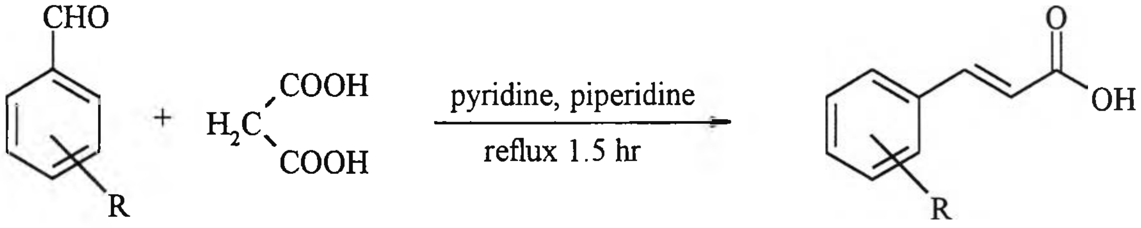
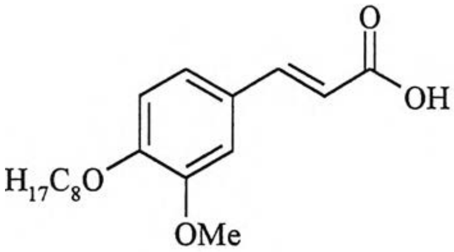
CHAPTER III
RESULTS AND DISCUSSION

3.1 Synthesis of Substituted *trans*-Cinnamic Acids

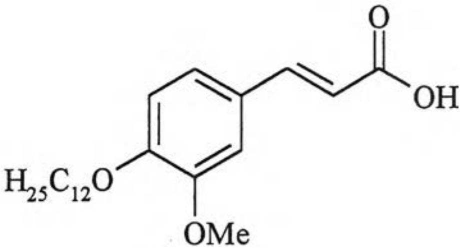
In this research, forty-seven substituted *trans*-cinnamic acids were synthesized by using Doebner condensation between one mole equivalent of malonic acid and one equivalent of selected aromatic aldehydes. The general equation is shown below.



The structures of all synthesized substituted *trans*-cinnamic acids were well-characterized using various spectroscopic techniques including IR, ^{1}H-NMR, ^{13}C-NMR and MS which will be discussed in the forthcoming section. The comparative results of the synthetic substituted *trans*-cinnamic acids are tabulated in Table 3.1. Two synthesized substituted *trans*-cinnamic acids (**C24** and **C25**) were disclosed to be new compounds based upon no report concerning these compounds in chemical literature.



C24



C25

Table 3.1 Physical properties and % yield of synthesized substituted *trans*-cinnamic acids

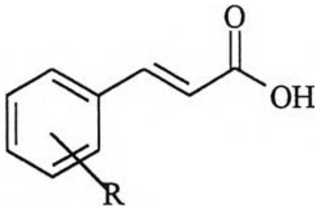
Cpds	Physical Properties		% Yield
	Appearance	m.p. (°C)	
C1	light white solid	165-167	57
C2	white mirror-like crystal	209-210	67
C3	light white solid	210-212	56
C4	light white solid	162-164	77
C5	white solid	250-251	75
C6	white crystal	215-217	93
C7	pale yellow crystal	179-180	73
C8	white needle crystal	258-259	98
C9	light pale green solid	233-235	75
C10	pale yellow needle crystal	195-197	33
C11	white solid	219-221	75
C12	pale yellow solid	210-212	48
C13	pale yellow needle crystal	185-186	80
C14	white mirror-like needle crystal	117-118	59
C15	white mirror-like needle crystal	173-174	62
C16	pale yellow solid	164-165	73
C17	pale yellow solid	160-162	90
C18	pale yellow mirror-like crystal	142-144	70
C19	small white solid	122-125	67
C20	pale yellow solid	200-203	92
C21	pale yellow solid	108-109	83
C22	pale yellow solid	155-156	82
C23	light white solid	124-125	93
C24	white solid	115-118	81
C25	pale yellow solid	60-62	60
C26	pale yellow needle crystal	185-187	93
C27	pale yellow crystal	180-182	64

Table 3.1 (cont.)

Cpds	Physical Properties		% Yield
	Appearance	m.p. (°C)	
C28	yellow crystal	188-189	78
C29	small yellow crystal	147-148	77
C30	pale yellow crystal	182-183	69
C31	pale yellow needle crystal	176-177	77
C32	pale yellow solid	124-126	40
C33	pale yellow mirror-like crystal	244-245	57
C34	brown solid	237-239	67
C35	yellow needle crystal	204-206	59
C36	brown solid	283-285	77
C37	green solid	216-217	82
C38	yellow solid	182-183	68
C39	pale yellow solid	172-173	85
C40	white needle mirror-like crystal	196-197	63
C41	pale yellow needle crystal	156-157	56
C42	pale yellow needle crystal	202-205	96
C43	white solid	225-226	72
C44	pale yellow solid	245-247	82
C45	white crystal	254-255	67
C46	pale yellow solid	210-212	76
C47	yellow-brown solid	245-248	83

3.2 Spectroscopic Data of Substituted *trans*-Cinnamic Acids

Infrared Spectroscopy (IR)



The IR absorption pattern for all substituted *trans*-cinnamic acids displayed the characteristic of common functional groups. O-H Stretching vibrations of acids were presented around 3150-3680 cm^{-1} (br). The absorption band at 1665-1716 cm^{-1} corresponded to the C=O stretching vibration of acid. C=C Stretching vibration at 1603-1644 cm^{-1} and that of C=C ring stretching at 1424-1611 cm^{-1} were also detected.

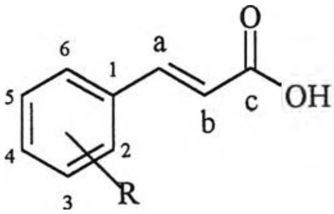
The IR characteristic absorption peaks of new synthetic *trans*-cinnamic acids (**C24** and **C25**) are presented in Table 3.2.

Table 3.2 FT-IR absorption band assignment of new synthetic *trans*-cinnamic acids (**C24** and **C25**)

Cpd	Wavenumber (cm^{-1})				
	O-H acid str.	C-H str.	C=O str.	C=C str.	C=C ring str.
C24	3325-3625 (br)	2930, 2955 (w)	1675 (s)	1629 (s)	1465, 1598 (s)
C25	3325-3625 (br)	2868, 2935 (w)	1683 (s)	1624 (s)	1470, 1603 (s)

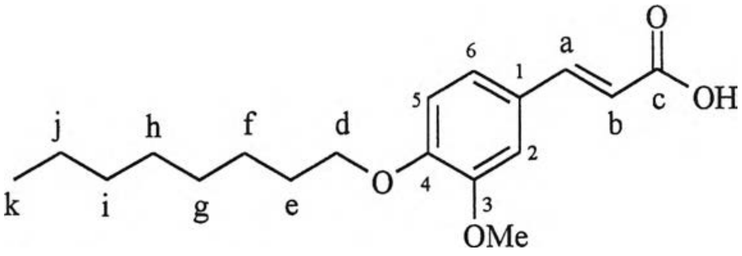
Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR

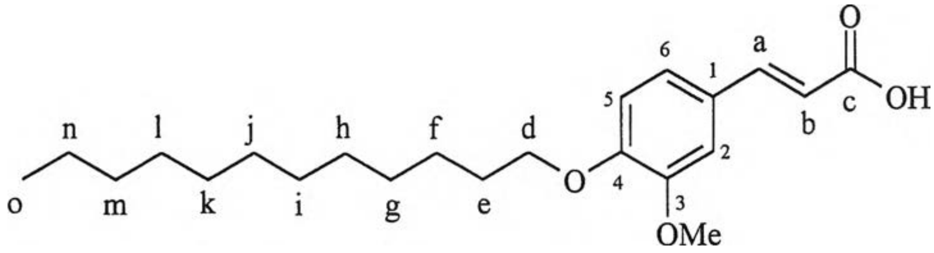


Acetone-d_6 and DMSO-d_6 were used as a solvent for most substituted *trans*-cinnamic acids. The ^{1}H-NMR spectra of substituted *trans*-cinnamic acids generally exhibited a doublet signal with 1H integration at 7.40-8.38 ppm (J = 15.09-16.75 Hz) which was Ar-C**H**= (H-a) and a doublet signal with 1H integration at 6.20-6.78 ppm (J = 15.56-16.73 Hz) which could be denoted for =C**H**-COOH (H-b). The coupling constant indeed represents *trans*- geometry in molecule. Another signal detected approximately 6.53-8.59 ppm could be assigned for aromatic protons.

The ^{1}H-NMR spectral assignments for new synthetic *trans*-cinnamic acids are summarized as shown in Table 3.3.



C24



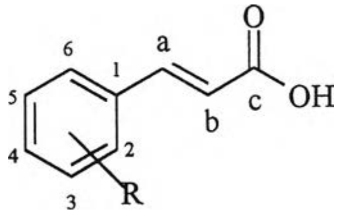
C25

Table 3.3 ^{1}H-NMR spectral assignments of new synthetic *trans*-cinnamic acids (**C24** and **C25**)

H	Chemical shift (ppm)	
	C24	**C25**
2	7.08 (d, J =1.83 Hz)	7.07 (d, J =1.83 Hz)
5	6.87 (d, J = 8.24 Hz)	6.87 (d, J = 8.24 Hz)
6	7.11 (dd, J = 8.24, 1.83 Hz)	7.11 (dd, J = 8.24, 1.84 Hz)
a	7.73 (d, J =15.87 Hz)	7.71 (d, J =15.87 Hz)
b	6.32 (d, J =15.86 Hz)	6.32 (d, J =15.86 Hz)
d	4.05 (t, J = 7.02 Hz)	4.08 (t, J = 7.02 Hz)
e	1.83-1.91 (m, 2H)	1.83-1.91 (m, 2H)
k	0.89 (t, J = 7.01 Hz)	-
o	-	0.88 (t, J = 6.72 Hz)
f-j*	1.25-1.50 (m, 10H)	-
f-n**	-	1.23-1.91 (m, 18 H)
$-OCH_3$	3.90 (s)	3.90 (s)

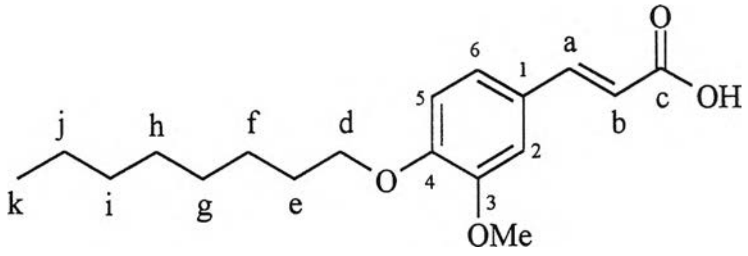
Note: * for **C24**, ** for **C25**

^{13}C-NMR

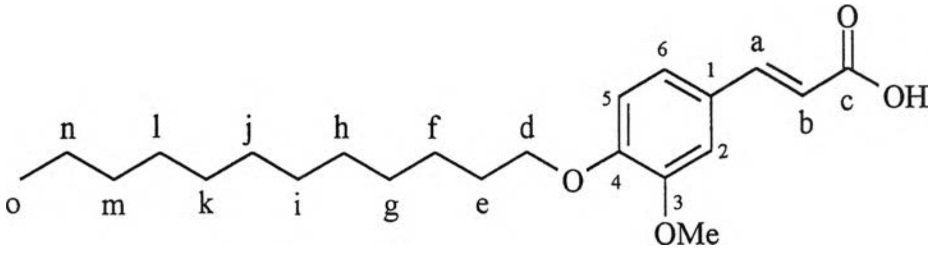


The ^{13}C-NMR spectra of substituted *trans*-cinnamic acids generally exhibited a signal belonging to carboxylic acid around 167-173 ppm. The signals of olefinic carbons (C-a and C-b) were detected in the range of 139-149 and 116-129 ppm, respectively. Another set of signal assigned to aromatic carbons as C-1, C-2, C-3, C-4, C-5 and C-6 was observed above 100 ppm in the range of 106.0-160.0 ppm.

The ^{13}C-NMR spectral assignments of new synthetic *trans*-cinnamic acids (**C24** and **C25**) are displayed in Table 3.4.



C24



C25

Table 3.4 ^{13}C-NMR spectral assignments of new synthetic *trans*-cinnamic acids (**C24** and **C25**)

C	Chemical shift (ppm)	
	C24	**C25**
1	126.8	129.8
2	110.2	109.2
3	151.2	154.2
4	147.0	146.2
5	112.2	111.3
6	123.1	126.8
a	149.5	149.8
b	114.7	114.8
c	172.6	171.4
d	69.0	69.2
e	31.8	31.9
f	29.3	29.6
g	29.2	29.6
h	28.9	29.6
i	25.9	29.5
j	22.6	29.3
k	14.1	29.0
l	-	28.9
m	-	25.9
n	-	22.7
o	-	14.1
$-OCH_3$	56.0	56.0

3.3 Synthesis and Spectroscopic Data of *trans*-Cinnamic Acid Derivatives

In this research, twelve cinnamamides were synthesized by the reaction between one mole equivalent of selected amine and one mole equivalent of cinnamoyl chloride in tetrahydrofuran. In addition, fifteen cinnamate esters were synthesized by esterification between one mole equivalent of selected alcohol and one mole equivalent of *trans*-cinnamic acid. Moreover, six sodium cinnamate and three calcium cinnamate derivatives were also prepared.

The IR absorption pattern for all cinnamamides displayed the characteristic of amide functional group. N-H Stretching vibrations were presented at 3419-3457 and 3247-3372 cm^{-1}. N-H Bending vibrations were also detected at 1514-1562 cm^{-1}.

The IR absorption pattern for all cinnamate esters displayed the characteristic of ester function group. To illustrate this, C=O stretching vibrations were presented at 1701-1734 cm^{-1} while C-O stretching vibrations were detected at 1214-1292 cm^{-1} and 1055-1185 cm^{-1}.

The IR absorption pattern for all sodium cinnamate and calcium cinnamate derivatives displayed almost the same absorption peaks as those of *trans*-cinnamic acids except for the absence of O-H stretching vibration.

The ^{1}H-NMR spectra of both cinnamamides and cinnamate esters displayed almost the same spectra as those *trans*-cinnamic acids.

The ^{13}C-NMR spectra of cinnamamides generally exhibited a signal of carbon which connected to a nitrogen atom (R′). In the case of a carbon which connected to a nitrogen atom (R′) was an alkyl chain, a signal was always observed in range of 39.6-48.3 ppm, whereas the detected signal in range of 133.6-140.3 ppm was usually observed when a carbon next to a nitrogen atom (R′) was an aromatic carbon.

The ^{13}C-NMR spectra of cinnamate esters generally exhibited a signal of carbon which connected to an oxygen atom (R′). When a carbon connected to an oxygen atom (R′) was an alkyl chain, the signal was detected in the range 60.3-72.6 ppm. In the case of a carbon next to an oxygen atom (R′) being an aromatic carbon, the signal was generally detected in the range of 147.5-151.7 ppm.

3.4 Herbicidal Potential

One of the major goals of this research is to find out the relationship between structures of substituted *trans*-cinnamic acids and herbicidal activity against *Mimosa pigra* Linn. and *Echinoloa crus-galli* (E.) Beauv. In addition, the results derived from this work were compared with those obtained when commercially available herbicides were tested as a reference.

3.4.1 Weed Growth Inhibition against *Mimosa pigra* Linn.

M. pigra was selected as bioassay species of inhibitory effect of tested compound because the weed is common found through out the country, seed size is not too small, the seed dormancy can be easily broken with high germination percentage. In addition, it had spread over almost all parts of Thailand for example, Chiangrai, Chiangmai, Lamphun, Tak, Kamphaengphet, Suphanburi, Saraburi, Bangkok and Narathiwat, etc.[51] The areas of distribution in Thailand are shown in Fig 3.1.

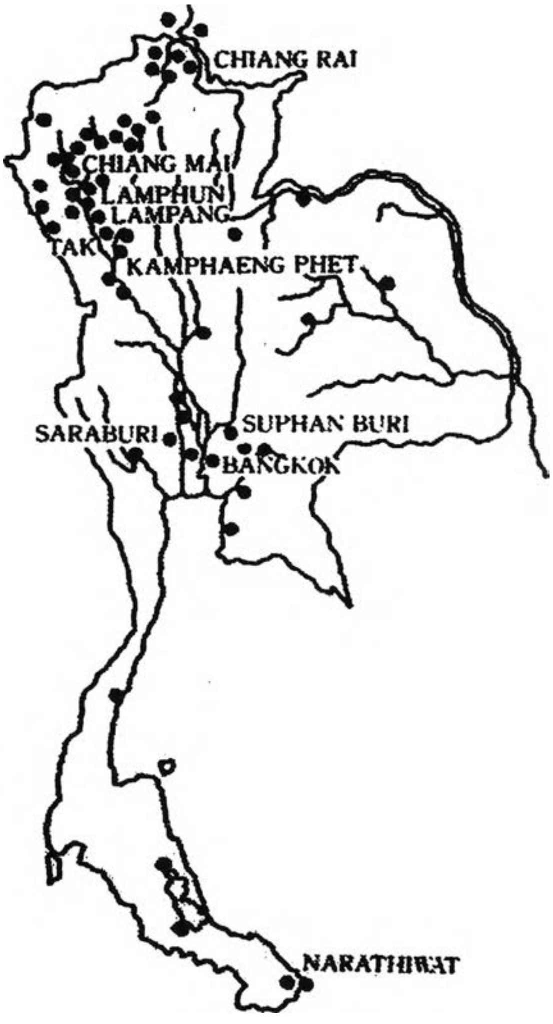
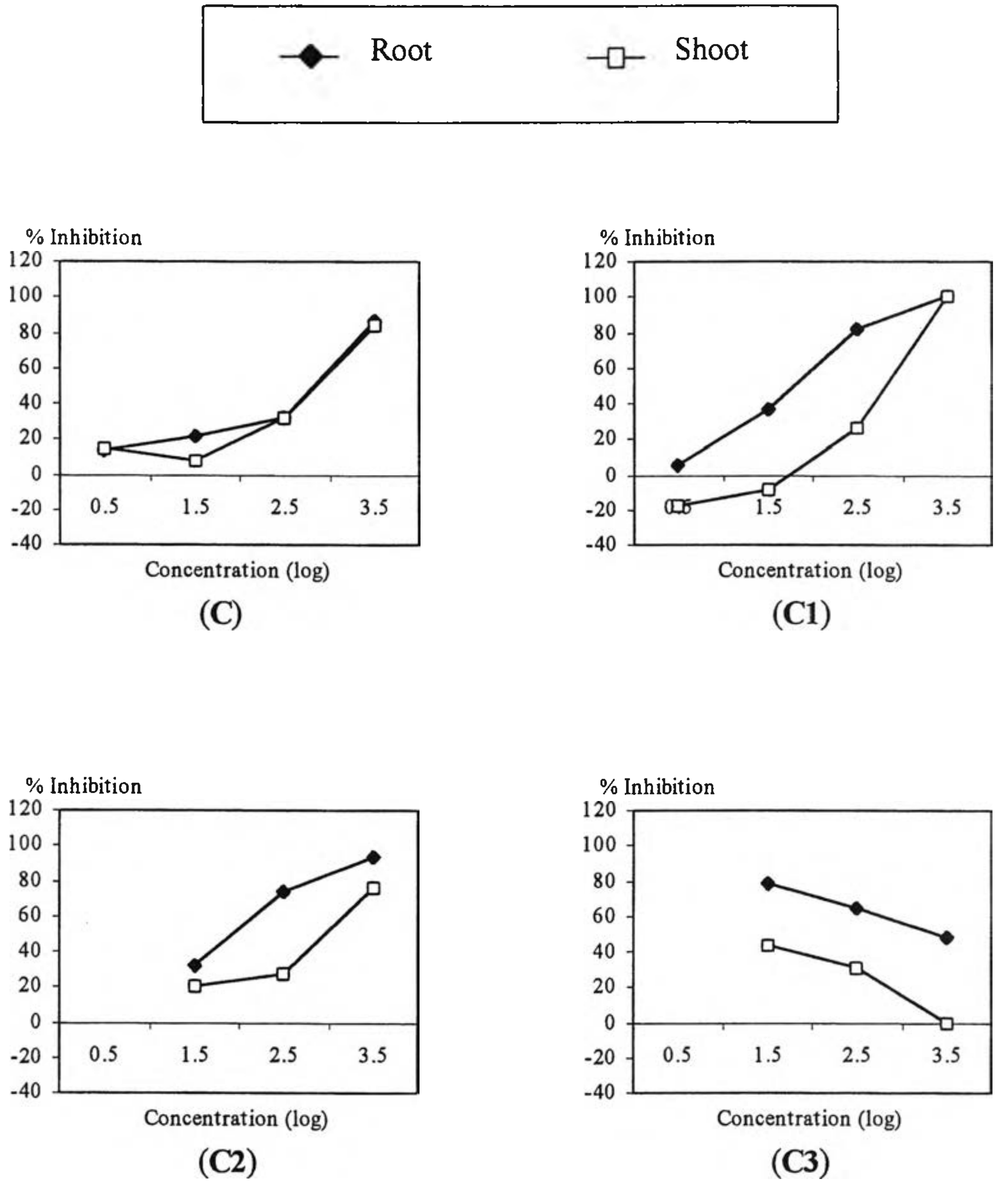


Fig 3.1 The area of *Mimosa pigra* distribution

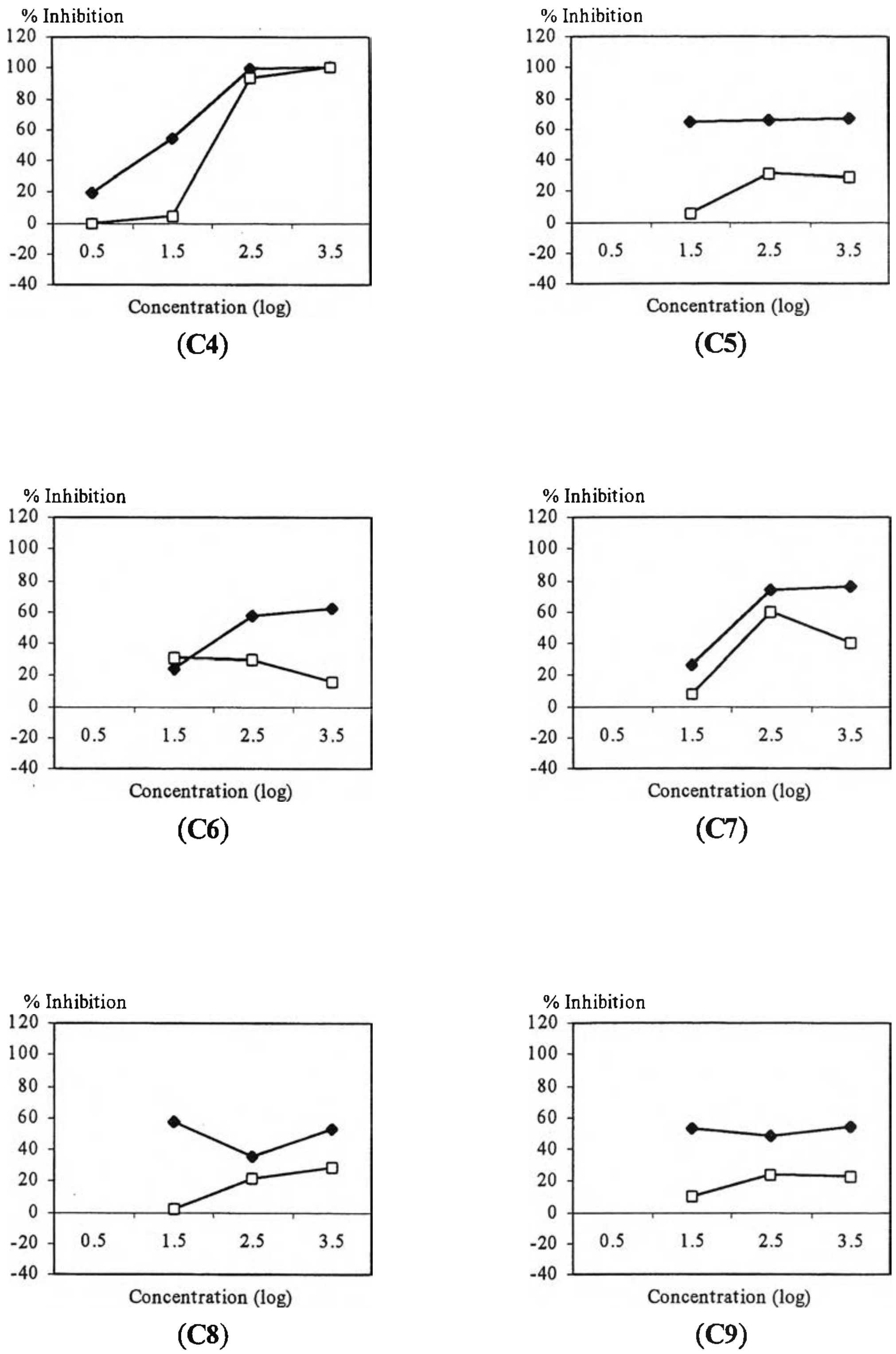
To our best knowledge, the biological activity test of substituted *trans*-cinnamic acids against giant mimosa has never been reported in chemical literature. The degree of inhibition/stimulation greatly depended on structures of forty-seven substituted *trans*-cinnamic acids. The results are summarized as shown in Fig 3.2.



