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A new benzil derivative from *Derris scandens*: Structure-insecticidal activity study

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ABSTRACT

Bioactivity-directed investigation of root extract of *Derris scandens* has led to the isolation and characterization of a new benzil derivative (**11**), along with ten known compounds (**1–10**). Their structures were determined on the basis of extensive spectroscopic (IR, MS, 1D and 2D NMR) data analysis and by comparison with the literature data. The insect antifeedant activity and growth inhibitory studies of these compounds were investigated against castor semilooper pest, *Achaea janata* using a no-choice laboratory bioassay. Several of the isolates displayed potent feeding deterrence and were also toxic or caused developmental abnormalities following topical administration. The new compound, derrisdione A was moderately active with an antifeedant index of 58.6 ± 1.7% at 10 μg/cm^3 against *A. janata*.

The focus on the use of natural product based agrochemicals has intensified recently, as they are biodegradable, eco-friendly, and safe to the environment. These plant based insecticides have the advantage of providing novel modes of action that can reduce the risk of cross resistance[1] as well as offering new leads for the design of target-specific molecules. *Derris scandens* (Fabaceae), known by its common name *Gonj* (Hindi), is widely distributed throughout India.[2] One of the potential applications of the Derris species is the use to the control of phytophagous pests. *D. scandens* root, is an excellent insecticide being harmful to the chewing and sucking insects but not human beings.[3] Insecticidal constituents, rotenone[4] and lonchocarpic acid[5] were isolated from the roots of *D. scandens*, which showed high insect antifeedant activity against the larvae of *Spodoptera litura*. It also been used as expectorants,[6] antitussives,[7] diuretics and anti-dysentery agents.[3] In previous studies, coumarins,[8] isoflavones,[9] flavones,[10] isoflavone glycosides[11] and phenyl coumarins[12] have been reported as chemical constituents from *D. scandens*.

As part of our program to screen the Indian medicinal plants for biologically active natural products,[13] chloroform extract of *D. scandens* showed potent insecticidal activity against castor semilooper pest, *Achaea janata*. This led us to undertake a bioactivity-directed investigation of the active component in the *D. scandens* extract. The phytochemical study of this active extract has now permitted the isolation of new benzil derivative (**11**), along with the known compounds (**1–10**). In this Letter, we report isolation, identification, and structure elucidation of new benzil derivative (**11**), its insecticidal activity and preliminary structure–activity relationship studies of the compounds (**1–11**) isolated from this plant. Structure of the new compound was established using IR, MS, 1D and 2D NMR (HSQC, HMBC, COSY and NOESY) spectroscopic techniques (Fig. 1).

The whole plant of *D. scandens* (5 kg) was shade dried, powdered, and extracted with chloroform in a soxhlet apparatus for 72 h. The resulting chloroform extract was evaporated to dryness under reduced pressure, affording syrupy residue (21 g). Then this chloroform extract was subjected to column chromatography on a silica gel column (60–120 mesh, 150 × 15 cm) and eluted with a step wise gradient of hexane/EtOAc (98:2, 95:5, 92:8, 90:10, 88:12 by volume) to give seven fractions (F_1, F_2, F_3, F_4, F_5, F_6 and F_7). Fraction F_2 was chromatographed on silica gel (60–120 mesh) column using hexane/EtOAc (99:1, 98:2 by volume) to give compound **1** (0.2 g) and compound **2** (0.08 g). Fraction F_4 was concentrated under reduced pressure to give compound **3** as a pale yellow solid (0.12 g). Fraction F_5 was further diluted with hexane to furnish compound **5** (5.8 g) as a solid. Upon filtration, the filtrate was concentrated to give compound **4** (4.6 g) as a pale yellow solid. Fraction F_6 was concentrated to give dark brown residue (2.5 g), which was chromatographed on a (100–200 mesh) silica gel column with an isocratic elution of the solvent system, hexane/chloroform/acetone (80:15:5 by volume) to give two sub fractions

