values are mean ± SE; [b]Azadirachtin at a dose of 1.5 µg/cm^2

drugs in late stages of clinical trials are of natural origin. On the basis of these observations and in continuation of our efforts on structural simplification of natural products, we were interested to make derivatization on these isolates (**1-3**) because of their potential biological activities coupled with the functionalities present on these scaffolds. In this article, eight analogues were prepared through alkylation, epoxidation and allylation aimed at elucidating the role of phenol group and double bond. All analogues were evaluated for their antifeedant activities against *spodoptera litura*. The results from these studies are reported herein.

As shown in **Scheme-I**, derivatives were prepared through the alkylation of hydroxyl groups and epoxidation of double bond. Thus, derris isoflavone (**1**), scandenin (**2**) and trihydroxy isoflavone (**3**) were treated with methyl iodide in the presence of K_2CO_3 in acetone under reflux conditions yielded the corresponding methylated products **4**, **6** and **9**, respectively. Similarly, compounds **2** and **3** were treated with allyl bromide in the presence of K_2CO_3 in acetone under reflux conditions yielded the corresponding allylated products **8** and **11**. The compounds **1-3** were treated with *m*-chloroperbenzoic acid in DCM under 0-5 °C yielded the corresponding epoxides **5**, **7** and **10** in moderate yields.

Antifeedant activity of synthesized compounds by no-choice laboratory bioassay method: The antifeedant activity for semi synthesized compounds (**4-11**) were tested for their viability in castor semilooper and tobacco caterpillar using a no-choice laboratory bioassay and azadirachtin was utilized as a standard for biological activity. Derris isoflavone-A (**1**) and 6,8-diprenyl-4,5,7-tri hydroxy isoflavone (**3**) showed potent insecticidal activity due to isoflavone moiety was responsible for feeding control. As appeared in Table-1, synthesized molecules **4**, **6**, **8** and **9** have low antifeedant activity compared to parent molecule, while compounds **5**, **7** and **10** have displayed potent antifeedant activity against the test insects. In topical bioassay, synthesized molecules **4**, **6**, **8** and **9** have low activity compared to parent molecule, while compounds **5**, **7** and **10** have displayed potent activity against these test insects (Table-2).

Compounds **4**, **6** and **9** have less insecticidal activity due to methylation of hydroxyl group of the B-Ring. Compounds **5**, **7** and **10** LC_{50} values are potent than parent molecules due to free hydroxyl group at the *para* position of B-ring, as well as epoxide formation at double bond. It is apparent from the results, antifeedancy and topical bioassay are directly proportional, recommending that comparable structures are necessary for antifeedant activity. These outcomes demonstrated that semi synthesized compounds (**5**, **7** and **10**) possess significant biological activity on the insect species analyzed from these examination.

Conclusion

We have isolated naturally occurring isoflavones, *i.e*. derris isoflavone-A, scandenin and 6,8-diprenyl-4',5,7-tri hydroxy isoflavone molecules from *Derris scanden* chloroform extract. These three molecules are subjected to methylation, epoxidation and allylation to attain a set of synthesized derivatives (**4-11**). Some of the synthesized compounds, *i.e.* **5**, **7** and **10** showed good antifeedant activity and topical bioassay activity.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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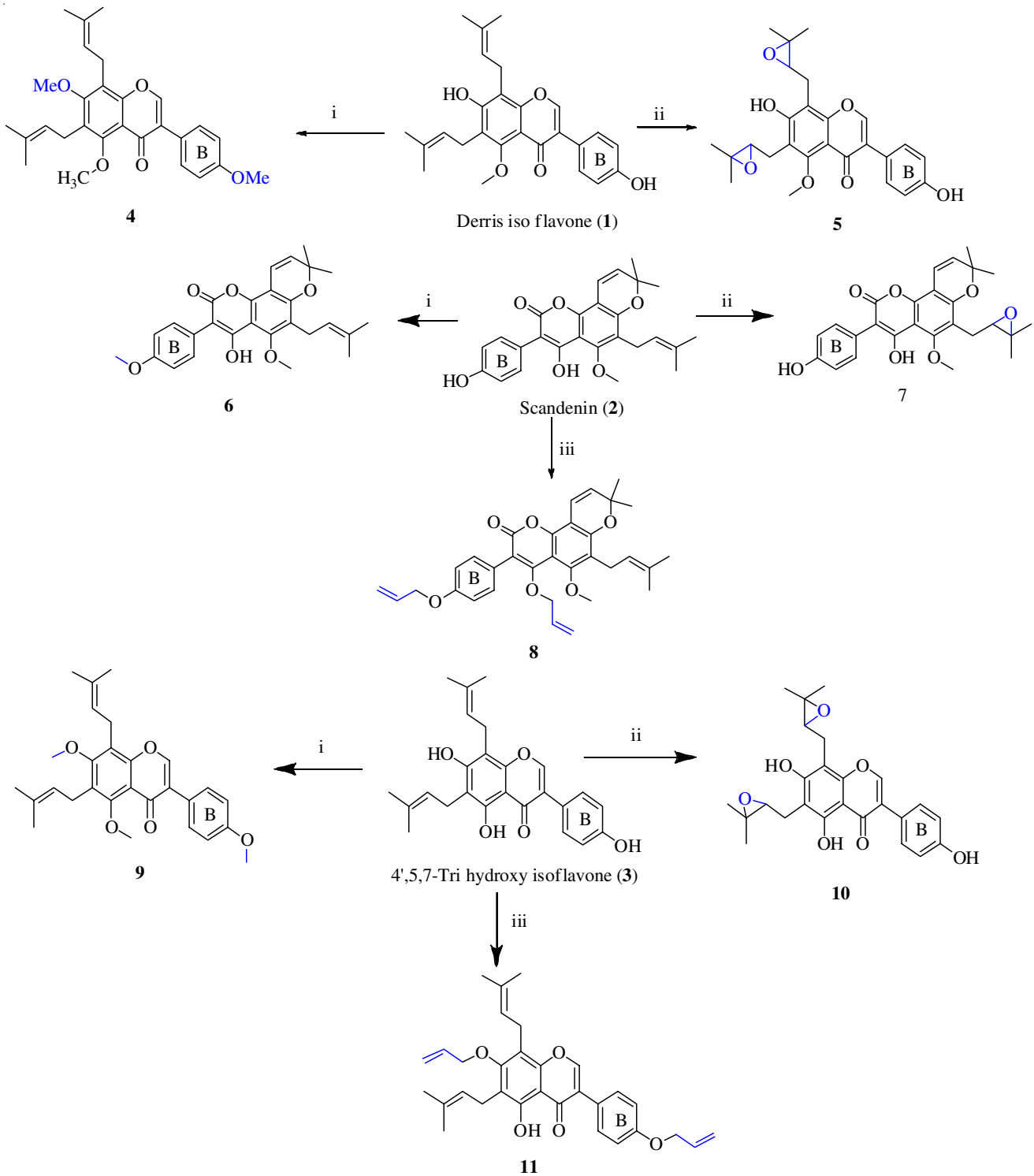

Scheme-I: Reagents and conditions: i) H_2SO_4, methanol, reflux, ii) DCM, *m*CPBA, room temperature, iii) NaH, allyl bromide, THF

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