(C) (C1)

(C2) (C3)

Fig 3.2 Inhibitory effect of substituted *trans*-cinnamic acids on root and shoot growth of *M. pigra* (%)

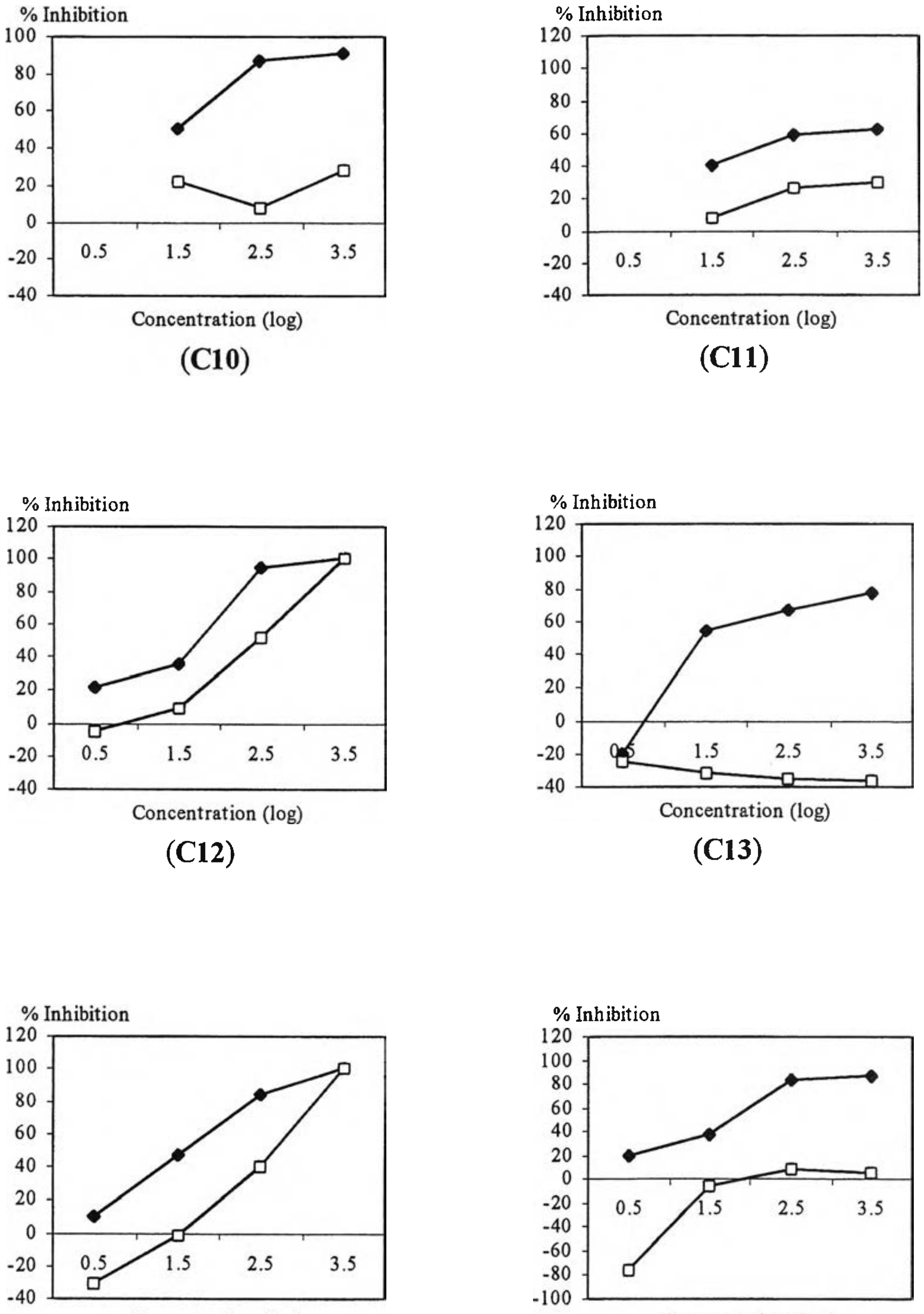


(C4) (C5)

(C6) (C7)

(C8) (C9)

Fig 3.2 (cont.)

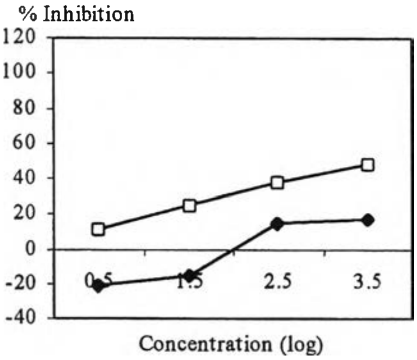


(C10) **(C11)**

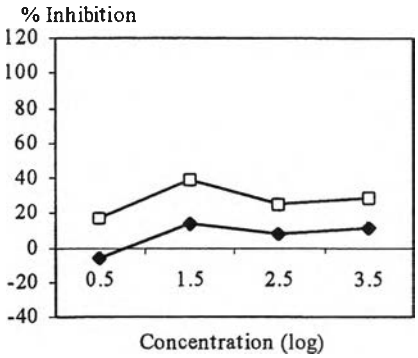
(C12) **(C13)**

(C14) **(C15)**

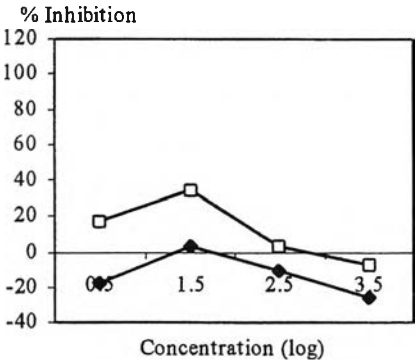
Fig 3.2 (cont.)



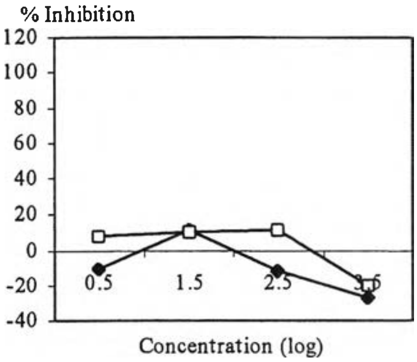
(C16)



(C17)



(C18)



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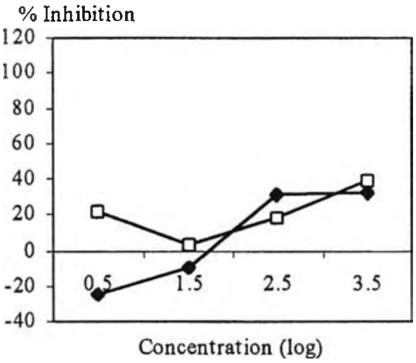

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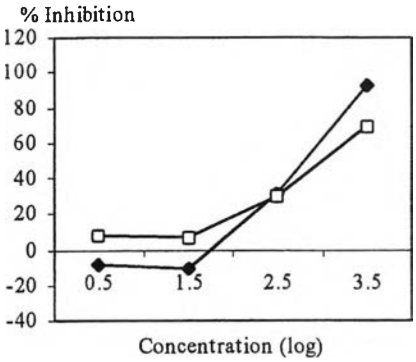

(C21)

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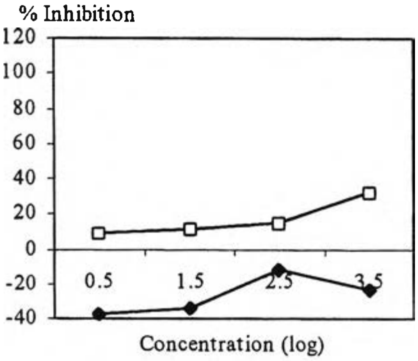

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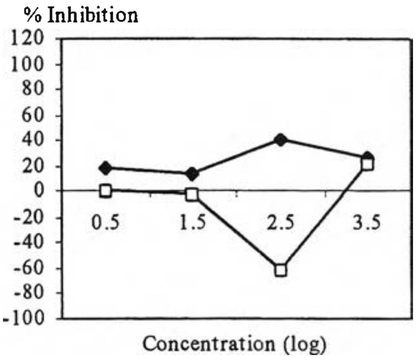

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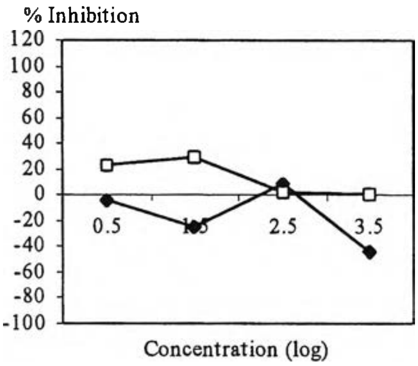
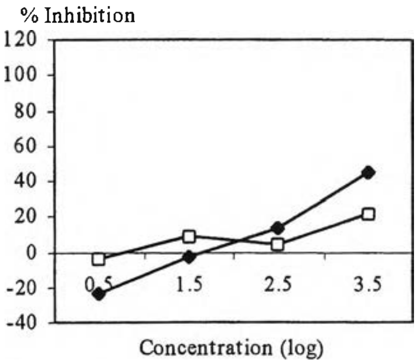
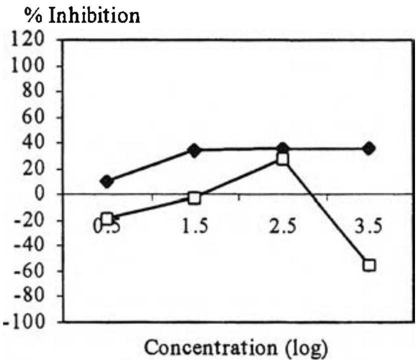


(C24)



(C25)



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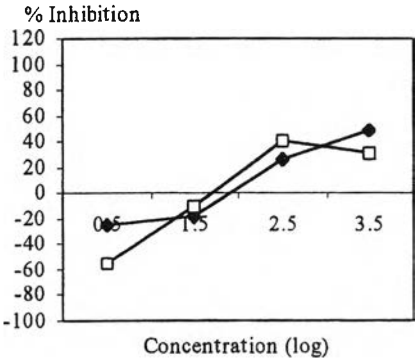

(C27)

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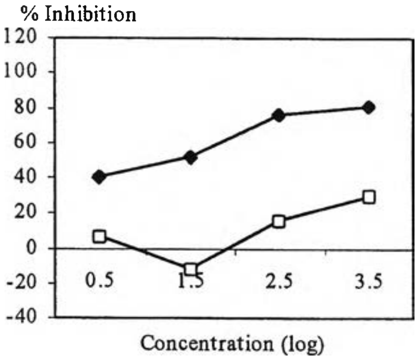

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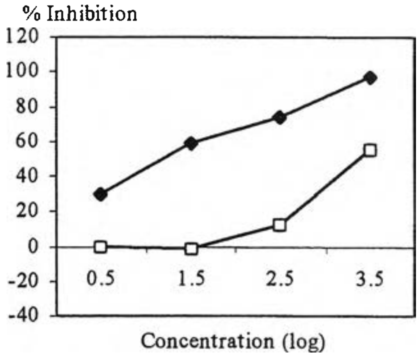

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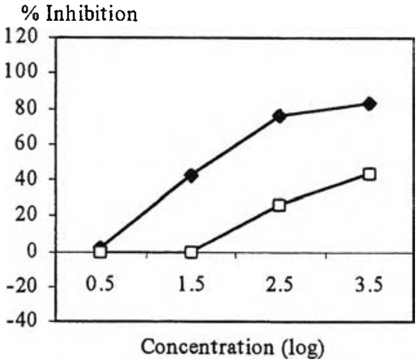

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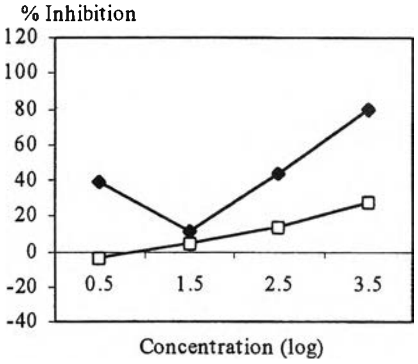

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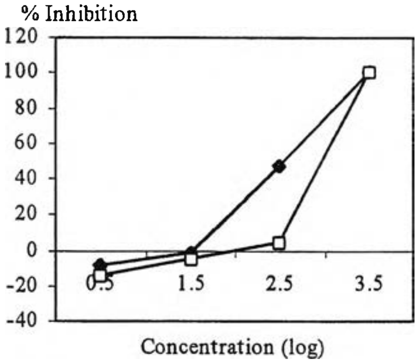

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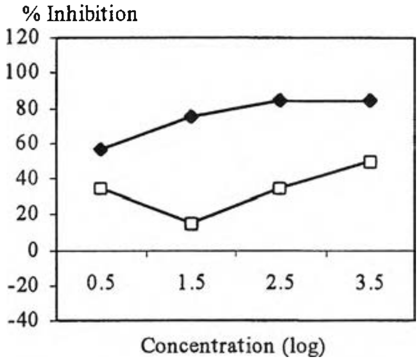

(C33)

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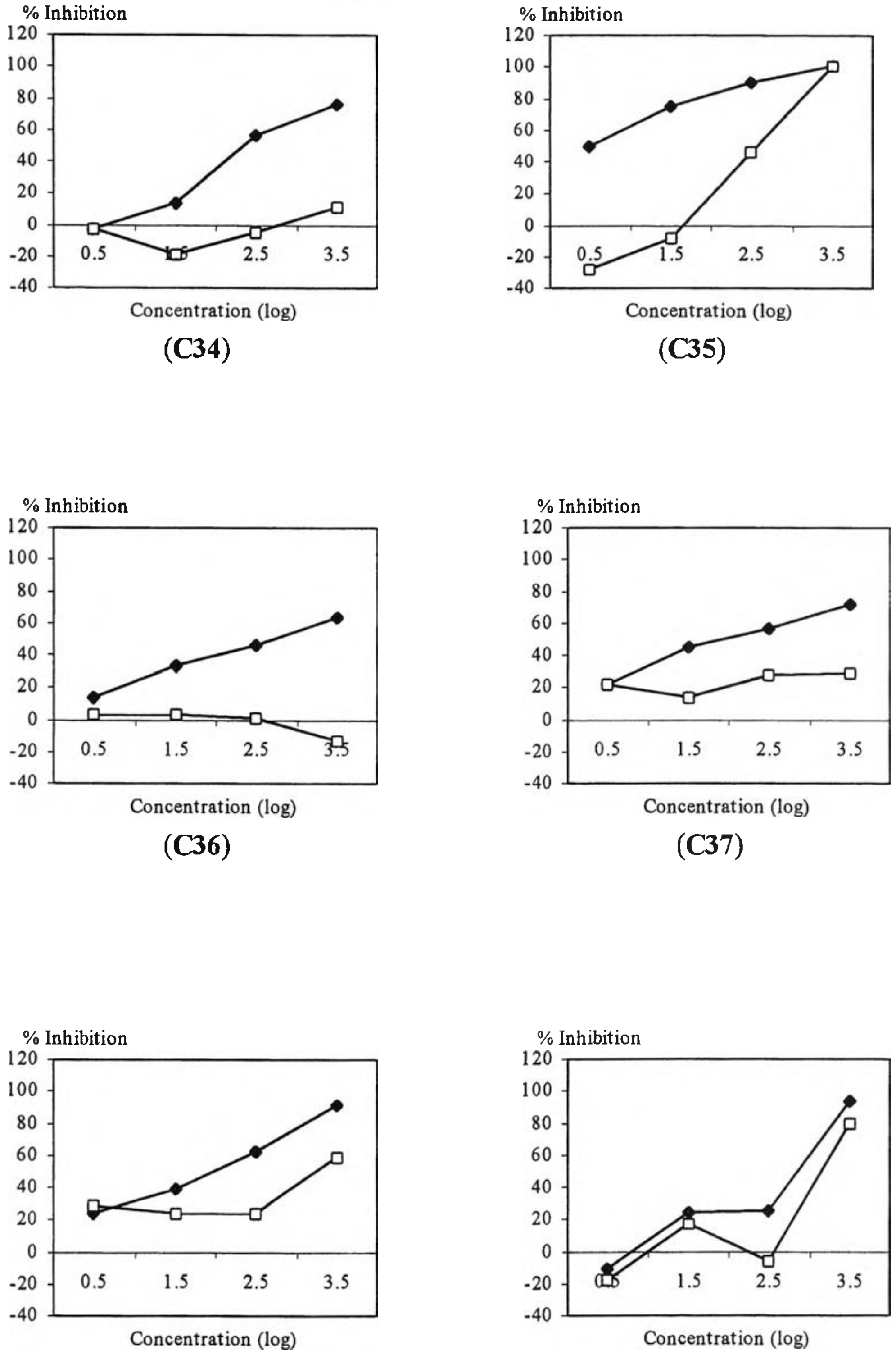

(C34) (C35)

(C36) (C37)

(C38) (C39)

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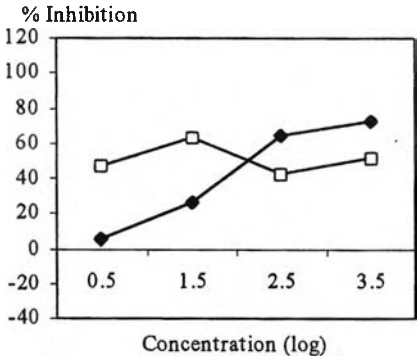

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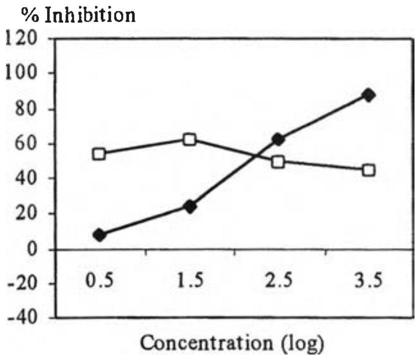

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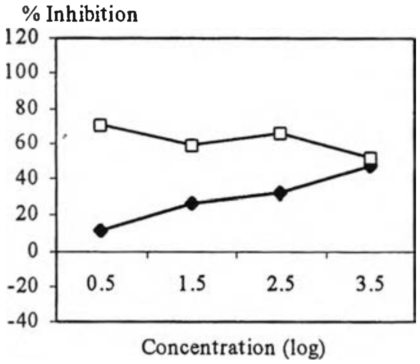

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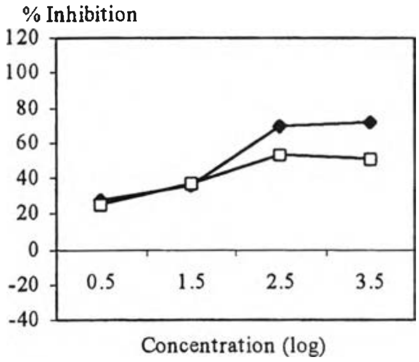

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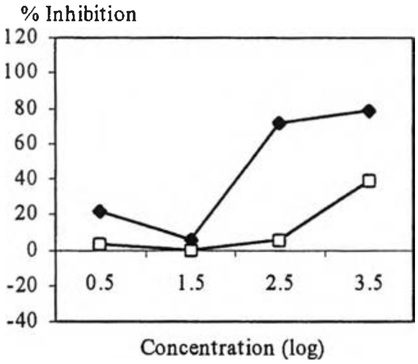

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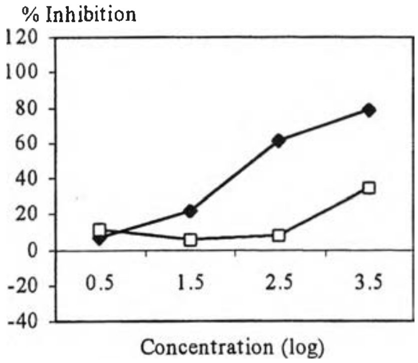

(C45)

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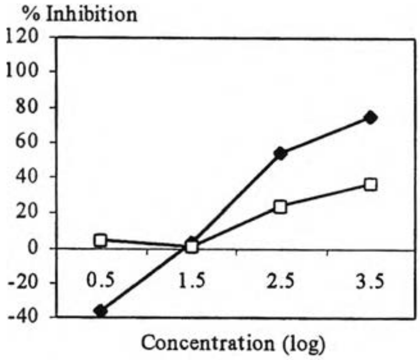

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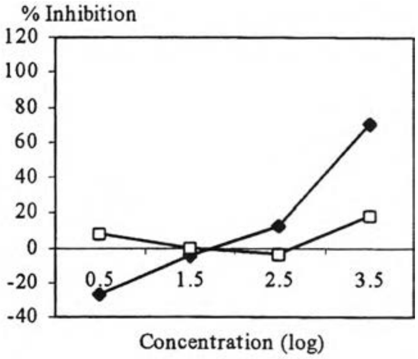


(C47)

Fig 3.2 (cont.)