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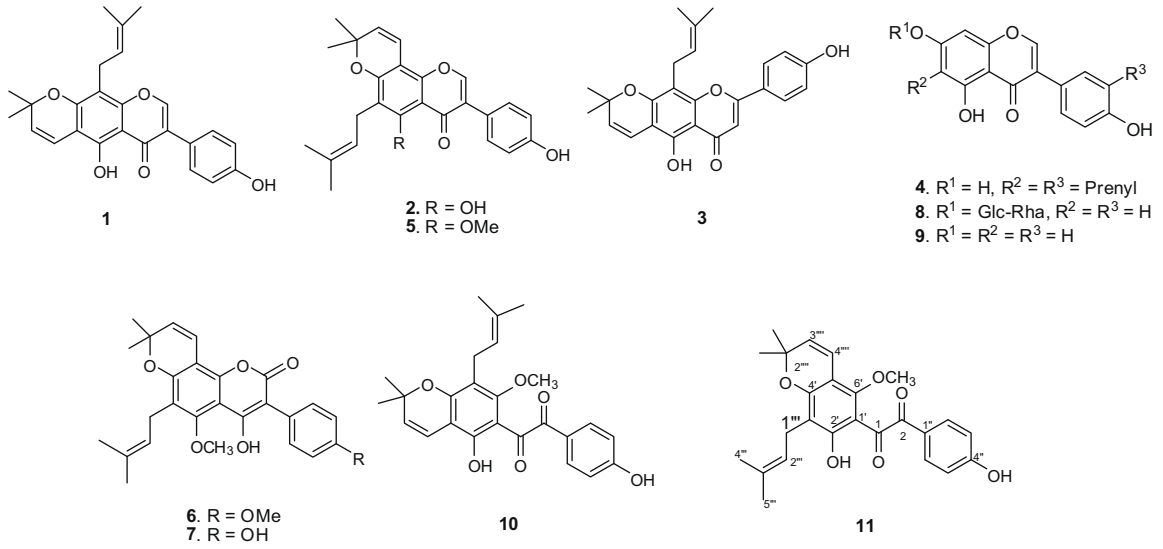

Figure 1. Compounds isolated from the chloroform extract of *Derris scandens*.

A and B. Sub fraction A was further fractionated on silica gel column with isocratic elution of chloroform/carbon tetrachloride/acetone (55:40:5 by volume) to give compound **6** (0.26 g) and compound **7** (1.2 g). Sub fraction B was subjected to HPLC fractionation (acetonitrile/water, 70:30, 4.0 mL/min). The analysis was performed on a reverse phase HPLC using Shimadzu LC-8A system linked to CR 4A data processor and the peaks were detected at 260 nm. The fractionation was carried out on a Waters NovaPak HR C18 (300 × 20 mm, 6 μ). Compound **10** (0.011 g) and compound **11** (0.012 g) were eluted at the retention time of 15.23 min and 17.20 min. Fraction F_6 was chromatographed on a silica gel column (60–120 mesh, 50 × 5 cm) and eluted with a step wise gradient of chloroform/methanol (90:10, 85:15 by volume) to give compounds **8** (2.8 g) and **9** (3.9 g). The known compounds were identified as scandenone (**1**),[14] osajin (**2**),[14] laxifolin (**3**),[15] lupalbigenin (**4**),[16] scandinone (**5**),[16] scandenin A (**6**),[16] scandenin (**7**),[16] sphaerobioside (**8**),[17] genistein (**9**),[18] and (**10**)[19] from ^{1}H and ^{13}C NMR data comparison with those reported in the literature.