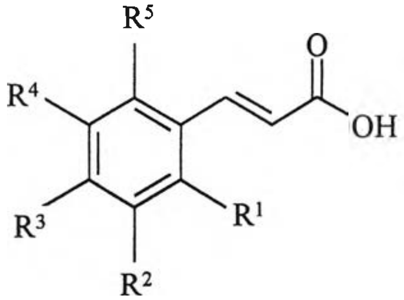
The above graphs revealed the correlation between tested substituted *trans*-cinnamic acids in the range of 3-3000 ppm and inhibitory effect on root and shoot growth of *M. pigra* (%). The substance possessing high activity should give the slope as increasing function in semi-logarithm graph (higher activity of each increase 1 unit of logarithm concentration of dose) and high percent root growth inhibition at 300 ppm. The inhibition of root is thought to be more essential for considering than that of percent shoot growth inhibition. This is because the roots are directly contacted to the tested chemical in cellulose, while the shoot growth is contributed from root and attributed to accumulated food from seed. Therefore, the profound effect of tested substance in this plant part might be misinterpreted. Percent root growth inhibition at 300 ppm was selected to be mainly contemplated. On the ground of low root growth inhibition always revealed by substance with low concentration (3 or 30 ppm) (e.g., some common herbicides with low level of dose were grossly encountered to be plant promoters: hormone-like herbicide) and substance with high concentration (3000 ppm) always desisted herb growth at high level (high percent root growth inhibition). The concentrations at such, the difference of inhibition activity of each tested substance would probably vanish. As follows, the general interpretations of these results are intensively concentrated at the first view on the slope of graph and percent root growth inhibition at dose level of 300 ppm.

Forty-seven synthesized substituted *trans*-cinnamic acids in this examination were divided into four subgroups based upon the difference in a main substituent on a benzene ring as (i) halocinnamic acids, (ii) alkoxy cinnamic acids, (iii) nitrogen-containing cinnamic acids and (iv) alkyl cinnamic acids and others.

(i) Halocinnamic acids (**C1-C12**)

Among twelve halocinnamic acids studied, it was found that the herbicidal activity was markedly depended on type and position of substituent. Using cinnamic acid (**C**) as a reference compound, it can be summarized as tabulated in Table 3.5.

Table 3.5 Inhibitory effect of halocinnamic acids at 300 ppm



Cpds	Position					Inhibitory effect at 300 ppm
	R^1	R^2	R^3	R^4	R^5	
C	H	H	H	H	H	32.13
C1	H	F	H	H	H	81.79
C2	H	H	F	H	H	73.85
C3	Cl	H	H	H	H	64.62
C4	H	Cl	H	H	H	99.38
C5	H	H	Cl	H	H	65.00
C6	Br	H	H	H	H	56.92
C7	H	Br	H	H	H	73.46
C8	H	H	Br	H	H	35.77
C9	Cl	H	Cl	H	H	47.69
C10	Cl	H	H	H	Cl	86.54
C11	H	Cl	Cl	H	H	58.85
C12	Cl	H	H	H	F	94.14

Considering all synthesized compounds in this group, Compounds **C1**, **C4**, **C10** and **C12** exhibited root growth of *M. pigra* more than 80% of control. The compounds having the substituent bearing on *meta-* position of a benzene ring showed higher activity than another position. In addition, the compound having chloro group as substituent revealed higher activity than fluoro and bromo groups, respectively.

(ii) Alkoxy cinnamic acids **(C13-C33)**

Twenty-one alkoxy cinnamic acids (**C13-C33**) were synthesized. Compounds **C13-C15** beared a methoxy group at *ortho-*, *meta-* and *para-* position, respectively. The variation of side chain was investigated from a series of Compounds **C15-C21**, where alkyl group was varied from $-CH_3$, $-C_4H_9$, $-C_6H_{13}$, $-C_8H_{17}$, $-C_{12}H_{25}$, $-CH_2Ph$ and Ph groups. Similar examination on the effect of side chain was performed in a series of Compounds **C22-C26**, where the substituent at position 3 was fixed as $-OCH_3$. Other side chain variation at position 2 was observed from $-C_4H_9$, $-C_6H_{13}$, $-C_8H_{17}$, $-C_{12}H_{25}$ and $-CH_2Ph$. Among alkoxy cinnamic acids studied, Compounds **C13**, **C14**, **C15**, **C16**, **C20**, **C25**, **C26**, **C27**, **C28**, **C29**, **C30**, **C32** and **C33** exhibited good tendency of growth inhibition. It is noteworthy that Compounds **C14**, **C15** and **C33** exhibited more than 80 percent growth inhibition activity considering at concentration 300 ppm. Compounds **C28**, **C29** and **C30** displayed more than 70 percent growth inhibition activity. The rest compounds revealed low inhibition.

(iii) Nitrogen-containing cinnamic acids (**C34-C39**)

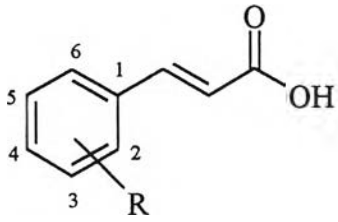
Three nitrocinnamic acids (**C34-C36**) were synthesized. In addition, nitrocinnamic acids (**C37-C39**) containing Cl group were prepared. All compounds gave good tendency of weed growth inhibition. Particularly, Compound **C35** revealed very interesting activity and gave 98 percent growth inhibition activity at 300 ppm.

(iv) Alkyl cinnamic acids and others (**C40-C47**)

Most compounds in this subgroup exhibited good tendency of inhibition, except for Compounds **C44** and **C45** which beared mono cyano group at *meta-* and *para-* position, respectively. Nonetheless, only Compound **C43** gave 70 percent growth inhibition activity. The other compounds displayed less than 70 percent growth inhibition activity.

Generally, the position and type of substituents were major factors to influence the herbicidal activity. To make the SAR study more comprehendible, the comparison of various substituents of forty-seven compounds could be summarized as follows:

1) Substituent on a benzene ring



Using Compound **C** (R = H) as a reference, the introduction of various substituents at 4-position lucidly reduced activity. The activity was observed in the series of:

OMe > F > CF_3 > Cl > CH_3 > *i*-Pr > NO_2 > *t*-Bu > H > OCH_2Ph > OC_4H_9

Comparing with the compounds having the same substituents but different in the position, it was found that the substituents bearing on the 3-position of the benzene ring had little effect on activity observed. For instance, 3-chlorocinnamic acid **(C4)** showed the highest activity in this series and the activity of 3-nitrocinnamic acid **(C35)** was higher than that of 3-methoxycinnamic acid **(C14)**. Moreover, it was found that the activity of 3-methoxycinnamic acid **(C14)** was higher than those of 3-fluorocinnamic acid **(C1)** and 3-bromocinnamic acid **(C7)**, respectively. The comparative activity is exhibited as follows:

Cl > NO_2 > OMe > F > Br > H

Considering the compounds with substituent at 2-position of the benzene ring, it was found that it had the lowest effect on activity observed. To illustrate this, 2-methoxycinnamic acid **(C13)** revealed the highest activity in this series and the activity of 2-bromocinnamic acid **(C6)** was higher than that of 2-nitrocinnamic acid **(C34)**. The comparative activity can be written as follows:

OMe > Br > NO_2 > H

The effect of the positions on root growth inhibition activity against *M. pigra* could also be visualized in Fig 3.3.

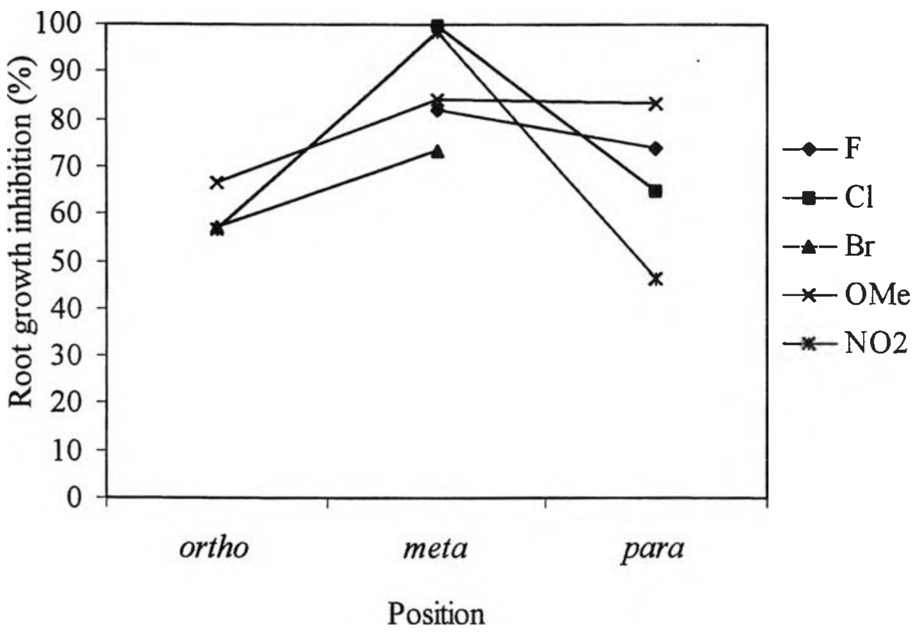


Fig 3.3 Inhibitory effect of substituents at various positions on a benzene ring of *trans*-cinnamic acids on root growth of *M. pigra* at 300 ppm (%)

It was found as presented in Fig 3.2 that the attractive percent growth inhibition against *M. pigra* at 300 ppm was noticed from *trans*-cinnamic acids containing methoxy groups at 3-position. The tendency of activity ranged from the highest to the lowest when the position of substituent are at *meta*-, *para*- and *ortho*-, respectively. When the substituents are nitro groups, the tendency of activity ranged from the highest to the lowest when the position of substituents are *meta*-, *ortho*- and *para*-, respectivery. Besides, the observed activity was markedly influenced by halogen substituents. When the substituents are fluoro or chloro groups, the activity were lessened from *meta*- to *para*- position. Moreover, when bromine was a substituent on an aromatic ring, the activity was found to be increased. The variant activity of bromo substituent could be arranged as *meta*- > *ortho*-.

The introduction of the second chlorine atom to chlorocinnamic acids such as dichlorocinnamic acids (**C9-C11**) was carried out. The activity of dichlorocinnamic acids was observed to be less than monosubstituted compound, except for 2,6-dichlorocinnamic acid (**C10**) where there were two chloro atoms at both *ortho*-position on a benzene ring. Moreover, it was found that Compound **C12** which contained Cl and F atoms at both *ortho*- positions on a benzene ring showed excellent activity. The activity was observed in this series as:

2-Cl-6-F > 2,6-diCl > 3,4-Cl

In the case of compounds with chloro (Cl) and nitro (NO_2) groups on a benzene ring (**C37**-**C39**), the activity observed was lower than that of the compounds having only chloro (Cl) or nitro (NO_2) group on a benzene ring. For instance, 2-chlorocinnamic acid (**C3**) and 3-nitrocinnamic acid (**C35**) showed higher activity than 2-chloro-5-nitrocinnamic acid (**C37**). 3-Chlorocinnamic acid (**C4**) and 2-nitrocinnamic acid (**C34**) illustrated higher activity than 5-chloro-2-nitrocinnamic acid (**C39**). 4-Chlorocinnamic acid (**C5**) and 3-nitrocinnamic acid (**C35**) also displayed higher activity than 4-chloro-3-nitrocinnamic acid (**C38**). Moreover, 4-chloro-3-nitrocinnamic acid (**C38**) showed the highest activity in this series and the activity of 2-chloro-5-nitrocinnamic acid (**C37**) was also found to be higher than that of 5-chloro-2-nitrocinnamic acid (**C39**). The effect of substituents on a benzene ring of these series is represented in Fig 3.4.

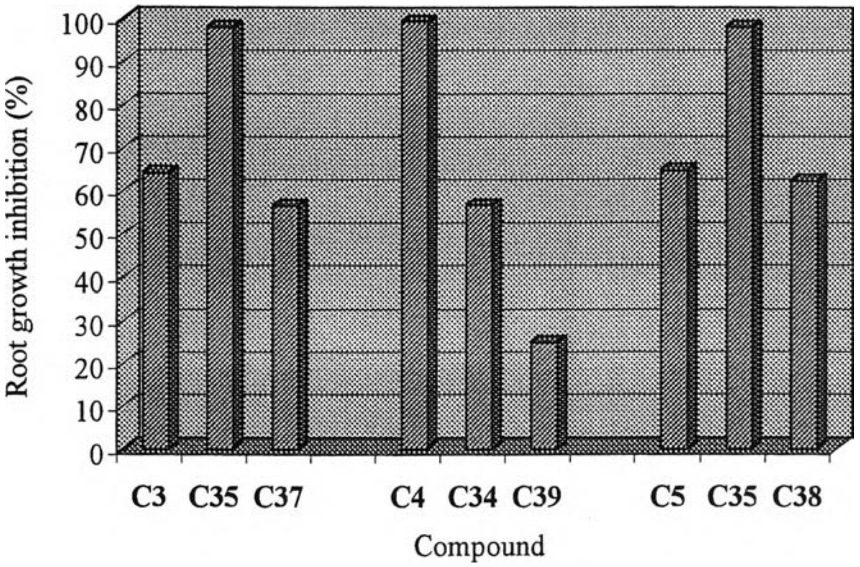


Fig 3.4 Inhibitory effect of various substituents on a benzene ring of *trans*-cinnamic acids on root growth of *M. pigra* at 300 ppm (%)

The order of activity observed in compounds bearing the chloro (Cl) group on a benzene ring could be arranged as follows:

3-Cl > 2-Cl-6-F > 2,6-diCl > 4-Cl > 4-Cl-3-NO_2 > 3,4-diCl > 2-Cl-5-NO_2 > 5-Cl-2-NO_2

Considering the series of methoxy group, it was found that most of them showed higher activity than the reference compound, *trans*-cinnamic acid (**C**) which was used as a reference compound. Five dimethoxycinnamic acids (**C27**-**C31**) were synthesized. It was found that the activity of dimethoxycinnamic acids was normally less than monomethoxycinnamic acids. For instance, the activity of 2,4-dimethoxycinnamic acid (**C28**) was lower than that of 4-methoxycinnamic acid (**C15**) and the activity of 3,4-dimethoxycinnamic acid (**C30**) was lower than that of 3-methoxycinnamic acid (**C14**). Moreover, 3,4-dimethoxycinnamic acid (**C30**) showed the highest activity in this series. The inhibition activity of 2,4-dimethoxycinnamic acid was higher than those of 2,5-dimethoxycinnamic acid (**C29**). 2,3-Dimethoxycinnamic acid (**C27**) exhibited the lowest activity in this series. The comparative activity in this series is exhibited as follows:

{[3-OMe, 4-OMe >] 3,4-diOMe} > {[4-OMe >] 2,4-diOMe} >
{[3-OMe >] 2,5-diOMe} >{[2-OMe, 3-OMe >] 2,3-diOMe}

Furthermore, it was found that the compound bearing three methoxy groups on a benzene ring (**C32**) displayed lower activity than that containing only one or two methoxy groups, respectively. The comparative order of activity observed was exhibited as follows:

3-OMe > 3,4-diOMe > 3,4,5-triOMe

The effect of methoxy groups on a benzene ring can also be visualized in Fig 3.5.

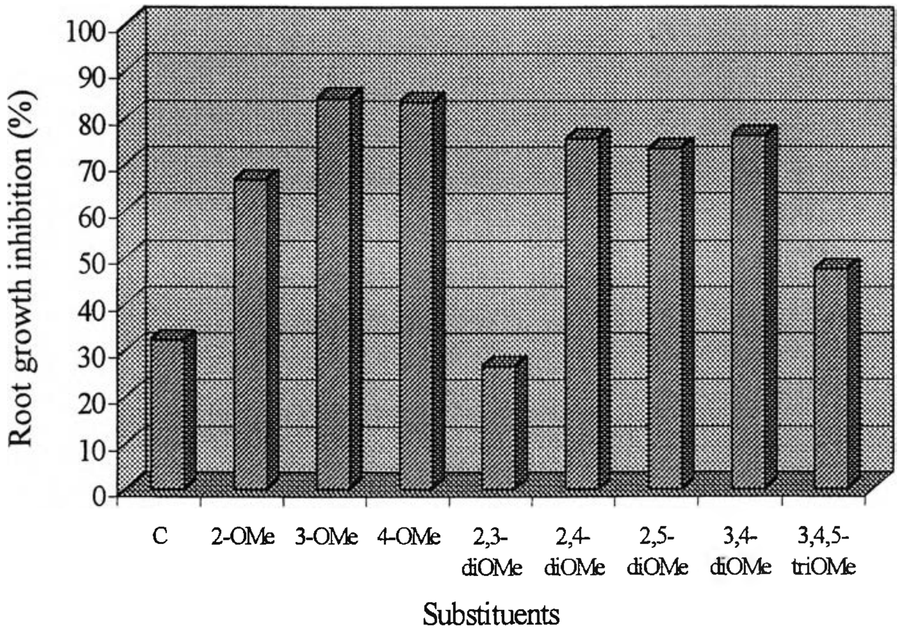
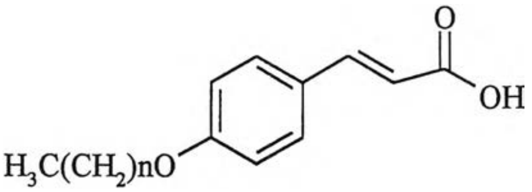


Fig 3.5 Inhibitory effect of one, two and three methoxy group on a benzene ring of *trans*-cinnamic acids on root growth of *M. pigra* at 300 ppm (%)

The variation of numbers of carbon atoms on a benzene ring of an alkoxy group at 4-position was investigated from a series of Compounds **C15–C19** which carbon atoms increased from 1, 4, 6, 8 and 12, respectively. In addition, 4-benzyloxycinnamic acid **(C20)** containing a benzyloxy group at 4-position of a benzene ring was included in this series. Among the six compounds of this group, 4-methoxycinnamic acid **(C15)** showed the highest activity (83%). The optimization of the number of carbon atoms in chain can be deduced and compound with one carbon atom **(C15)** exhibited the highest activity.



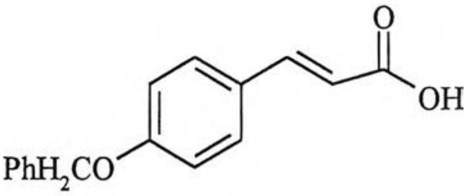
C15 n = 0

C16 n = 3

C17 n = 5

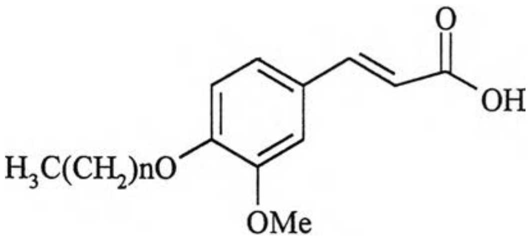
C18 n = 7

C19 n =11

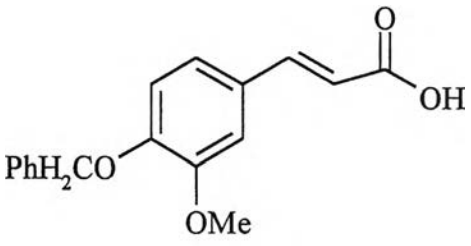


C20

The deviation of the numbers of carbon atoms in an alkoxy part at 4-position in a benzene ring containing 3-OMe was investigated. A series of Compounds **C22-C25** which carbon atoms varied from 4, 6, 8 and 12 was studied. In addition, 4-benzyloxy-3-methoxycinnamic acid **(C26)** and 3,4-dimethoxycinnamic acid **(C30)** which have a methoxy group and a benzyloxy group at 4-position on a benzene ring were studied. Among them, only 3,4-dimethoxycinnamic acid **(C30)** showed the highest activity (76 %). The best activity observed when an alkoxy side chain contained only one carbon. The results were found to be coincide with those in previous section.



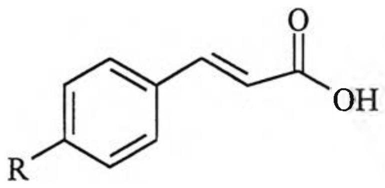
C30 n = 0
C22 n = 3
C23 n = 5
C24 n = 7
C25 n = 11



C26

2) Effects of alkyl substituents

The examination on the effects of branch chain of alkyl substituents was performed employing a series of 3 compounds: **C40-C42.** It was found that increasing the number of carbon atom provided the diminishing of growing inhibition activity. When the substituent at 4-position on a benzene ring was changed from CH_3 to CF_3 group, it was found that it provided the increasing of growth inhibition activity from 64 to 70 %.