Compound **11** was obtained as yellow amorphous solid with the molecular formula $C_{25}H_{26}O_6$, as determined by the HR-EI mass spectrum (*m/z* 423.1827 [M$^+$+H]). The UV spectrum showed absorption maxima at λ_{max} (MeOH) 228 nm, 202 nm and 262 nm which are typical of benzil derivative. IR spectrum displayed a broad band of O–H stretching at 3550 cm^{-1} and a sharp band of –C=O stretching at 1640 cm^{-1} (chelated carbonyl). Resonances of two carbonyl carbons (δ 197.94 and δ 189.50) were present in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum (in MeOH-d_4)[20] showed a singlet signal of methoxyl group at δ 3.46 (s). A pair of doublets at δ 7.85 (J = 8.5 Hz) and δ 6.87 (J = 8.5 Hz) appearing as AA′BB′ pattern, suggested the presence of 1,4-di substituted aromatic ring. The presence of chromene ring was established by the signals due to two methyl groups (δ 1.43, each 3H) and vicinal olefinic protons at δ 6.32 and δ 5.56. In addition, there were characteristic signals of 3,3′-dimethyl allyl (prenyl) group at δ 5.21(t, 1H, J = 7.4 Hz, H-2‴), 3.29 (d, 2H, J = 7.4 Hz, H-1‴), 1.87 (s, 3H, H-4‴) and 1.68 (s, 3H, H-5‴). The ^{13}C NMR spectrum[20] displayed the presence of 25 carbon atoms, and were further classified by DEPT experiments into categories of one methylene, seven methines, five methyls and 12 quaternary carbons including two carbonyls. On the basis of these characteristic features, database and literature searches led the skeleton of **11** as a benzil derivative frame work with two aromatic rings (subunits A and B).[19,21]

Comparison of the NMR data with those reported for **10** was indicative of a similar structure except for the positions of chromene ring and prenyl moiety.[19] Placement of prenyl moiety to C-3′ was further confirmed by an HMBC experiment (Fig. 2), revealing correlation of H-1‴ (δ 3.29) to C-2′ (δ 163.70), C-3′ (δ 126.03) and C-4′ (δ 160.76), H-2‴ to C-1‴ (δ 29.06), C-3′ (δ 126.03), C-5‴ (δ 25.77) and C-4‴ (δ 17.87). Whereas, the correlation of H-4‴′ (δ 6.32) to C-5′ (δ 106.5), C-6′ (δ 157.15) and C-4′ (δ 160.76) suggested that chromene ring was fused to C-4′ and C-5′ (subunit-A). The presence of the methoxyl group at C-6′ could also be inferred through HMBC correlations, which showed a cross peak with C-6′ (δ 157.15). The location of the hydroxyl group at C-2′ was justified based on its hydrogen bonding with carbonyl at C-1 (δ 197.94).[19] With respect to the second aromatic ring (subunit-B) of **11**, H-2″, H-6″ protons at δ 7.85 (d, 2H, J = 8.5 Hz) exhibited HMBC cross peaks with the quaternary carbon at C-1″ (δ 131.84), carbonyl carbon at C-2 (δ 187.50) and C-6″ (δ 131.84). Further, the correlation from H-3″ to C-4″ (δ 160.15) and C-5″ (δ 115.47) confirmed that the aromatic ring of subunit B is 1,4-disubstituted.

Further evidence regarding the connectivities of the subunits A and B was accomplished by its electron impact mass spectrum (EI-MS), showing intense peak at *m/z* 423. The fragmentation pattern in the electron impact mass spectrum (EI-MS) showing the base peak at *m/z* 121 corresponds to the ion of subunit B and strong peak at *m/z* 301 corresponded to the ion of subunit A, suggesting these two units were joined together. Thus, based on these data,

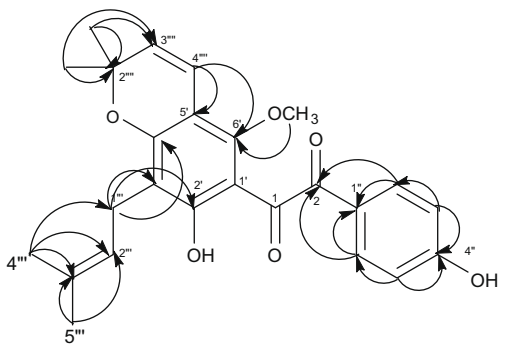

Figure 2. Key HMBC correlations of compound **11**.

compound **11** was characterized as, 1-(5-hydroxy-7-methoxy-2,2-dimethyl-8-(3-methyl-but-2-enyl)-2*H*-chromen-6-yl)-2-(4-hydroxyphenyl)ethane-1,2-dione for which we proposed trivial name as derrisdione A (see Fig. 3).

The antifeedant activities of the isolates were evaluated for their efficacy against castor semilooper pest, *A. janata* by using the conventional no-choice disk method (Table 1).[22] The most potent insect antifeedant, azadirachtin A, was used as an active control for comparison. Initially, the activities of these compounds were tested at 1 μg/cm^2 and at 2 μg/cm^2 against *A. janata*, for which the results were not encouraging. Hence, the dosages of the compounds for our study were fixed at 10 μg/cm^2. As shown in Table 1, all the isolates exhibited remarkable activity with the inhibition range from 100% to 1.3%. Among the test compounds, osajin (**2**), scandenin (**7**), sphaerobioside (**8**), genistein (**9**) and **10** displayed good antifeedancy against *A. janata*. Osajin (**2**), which has the chromene ring in the angular position, exhibited 100% antifeedant activity, while its structural analogue, scandenone (**1**) with the chromene ring in the linear position showed a very mild antifeedant index of 6.2. Similarly, genistein (**9**) demonstrated an antifeedant index of 97.7, while and its diglycoside, sphaerobioside (**8**) exhibited 96.2% of antifeedant index. These results clearly indicated fact that an isoflavone scaffold is primarily responsible for feeding deterrence, and the presence as well as position of chromene ring plays an important role, as all the potent compounds possess chromene moiety in angular position. This observation was confirmed by the fact that laxifolin (**3**), which is a flavone that lacked antifeedant activity, while osajin, an isoflavone with a potent feeding deterrence. Moreover, introduction of the sugar moiety gave no remarkable advantage for the activity in sphaerobioside (**8**).

With respect to the antifeedant activities of benzil derivatives, compound **10** with chromene ring in the linear position is a good antifeedant with an index of 96.8%, while its angular isomer, derrisdione A (**11**), the antifeedant activity was reduced to half (AF Index 58.6). It is note worthy to mention that the angular isomer being more effective with the isoflavones, while the linear isomer in the case of benzil compounds (**10** and **11**), which was reverse to isoflavones. Among the phenyl coumarins (**6** and**7**), scandenin was the most effective antifeedant. Whereas, scandenin A (**6**), in which the hydroxyl group in the B ring is methylated, failed to show any activity. It is important to mention that B ring with a hydroxyl group is the common structural unit in all the potent antifeedant compounds.

Another interesting feature is that, apart from causing feeding inhibition, several of the isolates also showed good toxicity (Table 2).[23] It must be pointed out that toxicity and antifeedancy are directly proportional, suggesting similar structural requirements for the toxicity studies too. It appears that the leaf surface application of the osajin (**2**), genistein (**9**), compound **10**, scandenin (**7**) and sphaerobioside (**8**), produced contact toxicity. The larvae that came into contact with the chemical substances died after 24 h. In these treatments absolute feeding inhibition was recorded

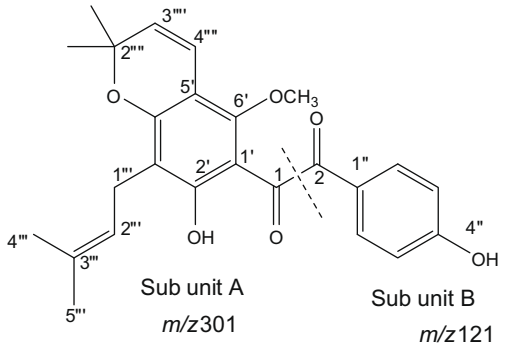

Figure 3. Mass fragmentation of compound **11**.

Table 1
Antifeedant activity of isolated compounds from *Derris scandens* against *A. janata* larvae by leaf disc method

Compounds	AFI ± SE[a] (10 μg/cm^2)	ED_{50} (95% CL[b]) (μg/cm^2)	χ^2 (Df)
$CHCl_3$ extract	93.0 ± 0.9	4.14 (3.43–4.82)	0.85 (3)
1	6.2 ± 0.6	NI	NI
2	100 ± 0.0	3.18 (2.73–3.59)	1.14 (3)
3	2.6 ± 0.5	NI	NI
4	22.4 ± 1.6	NI	NI
5	1.3 ± 0.3	NI	NI
6	4.0 ± 0.9	NI	NI
7	96.5 ± 1.0	3.85 (3.30–4.38)	3.67 (3)
8	96.2 ± 1.0	3.37 (2.77–3.91)	0.93 (3)
9	97.7 ± 0.9	3.22 (2.62–3.37)	1.66 (3)
10	96.8 ± 1.1	3.31 (2.67–3.81)	1.89 (3)
11	58.6 ± 1.7	7.18 (6.06–9.00)	0.81 (3)
Azadirachtin[c]	100 ± 0.0	0.72 (0.64–0.79)	1.61 (3)

[a] Values are mean ± SE, no feeding in solvent treated controls. NI—not included in statistical data as the activity was low (AFI is below 25).
[b] Confidence level.
[c] Azadirachtin at a dose of 1.25 μg/cm^2.