C40 R = CH_3
C41 R = *i*-Pr
C42 R = *t*-Bu
C43 R = CF_3

The replacement of H atom at 4-position with 1-naphthyl ring in Compound **C46** exhibited the growth activity more potency than that of the reference compound (**C**). While the change of H atom at 4-position on a benzene ring with 9-anthracenyl moiety as in Compound **C47** showed extremely low activity and even less than the reference compound (**C**).

Percent root growth inhibition against *Mimosa pigra* at 300 ppm of all synthesized substituted *trans*-cinnamic acids could be summarized and represented in Fig 3.6.

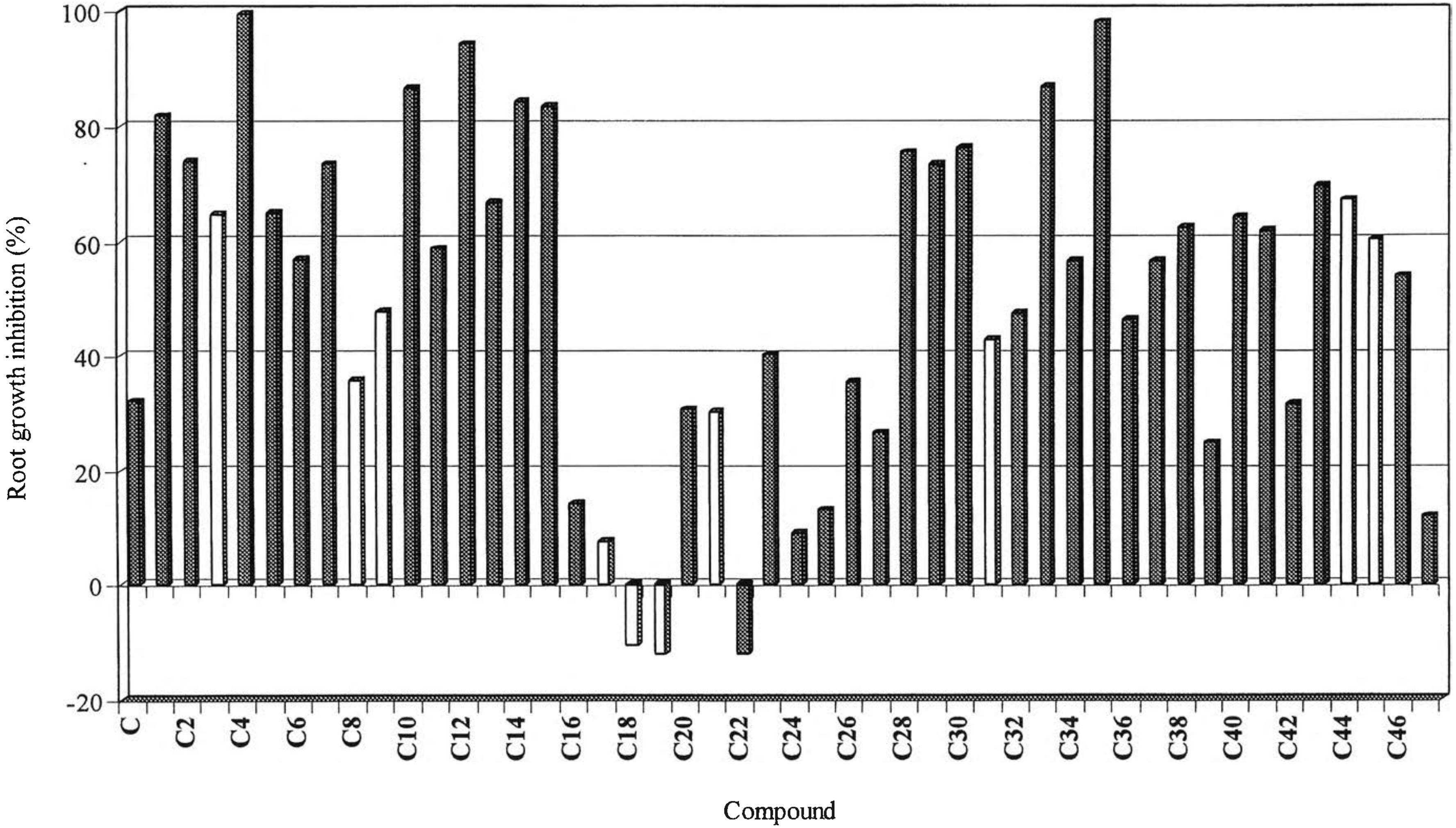


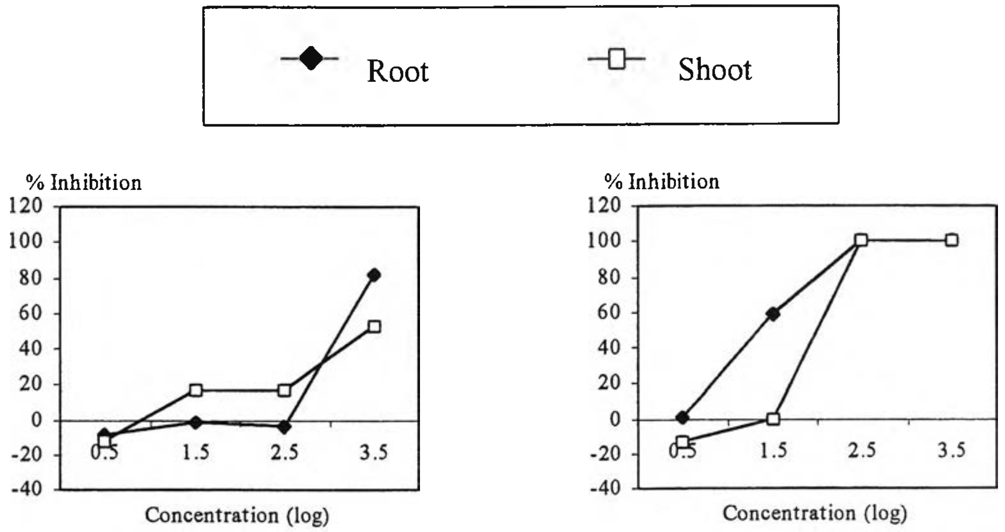
Fig 3.6 Inhibitory effect of substituted *trans*-cinnamic acids on root growth of *M. pigra* at 300 ppm (%)

4-Fluorocinnamic acid (**C2**), 3-bromocinnamic acid (**C7**), 2,4-dimethoxycinnamic acid (**C28**), 2,5-dimeyhoxycinnamic acid (**C29**), 3,4-dimethoxycinnamic acid (**C30**) and 4-trifluorocinnamic acid (**C43**) exhibited percent growing inhibition activity against *M. pigra* Linn. above 70. 3-Fluorocinnamic acid (**C1**), 3-chlorocinnamic acid (**C4**), 2,6-dichlorocinnamic acid (**C10**), 2-chloro-6-fluorocinnamic acid (**C12**), 3-methoxycinnamic acid (**C14**), 4-methoxycinnamic acid (**C15**), 3,4-methylenedioxycinnamic acid (**C33**) and 3-nitrocinnamic acid (**C35**) exhibited percent growing inhibition activity against *M. pigra* Linn. above 80. Most of them revealed promising tendency for the development as new herbicide for *Mimosa pigra*.

3.4.2 Weed Growth Inhibition against *Echinochloa crus-galli* (E.) Beauv.

Another weed selected for performing bioassay in this study was *Echinochloa crus-galli* (E.) Beauv. (barnyardgrass) which is a noxious weed distributed both paddy and upland field.

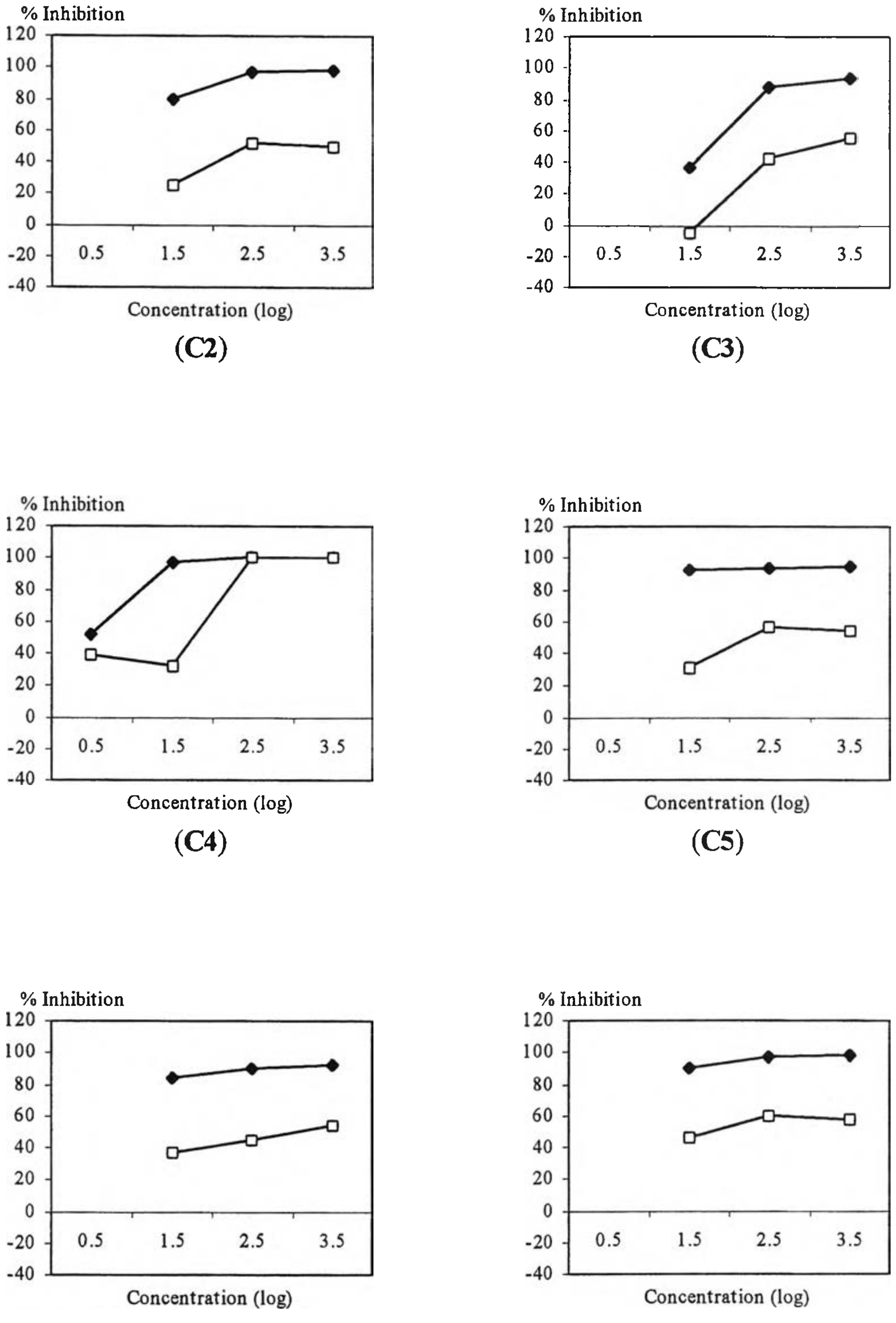
The biological test of substituted *trans*-cinnamic acids against barnyardgrass has also never been reported in literature. Synthesized substituted *trans*-cinnamic acids were in fact found to possess inhibitory effect on growth of *Echinochloa crus-galli*. The degree of inhibition/stimulation greatly depended on the difference in structures of forty-seven substituted *trans*-cinnamic acids. The results are summerized as shown in Fig 3.7.



(C)

(C1)

Fig 3.7 Inhibitory effect of substituted *trans*-cinnamic acids on root and shoot growth of *E. crus-galli* (%)

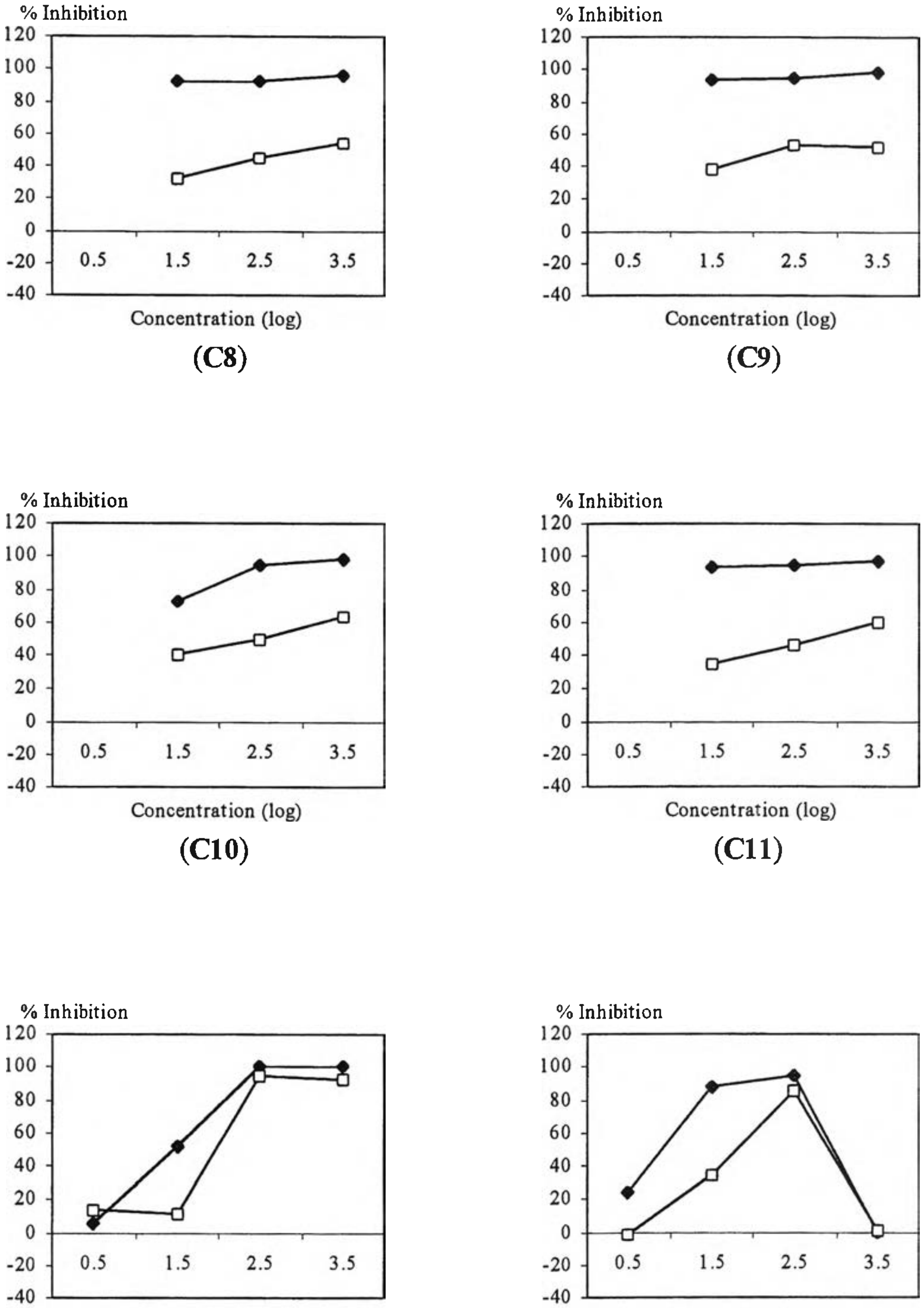


(C2) (C3)

(C4) (C5)

(C6) (C7)

Fig 3.7 (cont.)

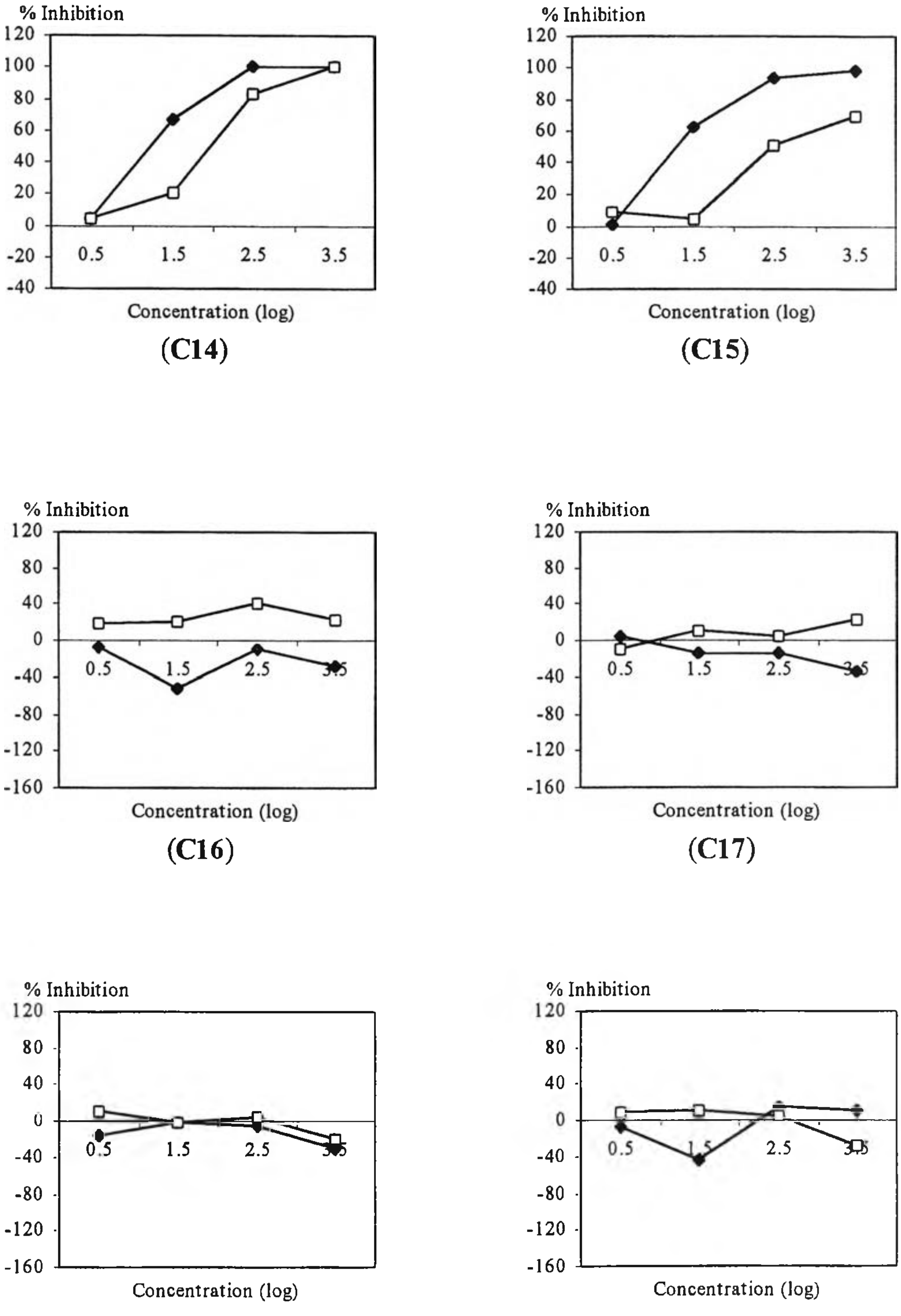


(C8) (C9)

(C10) (C11)

(C12) (C13)

Fig 3.7 (cont.)



(C14)

(C15)

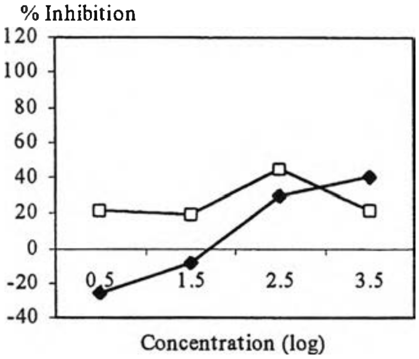
(C16)

(C17)

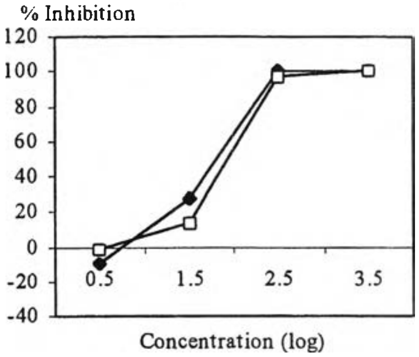
(C18)

(C19)

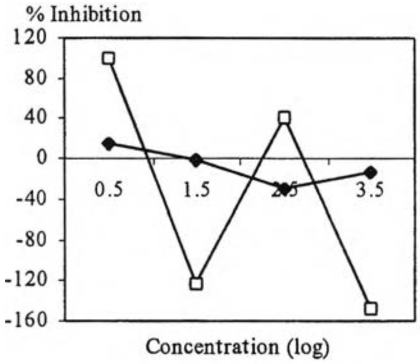
Fig 3.7 (cont.)



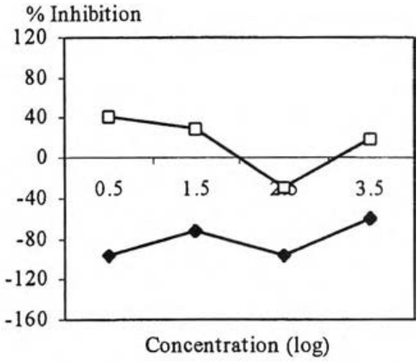
(C20)



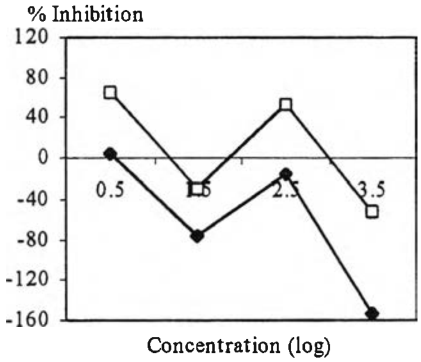
(C21)



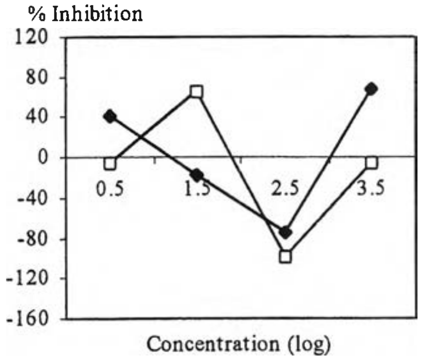
(C22)



(C23)

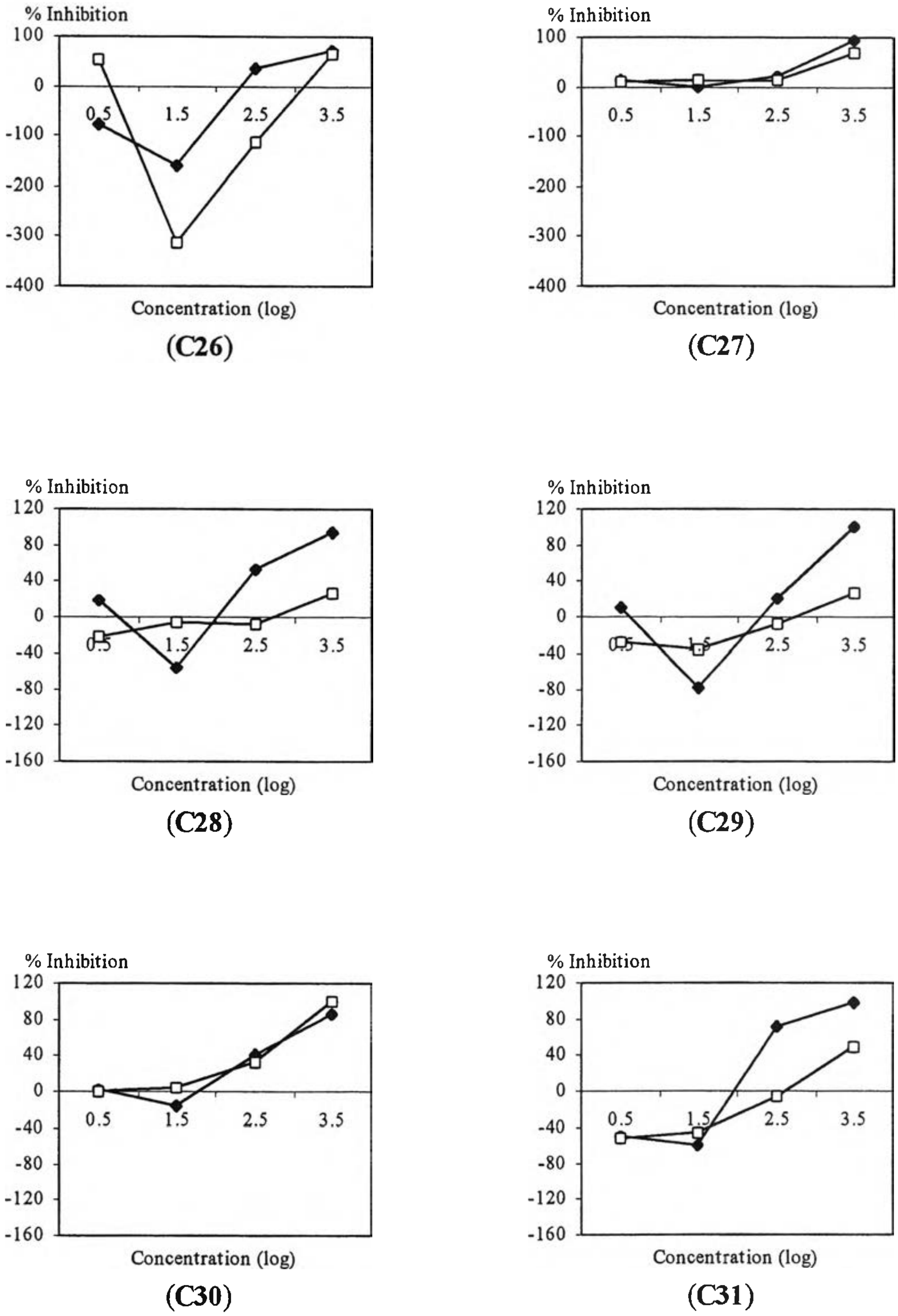


(C24)



(C25)

Fig 3.7 (cont.)

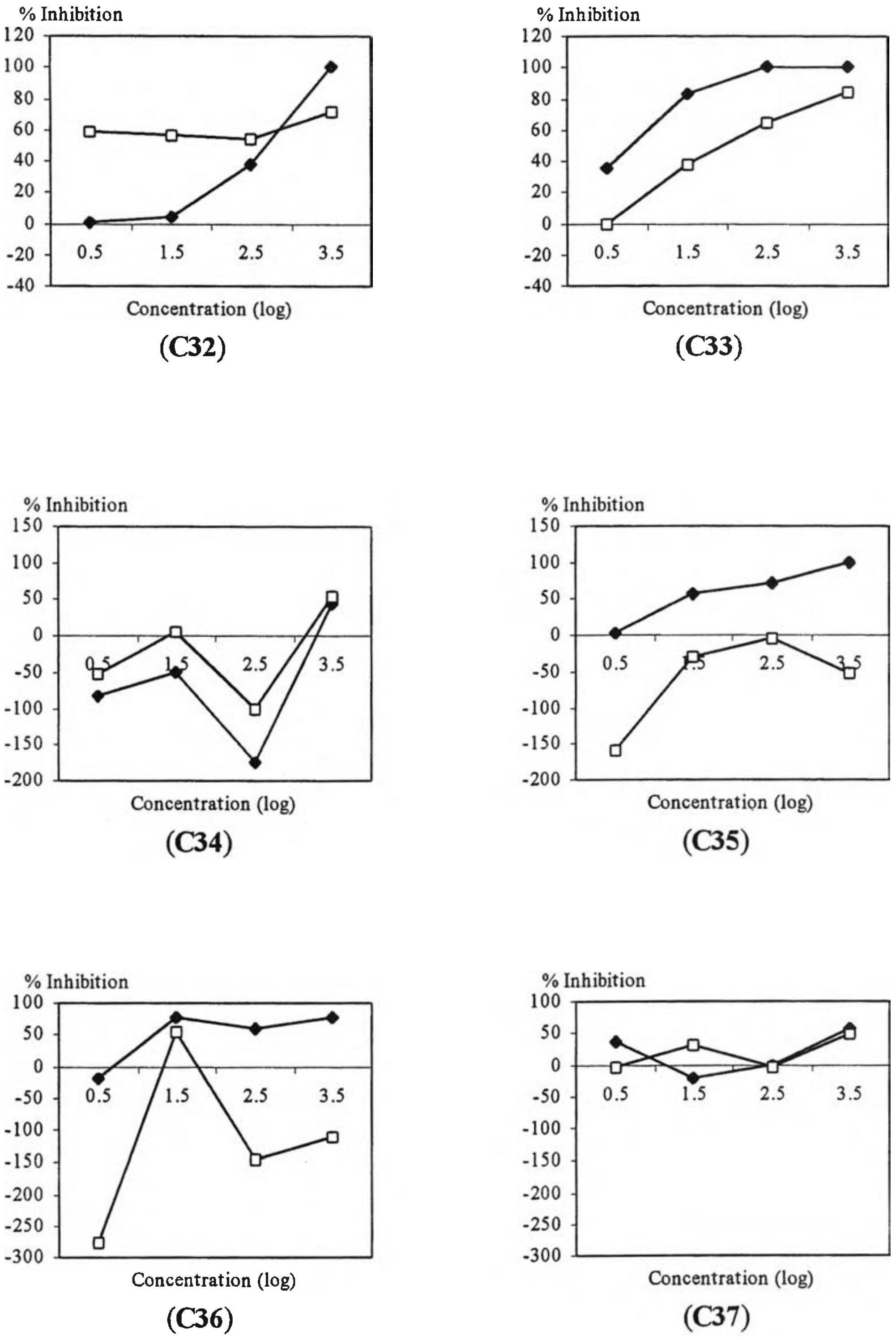


(C26) (C27)

(C28) (C29)

(C30) (C31)

Fig 3.7 (cont.)

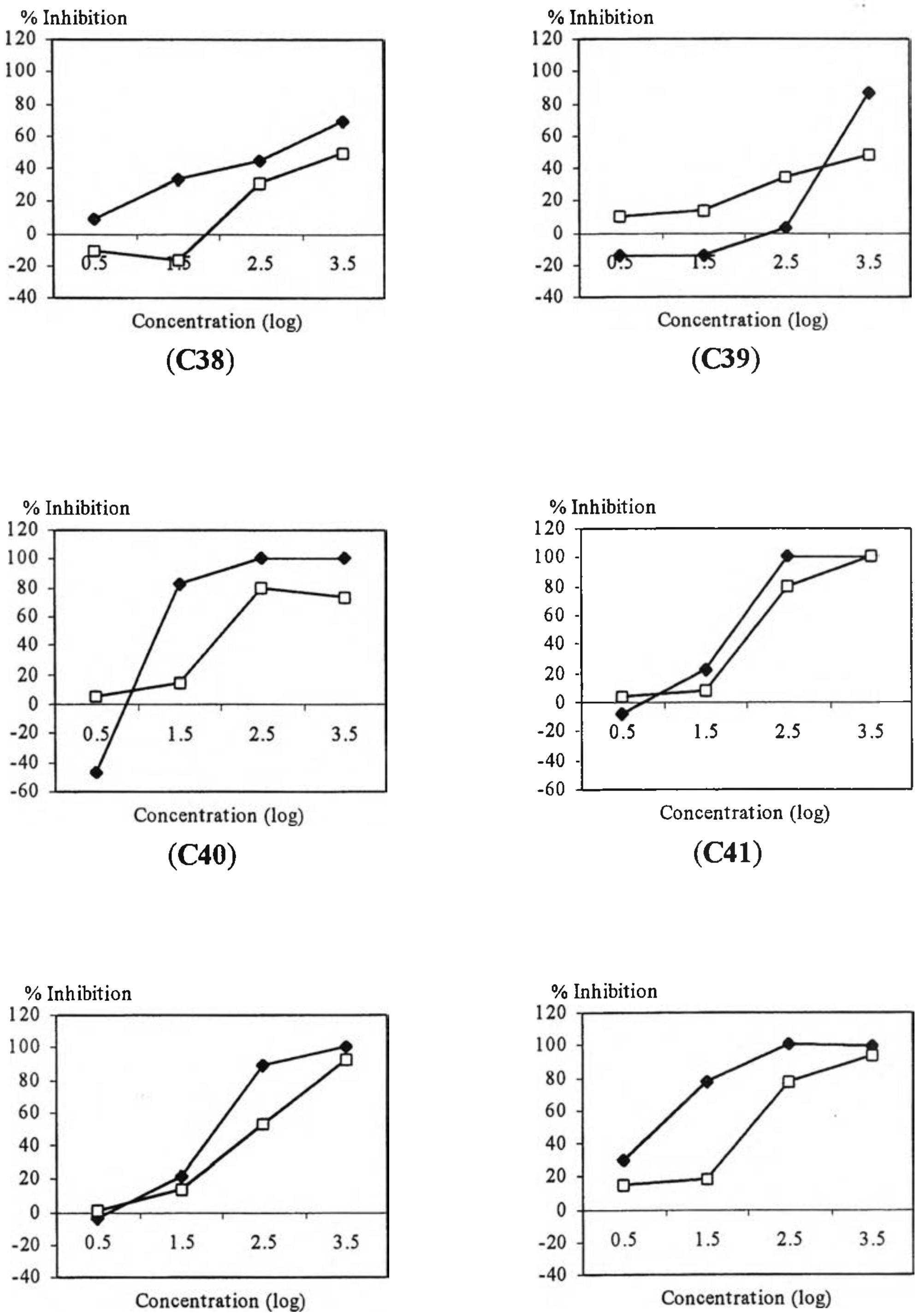


(C32) (C33)

(C34) (C35)

(C36) (C37)

Fig 3.7 (cont.)

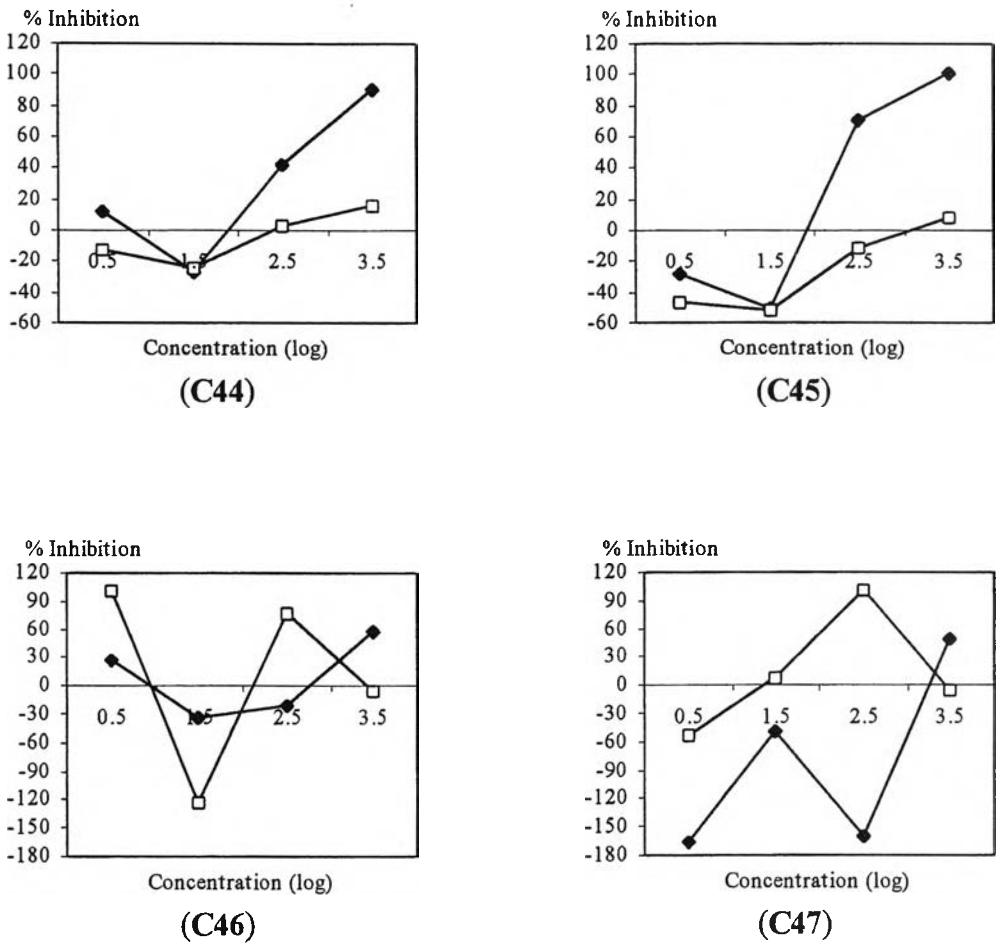


(C38) (C39)

(C40) (C41)

(C42) (C43)

Fig 3.7 (cont.)



(C44) **(C45)**

(C46) **(C47)**

Fig 3.7 (cont.)

The above graphs revealed the correlation between root and shoot growth inhibition and concentration of tested substituted *trans*-cinnamic acids in the range of 3-3000 ppm. Considering data of this graph by the same means as presented in Fig 3.2 (Inhibitory effect of substituted *trans*-cinnamic acids on root and shoot growth of *M. pigra* (%)), it gave different result from those obtained for *M. pigra* Linn. Most compounds did not show good correlation between the concentration used and percent growth inhibition observed. Therefore, their results would be excluded from this examination, except for 4-fluorocinnamic acid (**C2**), 2-chlorocinnamic acid (**C3**), 4-chlorocinnamic acid (**C5**), 2-bromocinnamic acid (**C6**), 3-bromocinnamic acid (**C7**), 4-bromocinnamic acid (**C8**), 2,4-dichlorocinnamic acid (**C9**), 2,6-dichlorocinnamic acid (**C10**), 3,4-dichlorocinnamic acid (**C11**), 4-methoxycinnamic acid (**C15**), 4-benzyloxycinnamic acid (**C20**), 3,4,5-trimethoxycinnamic acid (**C32**), 3-nitrocinnamic acid (**C35**), 4-chloro-3-nitrocinnamic acid (**C38**) and 4-*tert*-

butylcinnamic acid (**C42**). The relationship between growth inhibition against *E. crus-galli* and cinnamic acid derivatives depended on only substituent on a benzylidene ring. The introduction of various substituents at 4-position lucidly reduced activity. The activity can be illustrated as follows:

$$F > OMe > Cl \cong Br > t\text{-}Bu > OCH_2Ph$$

Comparison the compounds bearing the same substituents but different in position, it was found that the compounds bearing bromo (Br) group at different positions on a benzene ring had tendency of activity from the highest to the lowest as : *meta* > *para* > *ortho*. Besides, the activity influenced by chloro (Cl) group could be arranged as *para* > *ortho*. In every case of addition of two Cl atoms on a benzene ring (Compounds **C9** –**C11**), it showed stronger activity than one Cl atom present on a benzene ring. The inhibitory effect of these compounds was high as 94-95%.

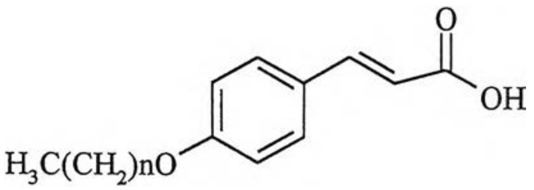
The addition of a Cl atom at 4-position of a benzene ring containing 3-NO_2 substituted group provided less active than only 3-NO_2 group present on a benzene ring. The comparative activity can be illustrated as follows:

$$3\text{-}NO_2 > 4\text{-}Cl\text{-}3\text{-}NO_2$$

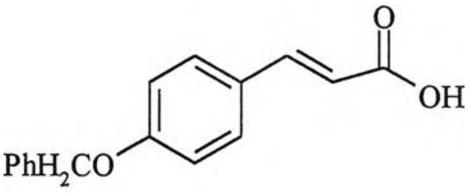
Another observation could be seen from the addition of three methoxy groups on a benzene ring (Compound **C32**). This compound displayed lower activity than a benzene ring with one OMe grouop. The comparative activity is exhibited as follows:

$$4\text{-}OMe > 3,4,5\text{-}triOMe$$

The variation of numbers of carbon atoms in an alkoxy moiety at 4-position of a benzene ring was investigated. A series of Compounds **C15-C19** which carbon atoms increased from 1, 4, 6, 8 and 12, respectively was studied, including 4-benzyloxycinnamic acid (**C20**) which contained a benzyloxy group at 4-position of a benzene ring. The inhibitory effect of 4-methoxycinnamic acid (**C15**) and 4-benzyloxycinnamic acid (**C20**) varied by the concentration. The growth inhibitory of Compound **C15** was 1, 62, 94 and 98% at concentration of 3, 30, 300 and 3000 ppm, respectively. So it might be concluded that Compound **C15** which was similar to *M. pigra*.



C15 n = 1
C16 n = 4
C17 n = 6
C18 n = 8
C19 n = 12



C20

Percent root growth inhibition against *Echinochloa crus-galli* at 300 ppm of all synthesized substituted *trans*-cinnamic acids could be summarized and presented in Fig 3.8.

Similar to that of *Mimosa pigra* Linn., 3-nitrocinnamic acid (**C32**) exhibited growth inhibition activity against *E. crus-galli* Beauv. higher than 70%. Moreover, 4-fluorocinnamic acid (**C2**), 2-chlorocinnamic acid (**C3**), 4-chlorocinnamic acid (**C5**), 2-bromocinnamic acid (**C6**), 3-bromocinnamic acid (**C7**), 4-bromocinnamic acid (**C8**), 2,4-dichlorocinnamic acid (**C9**), 2,6-dichlorocinnamic acid (**C10**), 3,4-dichlorocinnamic acid (**C11**), 4-methoxycinnamic acid (**C15**) and 4-*tert*-butylcinnamic acid (**C42**) could inhibit root growth of barnyard grass higher than 80%, which should be further studied and developed as new herbicide for *E. crus-galli*.