Table 2
Toxicity of compounds (**1**–**11**) against *A. janata* larvae by leaf disc method after 24 h of treatment

Compounds	Toxicity (%) ± SE[a] (10 μg/cm^2)	LD_{50} (95% CL[b]) (μg/cm^2)	χ^2 (Df)
$CHCl_3$ extract	90.6 ± 0.6	4.7 (4.10–5.45)	0.73 (3)
1	6.8 ± 0.9	NI	NI
2	98.2 ± 0.5	3.54 (0.86–5.45)	3.17 (3)
3	0.0 ± 0.0	NI	NI
4	0.0 ± 0.0	NI	NI
5	14.6 ± 0.9	NI	NI
6	0.0 ± 0.0	NI	NI
7	86.4 ± 1.4	5.28 (4.50–6.17)	1.01 (3)
8	97.8 ± 1.0	3.87 (1.14–6.07)	5.65 (3)
9	100 ± 0.0	3.29 (0.91–4.99)	4.07 (3)
10	100 ± 0.0	3.56 (1.42–5.25)	5.58 (3)
11	18.2 ± 1.1	NI	NI
Azadirachtin[c]	100 ± 0.0	0.67 (0.59–0.74)	3.42 (3)

[a] Values are mean ± SE. NI—not included in statistical data as the activity was low (below 20%).
[b] Confidence level.
[c] Azadirachtin at a dose of 1.25 μg/cm^2.

Table 3
Effect of isolated compounds from *Derris scandens* on larval growth parameters of *A. janata* by topical application method

Compound	Larval duration (days) ± SE[a]		Larval mortality (%) ± SE[a]	
	4 μg/larva	2 μg/larva	4 μg/larva	2 μg/larva
$CHCl_3$ extract	9.1 ± 0.1	8.7 ± 0.4	36.2 ± 1.0	15.2 ± 0.8
1	9.8 ± 0.1	9.4 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
2	11.2 ± 0.1	10.4 ± 0.3	33.4 ± 1.3	12.2 ± 0.6
3	11.1 ± 0.4	8.5 ± 0.5	25.2 ± 1.4	20.6 ± 1.3
4	9.7 ± 0.6	7.7 ± 0.1	18.8 ± 1.1	0.0 ± 0.0
5	10.5 ± 0.3	8.2 ± 0.1	17.0 ± 1.0	6.8 ± 1.0
6	11.1 ± 0.3	9.3 ± 0.2	15.2 ± 1.0	11.6 ± 1.1
7	10.8 ± 0.3	8.2 ± 0.1	42.6 ± 1.0	0.0 ± 0.0
8	11.3 ± 0.5	10.8 ± 0.1	31.8 ± 1.2	13.0 ± 1.2
9	10.3 ± 0.3	7.8 ± 0.3	48.6 ± 1.0	31.0 ± 0.5
10	8.5 ± 0.1	7.8 ± 0.2	39.3 ± 1.0	15.1 ± 0.5
11	10.5 ± 0.8	9.3 ± 0.4	0.0 ± 0.0	0.0 ± 0.0
Azadirachtin[b]	—	—	100 ± 0.0	—
Control (solvent)	7.3 ± 0.1	7.3 ± 0.1	0.0 ± 0.0	0.0 ± 0.0

[a] Values are mean ± SE.
[b] Azadirachtin at a dose of 0.2 μg/larva.