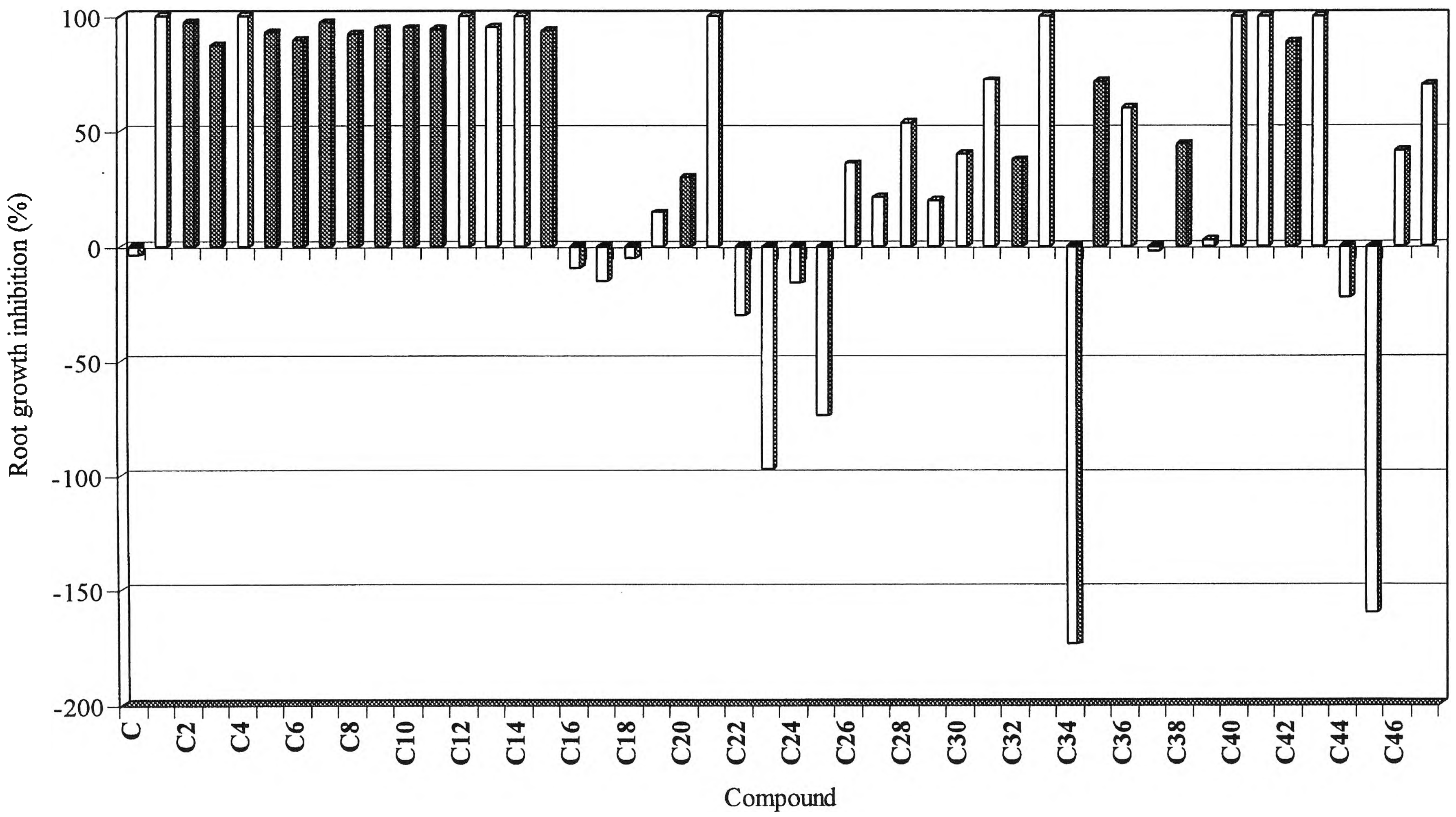


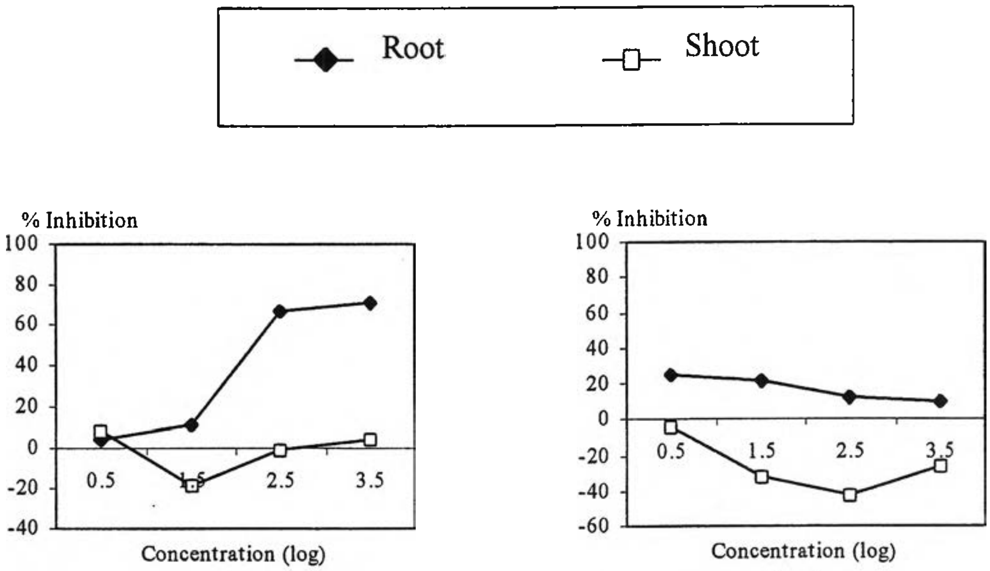
Fig 3.8 Inhibitory effect of substituted *trans*-cinnamic acids on root growth of *E. crus-galli* at 300 ppm (%)

3.5 Herbicidal Potential of *trans*-Cinnamic Acid Derivatives

From the above result of herbicidal potential against giant mimosa and barnyard grass, some selected compounds were prepared and evaluated for their herbicidal potential. Considering the root growth inhibition against *M. pigra*, the selected compounds for further study were based on 3,4-methylenedioxycinnamic acid (**C33**) and 3-nitrocinnamic acid (**C35**), which gave high inhibition effect at both 30 and 300 ppm concentration. The *trans*-cinnamic acid derivatives studied can be divided into 3 categories: 1) amide derivatives 2) ester derivatives and 3) sodium and calcium cinnamate derivatives.

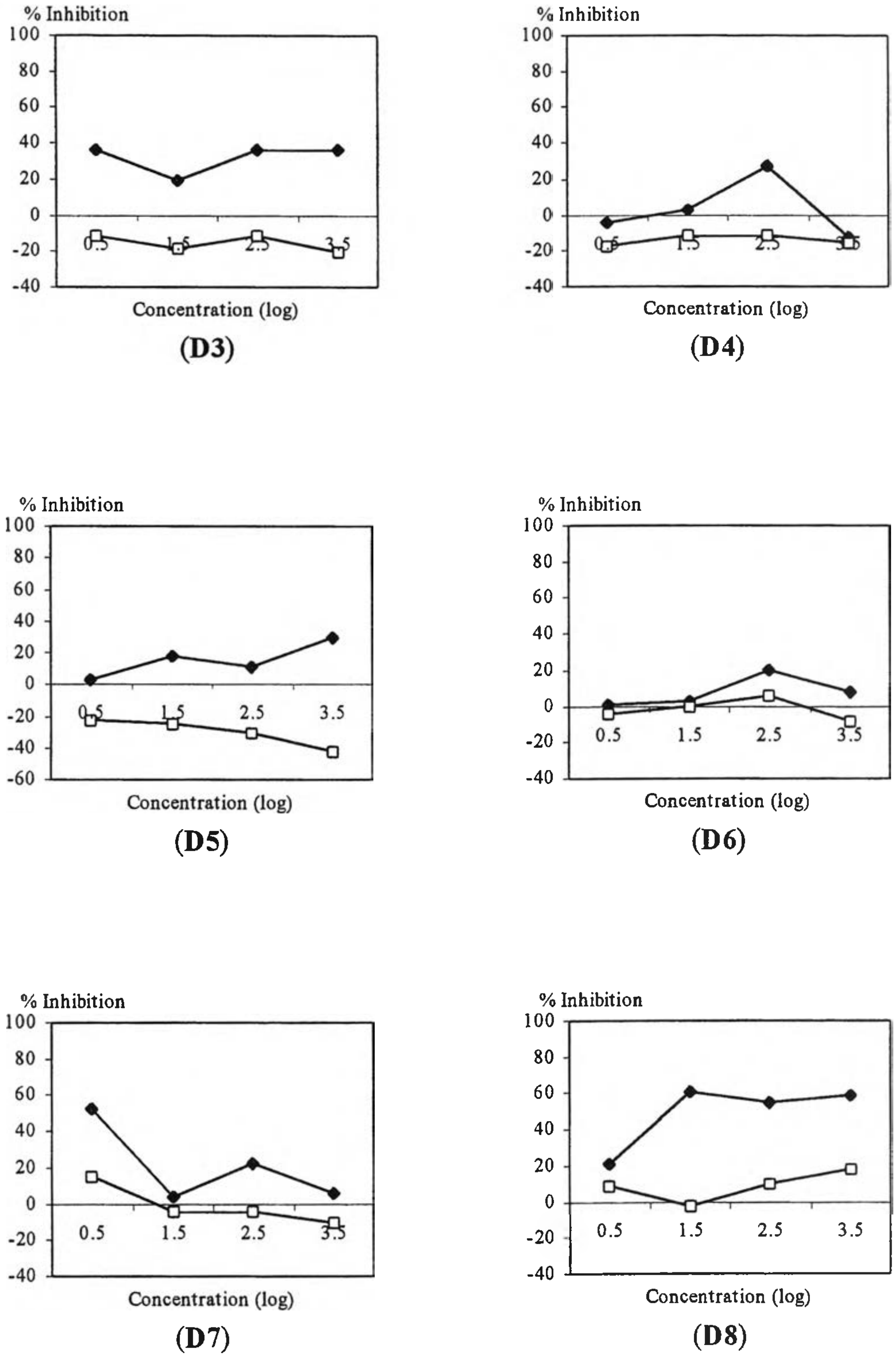
3.5.1 Cinnamamides (D1 – D12)

The selected substituted *trans*-cinnamic acids for this study were 2-nitrocinnamic acid (**C34**), 4-methylcinnamic acid (**C40**) and 4-*iso*-propylcinnamic acid (**C41**). The reason beyond this selection was their tendencies of inhibition were found to possess moderate activity (55-65% at 300 ppm concentration). Thus, the derivatization of the parent compounds with moderate activity may lead to the disclosure of compounds with increasing interested activity. The results of synthesized cinnamamides against *M. pigra* are shown in Fig 3.9.



(D1) (D2)

Fig 3.9 Inhibitory effect of cinnamamides on root and shoot growth of *M. pigra* (%)



(D3)

(D4)

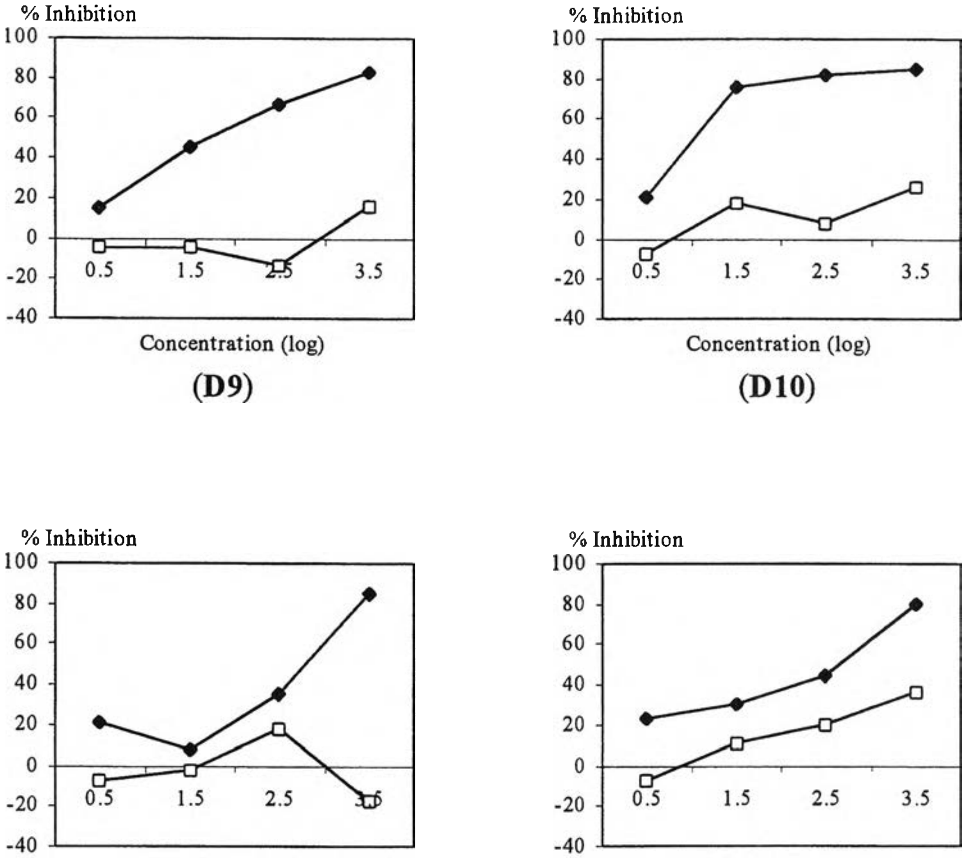
(D5)

(D6)

(D7)

(D8)

Fig 3.9 (cont.)



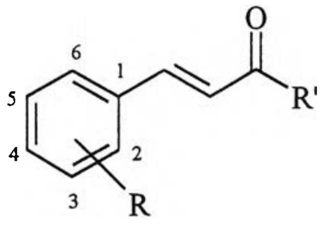
(D9) (D10)

(D11) (D12)

Fig 3.9 (cont.)

From the above graphs, most amide derivatives did not exhibit inhibition by the concentration against *M. pigra* except for (*N*-butyl)-4-methylcinnamamide (**D1**), (*N*-2,4-dichlorophenyl)-3-nitrocinnamamide (**D9**), (*N*-2,4-dichlorophenyl)-3,4-methylenedioxycinnamamide (**D10**) and (*N*-phenyl)-3,4-methylenedioxy-cinnamamide (**D12**). Although those compounds showed stronger inhibition at higher concentration, but (*N*-2,4-dichlorophenyl)-3,4-methylenedioxycinnamamide (**D10**) exhibited the excellent growth inhibition activity as high as 82% at 300 ppm. (*N*-butyl)-4-methylcinnamamide (**D1**) exhibited good growth inhibition as same as (*N*-2,4-dichlorophenyl)-3-nitrocinnamamide (**D9**) about 66% at the same concentration.

Comparing each amide derivative with its parent compound, it was found that in every case of amide derivative, it exhibited growth inhibition activity less than its parent compound except (*N*-butyl)-4-methylcinnamamide (**D1**) which revealed the growth inhibition activity higher than its parent compound. The degree of inhibition activity of the amide derivatives were range from the highest to the lowest as follow:



R = 3-NO_2: **C35** (R′ = OH) > **D9** (R′ = *N*-2,4-dichlorophenyl)

R = 3,4-OCH_2O-: **C33** (R′ = OH) > **D10** (R′ = *N*-2,4-dichlorophenyl) > **D12** (R′ = *N*-phenyl)

The summarized results are shown in Fig 3.10.

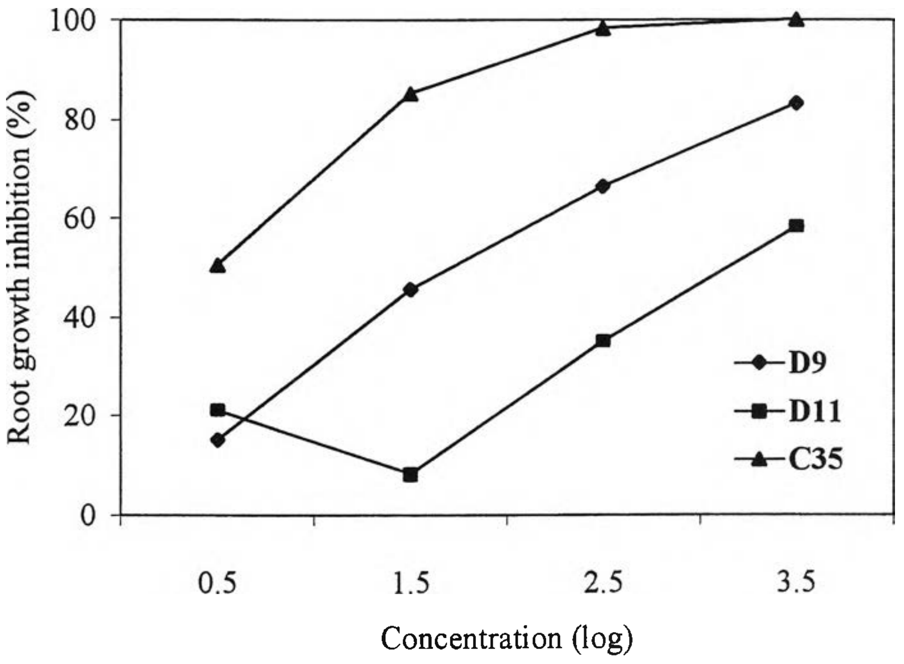


Fig 3.10 Inhibitory effect of cinnamamides and their parent compounds on root growth of *M. pigra* (%)

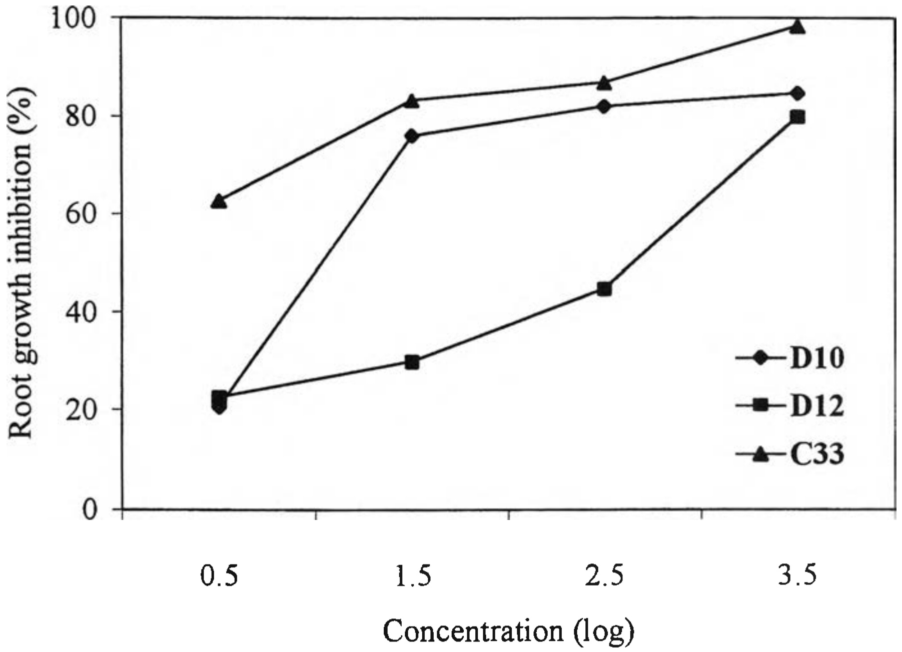
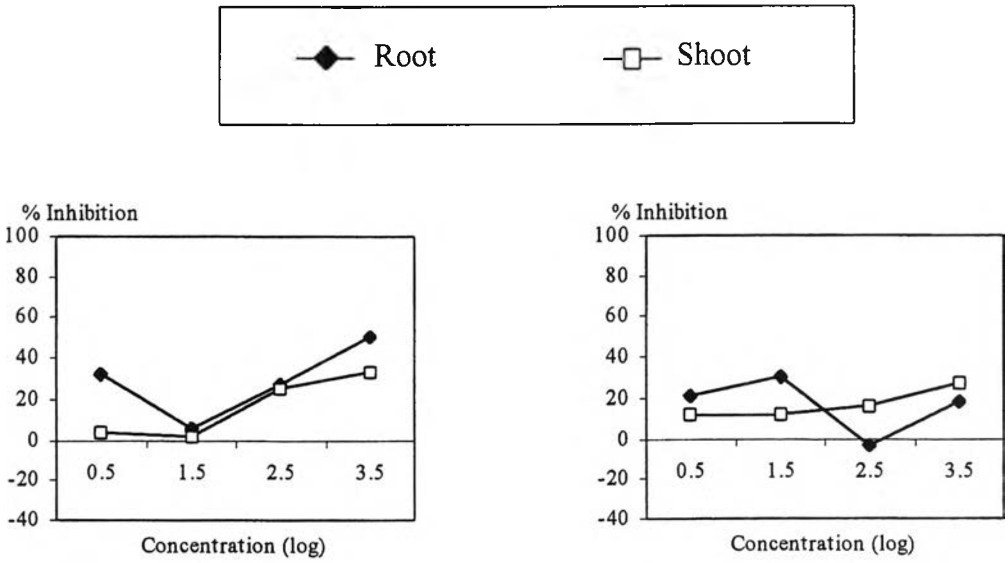


Fig 3.10 (cont.)

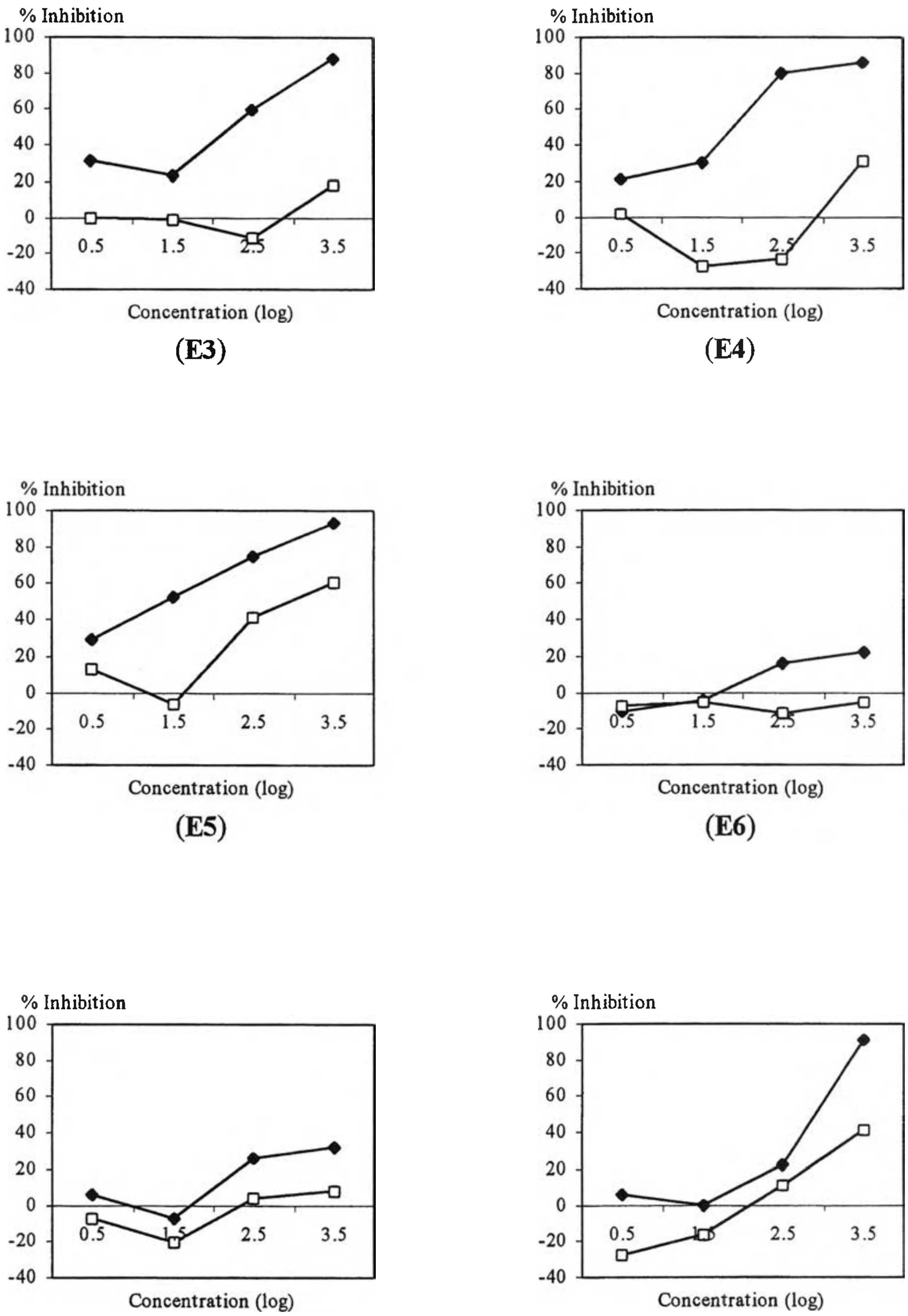
3.5.2 Cinnamate Esters (E1 – E15)

Fifteen cinnamate esters were synthesized and the results of growth inhibition activity against *M. pigra* of those cinnamate esters are shown in Fig 3.11.



(E1) **(E2)**

Fig 3.11 Inhibitory effect of cinnamate esters on root and shoot growth of *M. pigra* (%)

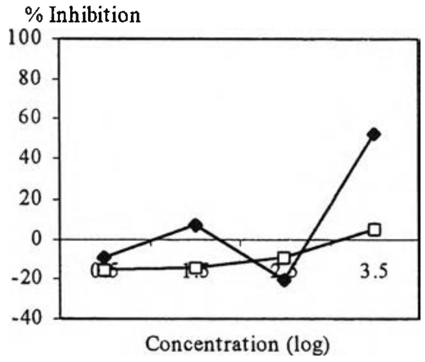


(E3) (E4)

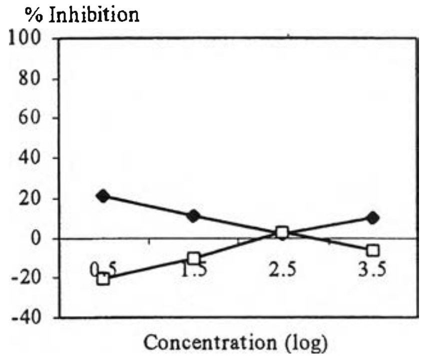
(E5) (E6)

(E7) (E8)

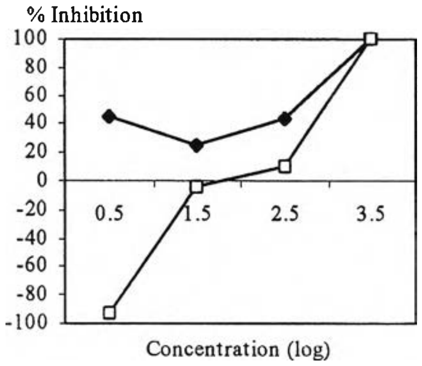
Fig 3.11 (cont.)



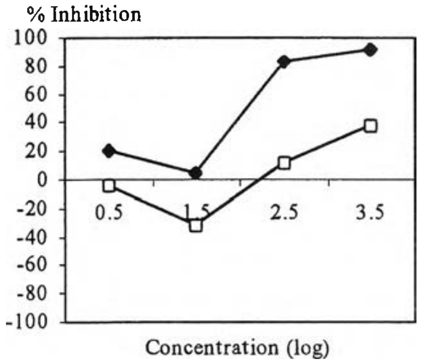
(E9)



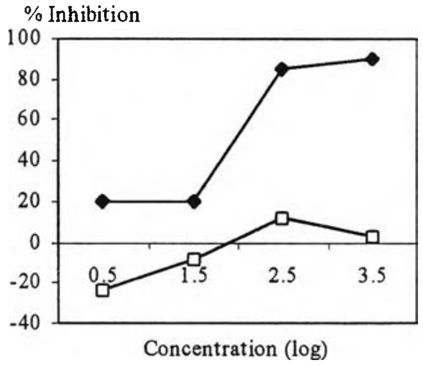
(E10)



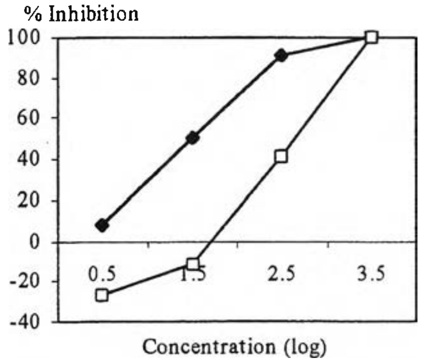
(E11)



(E12)

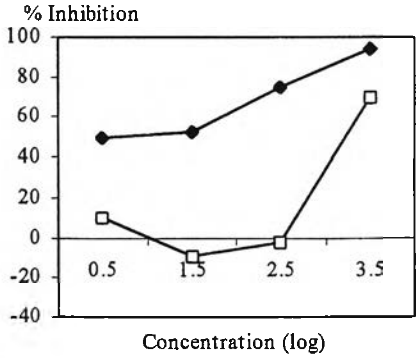


(E13)



(E14)

Fig 3.11 (cont.)

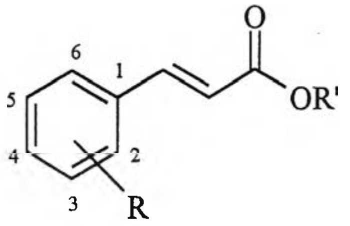


(E15)

Fig 3.11 (cont.)

From the above graphs, ethyl 3-nitrocinnamate (**E4**), ethyl 3,4-methylenedioxycinnamate (**E5**), 2,4-dichlorophenyl 3-nitrocinnamate (**E14**) and 2,4-dichlorophenyl 3,4-methylenedioxycinnamate (**E15**) which gave reasonable tendency of inhibition, only 2,4-dichlorophenyl 3-nitrocinnamate (**E14**) showed the highest growth inhibition activity as high as 90%. Ethyl 3-nitrocinnamate (**E4**), ethyl 3,4-methylenedioxycinnamate (**E5**) and 2,4-dichlorophenyl 3,4-methylenedioxycinnamate (**E15**) exhibited root growth inhibition activity, 79, 75 and 75, respectively.

Comparing root growth inhibition activity of each ester derivative with its parent compound, it was found that the ester derivatives exhibited less growth inhibition activity than its parent compound. The comparative activity was found to render as:



R = 3,4-OCH_2O-: **C33** (R′ = H) > **E5** (R′ = CH_2CH_3) ≅ **E15**

(R′ = 2,4-dichlorophenyl)

R = 3-NO_2: **C35** (R = H) > **E14** (R = 2,4dichlorophenyl) > **E4** (R = CH_2CH_3)

The summarized results are shown in Fig 3.12.

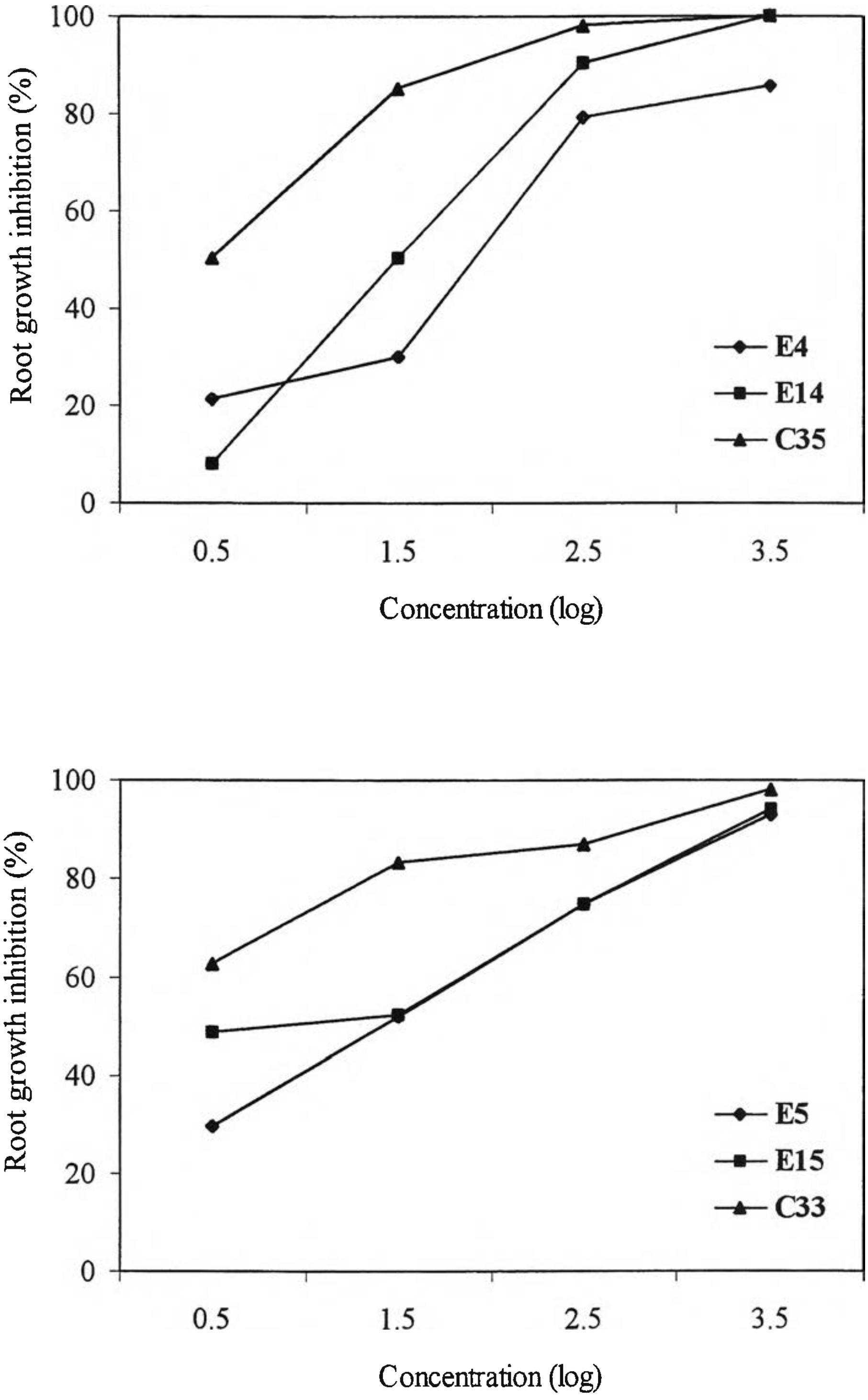
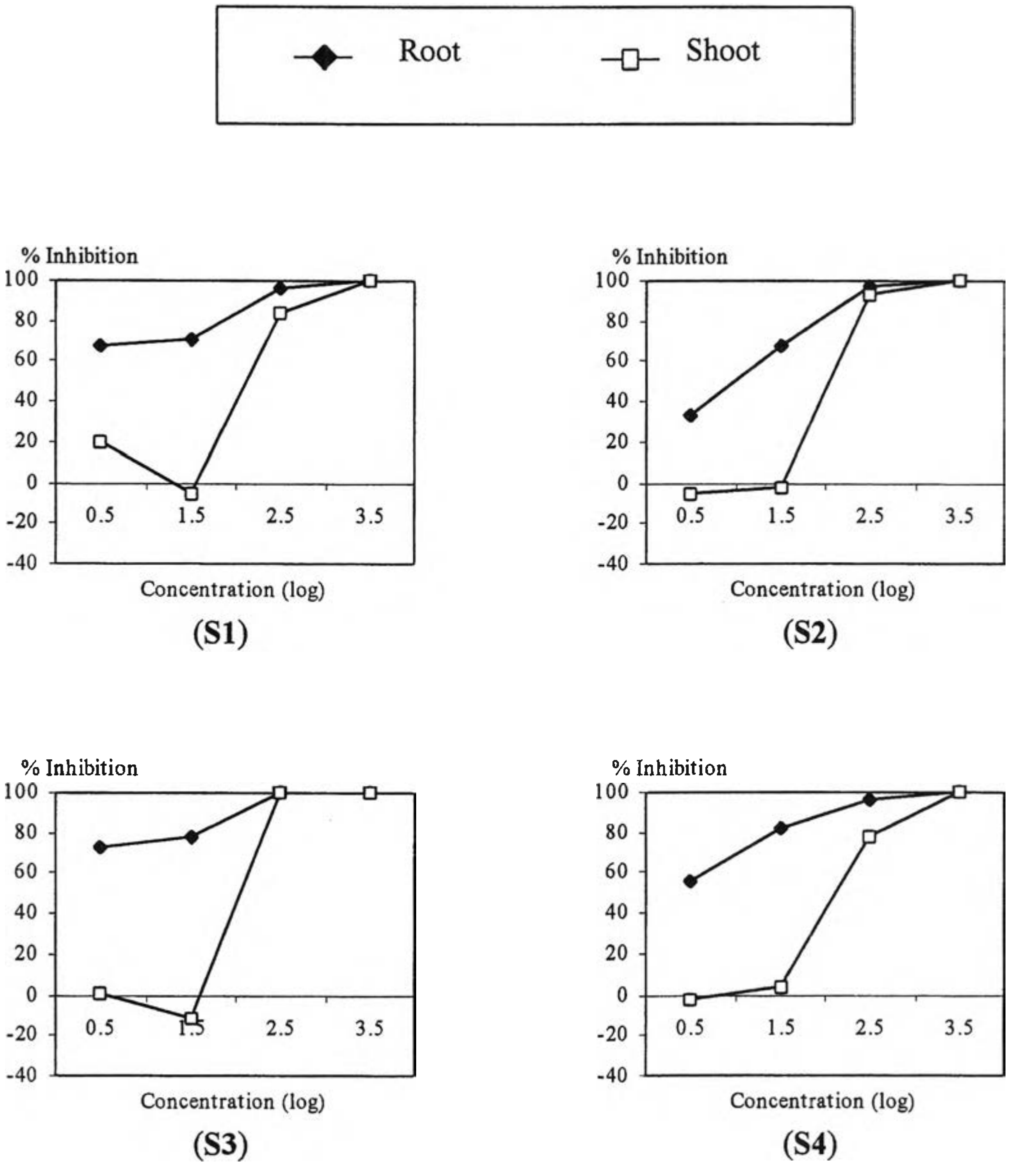


Fig 3.12 Inhibitory effect of cinnamate esters and their parent compounds on root growth of *M. pigra* (%)

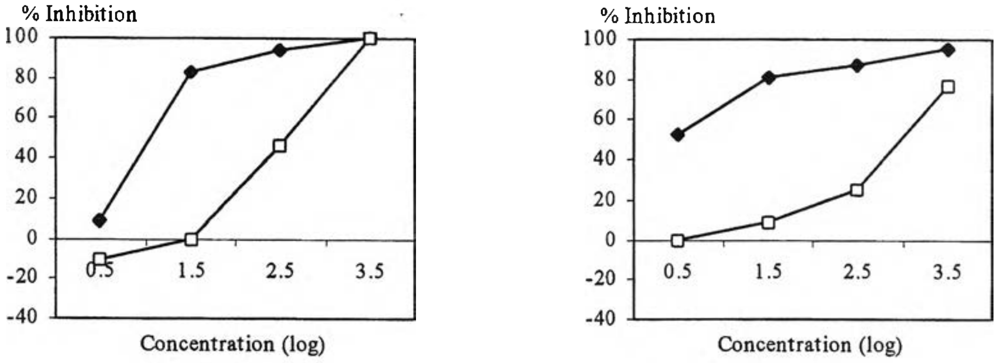
3.5.3 Sodium Cinnamate Derivatives (S1 - S6)

Sodium salts from four parent compounds: 3-fluorocinnamic acid (**C1**), 3-chlorocinnamic acid (**C4**), 3-bromocinnamic acid (**C7**) and 3-methoxycinnamic acid (**C14**) were prepared to study the effect of 3-position substituent on a benzene ring. The results are shown in Fig 3.13.



(S1) **(S2)** **(S3)** **(S4)**

Fig 3.13 Inhibitory effect of sodium cinnamate derivatives on root and shoot growth of *M. pigra* (%)



(S5) (S6)

Fig 3.13 (cont.)

From the above graphs it was found that sodium salts of various 3-position substituents on a benzene ring derivatives provided high growth inhibition activity. The comparative activity of all sodium cinnamate derivatives prepared could be illustrated as follows: **S1 ≅ S2 ≅ S4 > S5 > S6.** The summarized results are shown in Fig 3.14 and the results of percent root growth inhibition of sodium cinnamate derivatives against *M. pigra* at 300 ppm are shown in Fig 3.15.

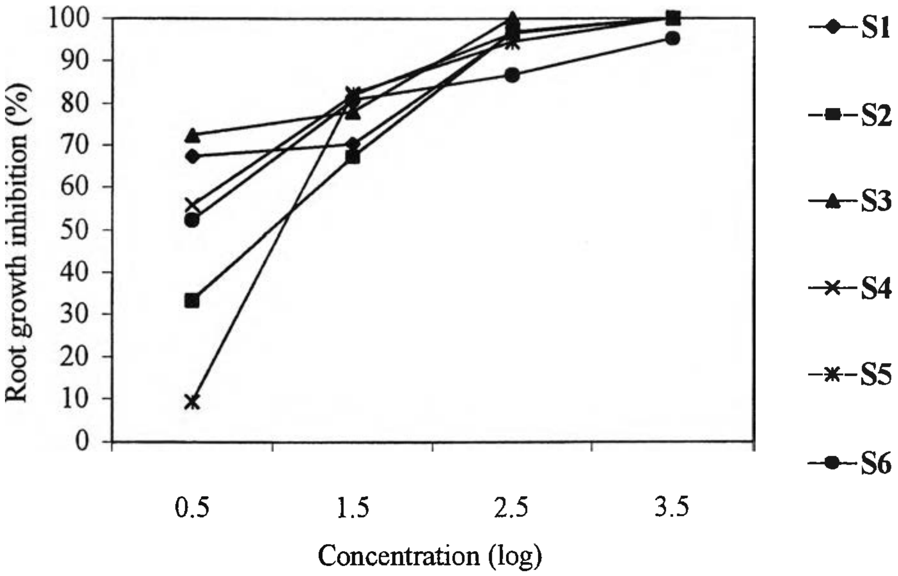


Fig 3.14 Inhibitory effect of the various 3-position substituent on a benzene ring of sodium cinnamate derivatives on root growth of *M. pigra* (%)

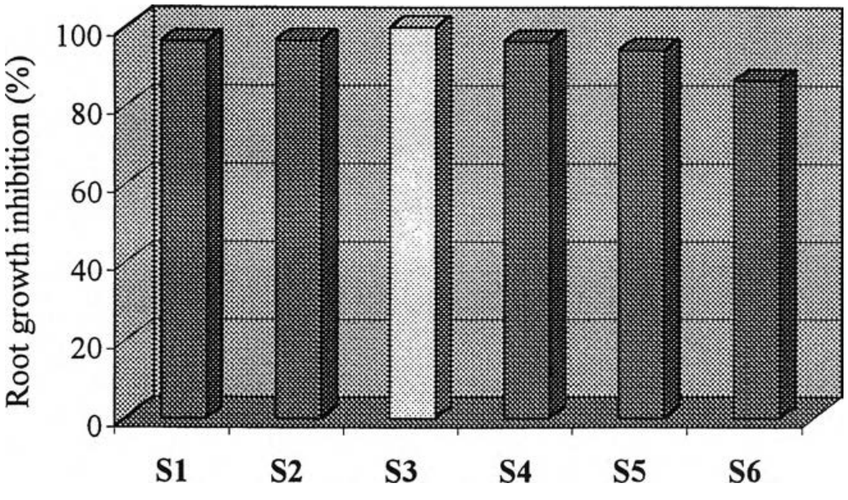


Fig 3.15 Inhibitory effect of sodium cinnamate derivatives on root growth of *M. pigra* at 300 ppm (%)

Comparing each sodium salt with its parent cinnamic acid, every case, the inhibition activity of sodium salt was superior to its parent compound. For instance, sodium 3-fluorocinnamate (**S1**) and sodium 3-methoxycinnamate (**S4**) showed the growth inhibition activity more than 3-fluorocinnamic acid (**C1**) and 3-methoxycinnamic acid (**C14**), respectively. In the case of sodium 3-chlorocinnamate (**S2**) and sodium 3-nitrocinnamate (**S5**), the growth inhibition activity was found to be slightly lower than those of their parent compounds (**C4** and **C35**). The activity of sodium 3,4-methylendioxycinnamate (**S6**) which contained 3,4-OCH_2O-bridge substituent, was found not much different from its parent compound. The summarized results are shown in Fig 3.16 and the comparison of percent root growth inhibition of sodium cinnamate derivatives and their parent compounds against *M. pigra* at 300 ppm are shown in Fig 3.17.