Table 4
Effect of isolated compounds from *Derris scandens* on pupal parameters of *A. janata* by topical application method

Compound	Pupal duration (days) ± SE[a]		Pupal weight (mg) ± SE[a]		Pupal mortality (%) ± SE[a]	
	4 μg/larva	2 μg/larva	4 μg/larva	2 μg/larva	4 μg/larva	2 μg/larva
$CHCl_3$ extract	14.1 ± 0.5	13.0 ± 0.5	508.2 ± 4.5	559.6 ± 9.0	39.6 ± 1.2	26.0 ± 1.0
1	11.9 ± 1.0	11.7 ± 0.1	572.6 ± 11.6	633.2 ± 7.5	27.6 ± 2.1	17.8 ± 1.2
2	15.5 ± 0.5	13.8 ± 0.7	504.8 ± 4.2	584.8 ± 4.2	45.6 ± 2.9	47.8 ± 1.0
3	14.1 ± 1.0	10.7 ± 0.1	552.0 ± 10.0	567.2 ± 6.2	27.4 ± 1.7	12.0 ± 1.8
4	12.9 ± 0.7	11.4 ± 0.1	587.0 ± 1.6	612.0 ± 4.5	32.2 ± 2.5	26.4 ± 1.1
5	12.5 ± 0.4	11.8 ± 0.7	592.0 ± 6.1	621.8 ± 4.2	23.4 ± 2.2	13.6 ± 1.0
6	10.5 ± 0.1	10.5 ± 0.1	605.0 ± 10.8	601.2 ± 4.4	32.8 ± 0.9	19.8 ± 2.0
7	11.3 ± 0.8	11.2 ± 0.4	514.2 ± 6.6	550.8 ± 5.8	24.8 ± 1.5	13.5 ± 1.5
8	14.4 ± 0.3	13.3 ± 0.6	504.8 ± 5.2	508.6 ± 4.6	41.2 ± 1.1	36.0 ± 1.9
9	14.8 ± 0.9	13.1 ± 0.2	532.0 ± 8.5	518.0 ± 5.1	22.5 ± 2.6	17.2 ± 2.7
10	13.5 ± 0.1	13.0 ± 1.1	515.4 ± 6.2	524.4 ± 5.8	31.6 ± 0.9	20.0 ± 1.8
11	12.5 ± 0.4	10.9 ± 1.0	597.8 ± 2.5	592.6 ± 6.0	36.2 ± 1.9	29.8 ± 0.8
Control	10.3 ± 0.1	10.3 ± 0.1	696.4 ± 2.6	696.4 ± 2.6	0.0 ± 0.0	0.0 ± 0.0

[a] Values are mean ± SE.

followed by the death of the exposed larvae. In genistein (**9**), compound **10**, scandenin (**7**) and sphaerobioside (**8**) consumption of a small amount of leaf was noted.

Perusal of the data on larval duration (Table 3) indicated**,** compounds **2**, **3**, **7**, **8**, **9**, **10** and chloroform extract significantly increased the total larval duration. These compounds showed slow and sustainable effects on larval development. The least effect was observed with compounds **11**and **4**. The chloroform extract and compounds **2**, **3**, **7**, **8**, **9** and **10** showed significant influences on larval mortality indicating it is susceptibly to the compounds. However, in Azadiractin, treatments at 0.2 μg/larva by topical application method resulted with 100% toxicity.

All the test compounds showed significant pupal mortality (Table 4), which is slightly higher than the larval toxicity. In case of pupal duration and pupal weight, the most potent were, chloroform extract and compounds **2**, **3**, **8**, **9**, **10** and least being compound **6** in both parameters. Scrutiny of the data on adult development (Table 5), indicated many intriguing observations. The chloroform extract and compounds **2**, **7**, **8**, **9** and **10** showed considerable reduction of adult emergence. The larval treatment with chloroform extract, and compounds **2**, **7**, **8**, **9**, **10** resulted with the adults that showed improper eclosion, shriveled wings and reduced abdominal segment growth. The tested compounds showed considerable reduction in adult emergence at 4 μg, while it was higher at 2 μg dosage.

Considering the advantages of using botanical insecticides for the pest management, it can be concluded that chloroform extract of *D. scandens*, could have great potential for the control of pests. From this active extract, a new benzil derivative, derrisdione A (**11**) and ten known compounds were isolated, and shown to be potent antifeedants. A comparison of their chemical structures indicated an isoflavone moiety is primarily responsible for antifeedant activity; introduction of chromene ring in angular position further increased the antifeedant activity. However, the introduction of sugar moiety on the isoflavonoid was not relative to the rate of antifeedant activity. The compound **11** (derrisdione A) being a new compound, had exhibited moderate antifeedant, toxic and growth inhibitory activities, and seems to be a promising candidate for the control of *A. janata* pest infestation in castor (*Ricinus communis* L.) fields.

Table 5
Effect of isolated compounds from *Derris scandens* on adult emergence of *A. janata* by topical application method

Compound	Adult deformity (%) ± SE[a]		Adult emergence (%) ± SE[a]	
	4 μg/larva	2 μg/larva	4 μg/larva	2 μg/larva
$CHCl_3$ extract	13.1 ± 1.1	8.2 ± 0.5	9.5 ± 0.3	37.3 ± 1.2
1	11.8 ± 1.2	5.5 ± 0.4	50.3 ± 1.6	63.6 ± 1.7
2	15.7 ± 1.0	10.0 ± 0.6	2.9 ± 0.4	18.0 ± 0.9
3	2.3 ± 1.8	0.0 ± 0.0	24.9 ± 0.2	59.6 ± 1.2
4	9.1 ± 0.6	9.5 ± 0.5	32.8 ± 0.2	62.7 ± 0.2
5	5.4 ± 0.9	3.5 ± 0.9	34.2 ± 0.9	65.3 ± 1.2
6	6.6 ± 1.5	0.0 ± 0.0	31.5 ± 0.6	71.5 ± 0.8
7	10.9 ± 0.5	0.0 ± 0.0	18.6 ± 0.6	75.3 ± 1.0
8	9.5 ± 1.9	0.0 ± 0.0	7.5 ± 0.3	32.7 ± 0.8
9	11.8 ± 0.9	10.6 ± 1.5	7.7 ± 0.2	27.0 ± 0.8
10	19.0 ± 0.7	16.2 ± 1.1	6.7 ± 0.9	34.5 ± 0.4
11	21.1 ± 1.2	19.5 ± 0.4	29.8 ± 0.7	35.4 ± 0.9
Control	0.0 ± 0.0	0.0 ± 0.0	98.8 ± 0.5	98.8 ± 0.5

[a] Values are mean ± SE.

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20. *Spectral data for compound* **11**: mp 86–88 °C; UV λ_{max} (MeOH): λ 228 202 nm and 262 nm. IR (KBr) ν_{max}: 3550, 2923, 2853, 1706, 1640, 1460, 1152, 761 cm^{-1}. ^{1}H NMR (300 MHz, MeOH-d_4): 3.46 (s, 3H, s, 6′-OMe), 7.85 (d, 2H, *J* = 8.5 Hz, H-2″, H-6″), 6.87 (d, 2H, *J* = 8.5 Hz, H-3″, H-5″), 5.21 (t, 1H, *J* = 7.4 Hz, H-2‴), 3.29 (d, 2H, *J* = 7.4 Hz, H-1‴), 1.87 (s, 3H, H-4‴), 1.68 (s, 3H, H-5‴), 6.32 (d, 1H,d, *J* = 10 Hz, H-4⁗), 5.56 (d, 1H, *J* = 10 Hz,H-3⁗), 1.43 (s, 6H, Me-2⁗).^{13}CNMR (75 MHz, MeOH-d_4): δ 197.94 (C-1), 189.50 (C-2), 106.72 (C-1′), 163.70 (C-2′), 126.03 (C-3′), 160.76 (C-4′), 106.15 (C-5′), 157.15 (C-6′), 113.28 (C-1″), 131.84 (C-2″,C-6″), 115.47 (C-3″, C-5″), 160.15 (C-4″), 29.06 (C-1‴), 121.78 (C-2‴), 131.67 (C-3‴), 17.87 (C-4‴), 25.77 (C-5‴), 77.31 (C-2⁗), 127.56 (C-3⁗), 115.86 (C-4⁗), 28.13 (2 × Me-2⁗), 62.97 (–OMe). HR-ESIMS *m/z*: −423.1827 $[M+H]^+$ (Calcd for $C_{25}H_{27}O_6$ 423.1808).
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