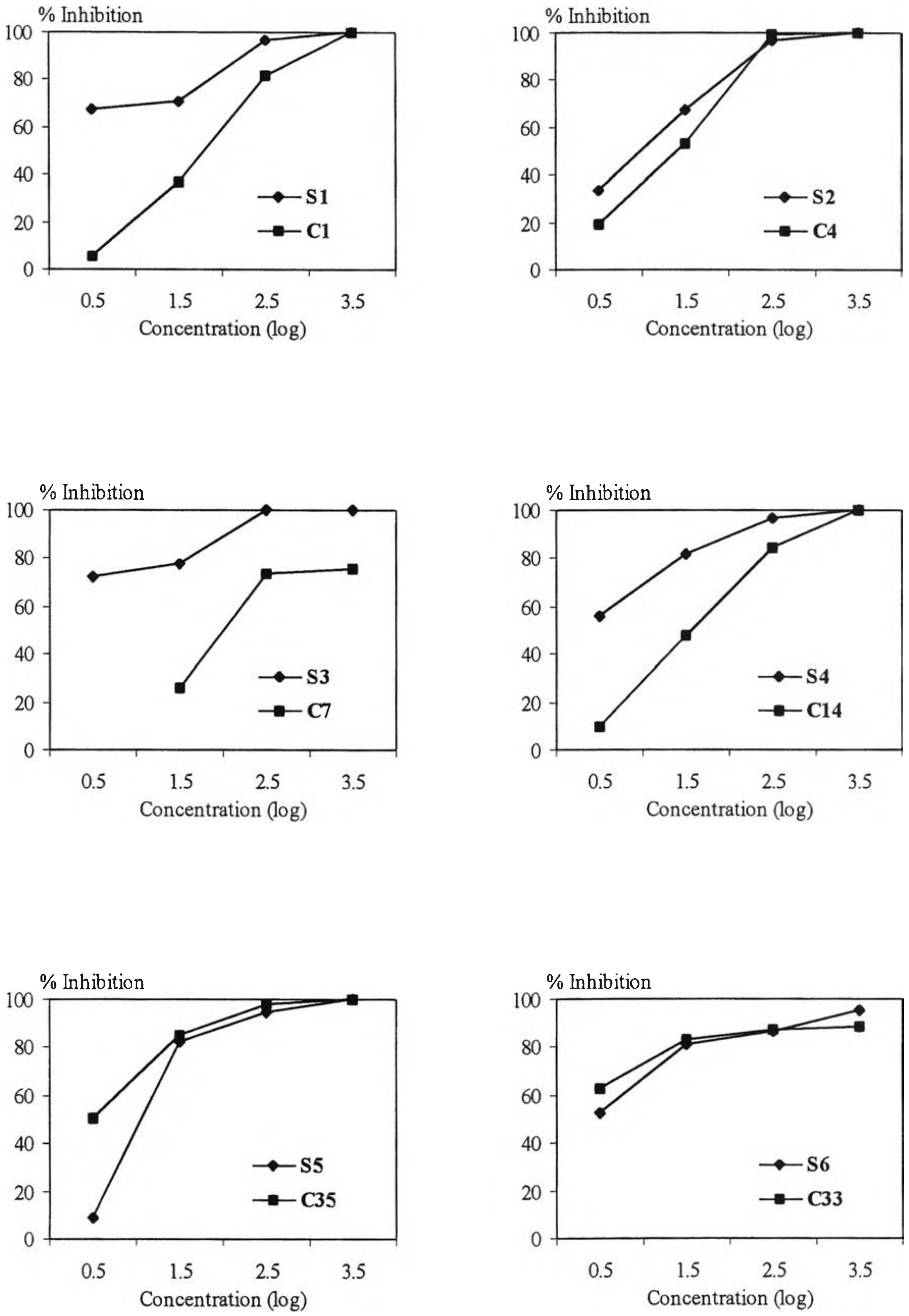


Fig 3.16 Inhibitory effect of sodium cinnamate derivatives and their parent compounds on root growth of *M. pigra* (%)

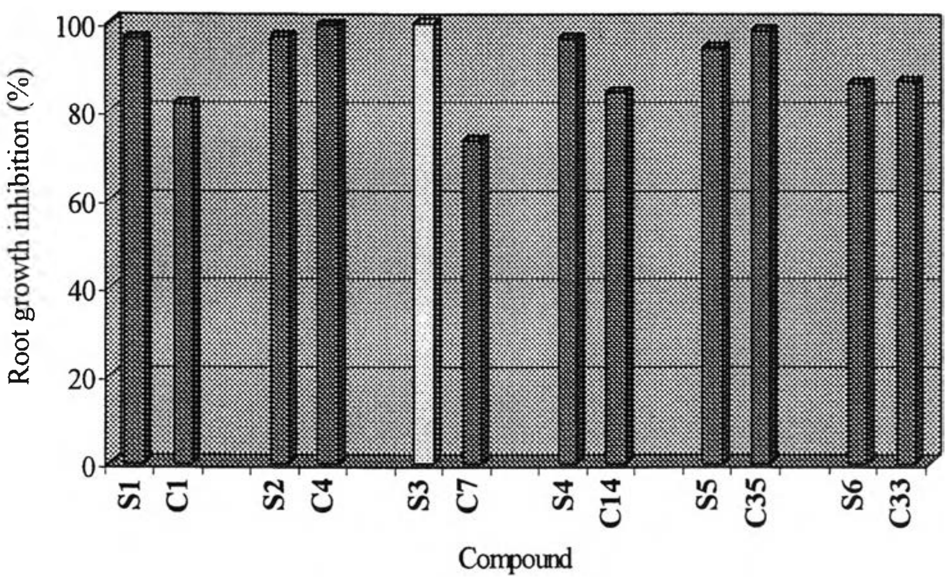
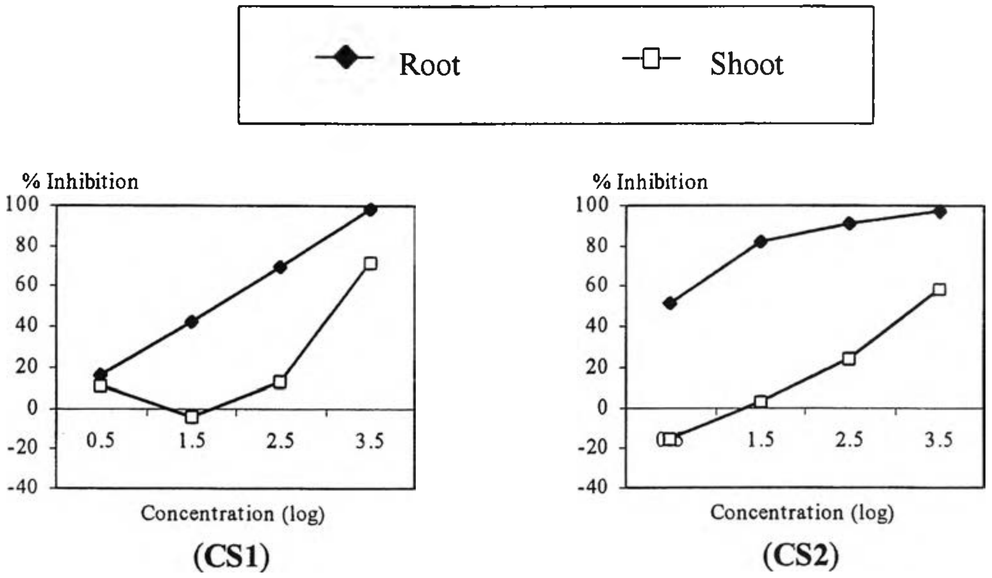


Fig 3.17 Inhibitory effect of sodium cinnamate derivatives and their parent compounds on root growth of *M. pigra* at 300 ppm (%)

3.5.4 Calcium Cinnamate Derivatives (CS1 - CS3)

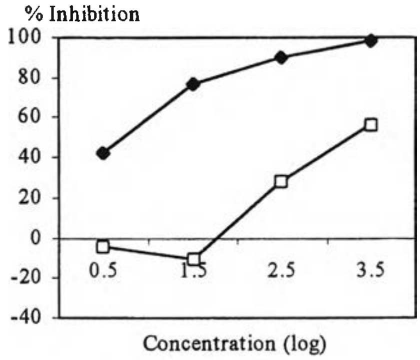
The preparation of calcium salt of 3-fluorocinnamic acid (C1) was manipulated in order to compare the effect of 3-position substitutent on a benzene ring of calcium cinnamate derivatives with sodium salts and the parent compounds. The results are presented as shown in Fig 3.18.



(CS1)

(CS2)

Fig 3.18 Inhibitory effect of calcium cinnamate derivatives on root and shoot growth of *M. pigra* (%)



(CS3)

Fig 3.18 (cont.)

From the above graphs, it was found that calcium 3-nitrocinnamate (**CS2**) and calcium 3,4-methylenedioxycinnamate (**CS3**) and calcium 3-fluorocinnamate (**CS1**) exhibited good activity. The comparative activity can be illustrated as follows: **CS2 ≅ CS3 > CS1**

Comparing the inhibitory effect of calcium cinnamate derivatives with their parent compounds, calcium 3-fluorocinnamate (**CS1**) and calcium 3-nitrocinnamate (**CS2**) showed little less growth inhibition activity than their parent compounds. In contrast to calcium 3,4-methylenedioxycinnamate (**CS3**) which contained 3,4-OCH_2O-bridge substituent, the growth inhibition activity was more than its parent compound. The summarized results are shown in Fig 3.19.

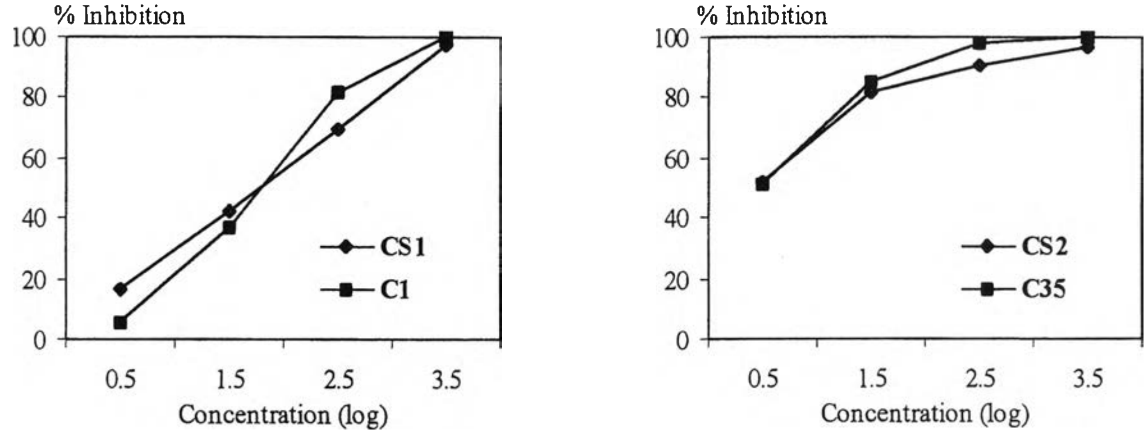


Fig 3.19 Inhibitory effect of calcium cinnamate derivatives and their parent compounds on root growth of *M. pigra* (%)

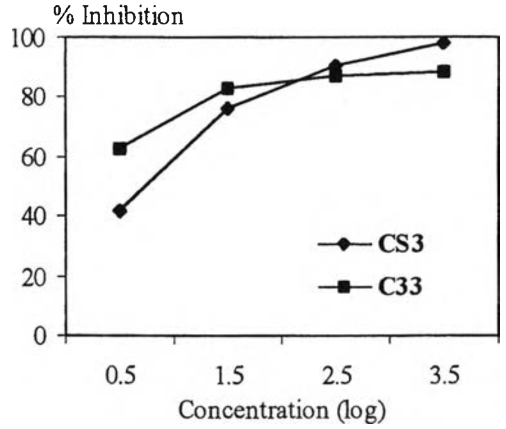


Fig 3.19 (cont.)

Comparing the growth inhibition of sodium and calcium cinnamate derivatives and their parent compounds against *M. pigra* at concentration of 300 ppm, the inhibition was rank from the highest to the lowest as follow: **S1** > **C1** > **CS1**, **C35** > **S5** > **CS2** and **CS3** > **C33** ≅ **S6**.

The activity of these series was represented in Fig 3.20.

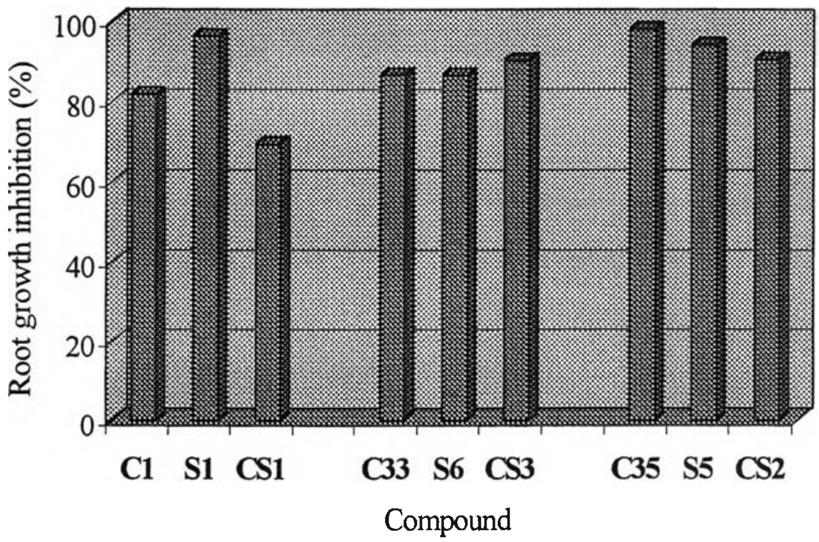
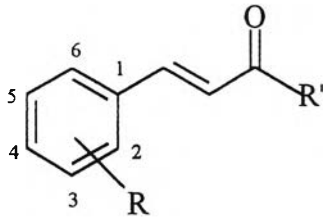


Fig 3.20 Inhibitory effect of sodium and calciun cinnamate derivatives and their parent compounds on root growth of *M. pigra* at 300 ppm (%)

Among cinnamamides, cinnamte esters, sodium and calcium cinnamte derivatives, it was disclosed that sodium and calcium derivatives exhibited the best growth inhibition activity. This was probably due to the increasing ability of its solubility.

The comparison of percent root growth inhibition of all derivatives with its parent compound against *M. pigra* could be exhibited as follows:



R = 3,4-OCH_2O-:

CS3 (R′ = OCa) > **C33** (R′ = OH) ≅ **S6** (R′ = ONa) >

D10 (R′ = *N*-2,4-dichlorophenyl) > **E15** (R′ = 2,4-dichlorophenyloxy) ≅

E5 (R′ = OCH_2CH_3) > **D12** (R′ = *N*-phenyl)

R = 3-NO_2:

C35 (R′ = OH) > **S5** (R′ = ONa) > **CS2** (R′ = OCa) ≅

E14 (R′ = 2,4-dichlorophenyloxy) > **E4** (R′ = OCH_2CH_3) >

D9 (R′ = *N*-2,4-dichlorophenyl)

The activities of these series are represented in Fig 3.21 and 3.22, respectively.

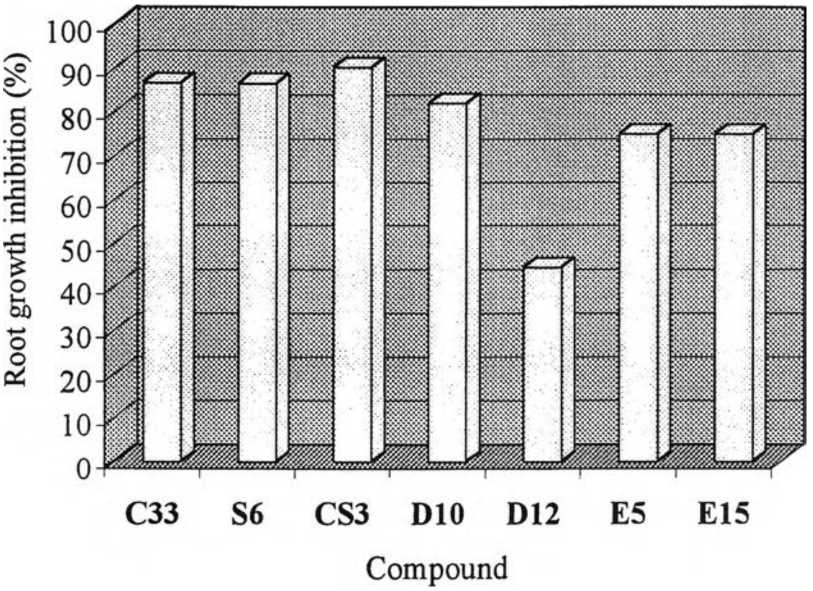


Fig 3.21 Inhibitory effect of 3,4-methylenedioxycinnamic acid and its derivative on root growth of *M. pigra* at 300 ppm (%)

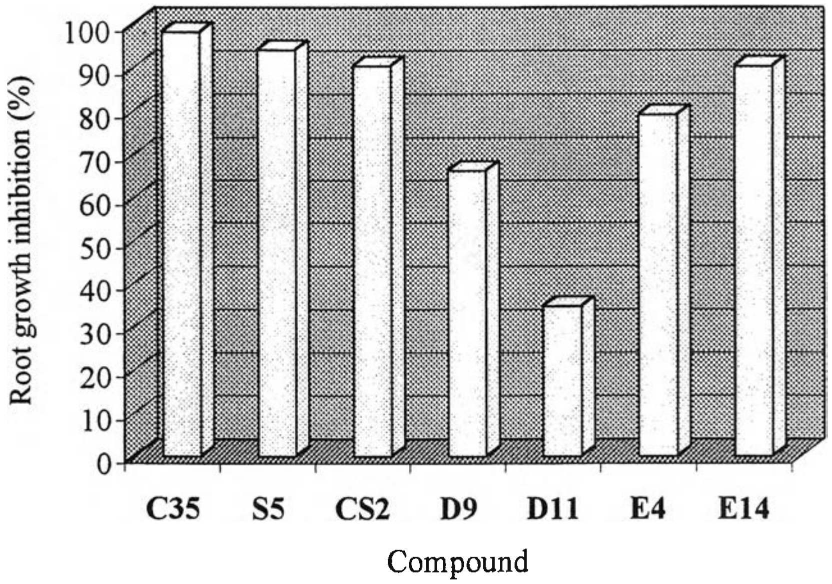
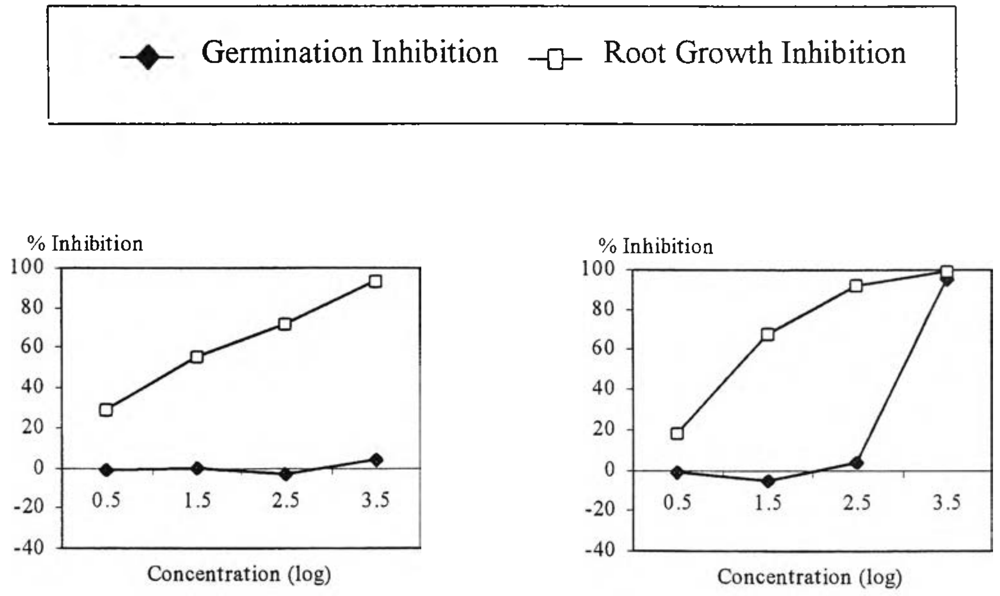


Fig 3.22 Inhibitory effect of 3-nitrocinnamic acid and its derivative on root growth of *M. pigra* at 300 ppm (%)

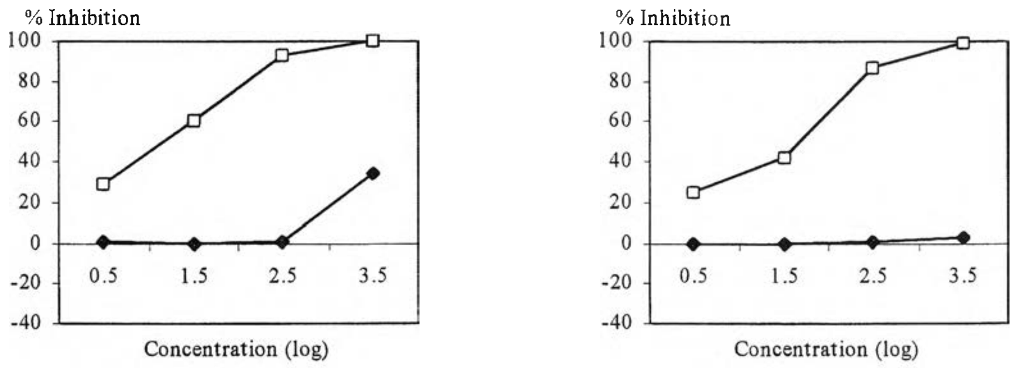
3.6 Weed Germination Inhibition

To clarify that the high herbicidal potential compounds could inhibition germination or not. Ten weeds selected for test, they were *Mimosa pigra* Linn., *Echinochloa crus-galli* Beauv., *Trianthema portulacastrum* Linn., *Celosia argentea* Linn., *Dactyloctenium aegyptium* Linn., *Euphorbia geniculata* Ort., *Tridax porcumbens* Linn., *Aeschynomene americana* Linn., *Cenchrus echinatus* Linn. and *Pennisetum pedicellatum* Trin. All of them were common weeds that can be found through out the country. From the used previous study, 3,4-methylenedioxycinnamic (**C33**) and 3-nitrocinnamic (**C35**) acids were the highest herbicidal potential since both of them exhibited high activity at both 30 and 300 ppm concentration as high as above 80%. The results of germination and root growth inhibition of 3,4-methylenedioxycinnamic (**C33**) and 3-nitrocinnamic (**C35**) acids against *T. portulacastrum*, *C. argentea*, *D. aegyptium*, *T. porcumbens*, *C. echinatus* and *P. pedicellatum* were failed because of low germination seeds. The results of germination and root growth inhibition of 3,4-methylenedioxycinnamic (**C33**) and 3-nitrocinnamic (**C35**) acids against *M. pigra*, *E. crus-galli*, *E. geniculata* and *A. americana* are presented as shown in Figs 3.23, 3.24, 3.25 and 3.26, respectively.



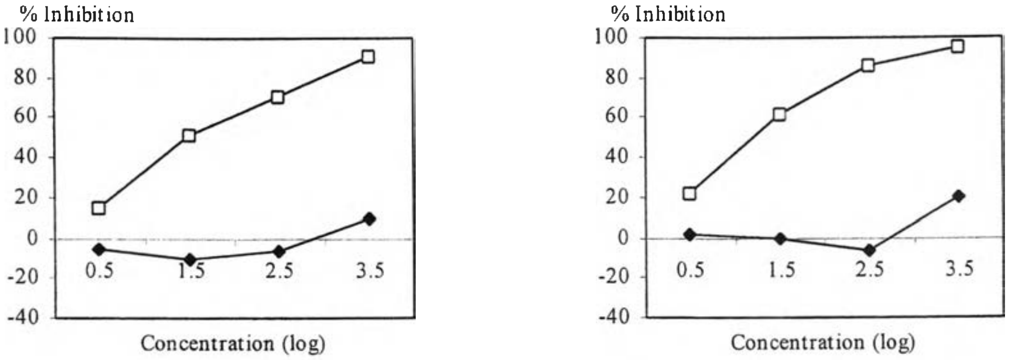
(C33) (C35)

Fig 3.23 Germination and root growth inhibition of 3,4-methylenedioxycinnamic (**C33**) and 3-nitrocinnamic (**C35**) acids against *M. pigra*



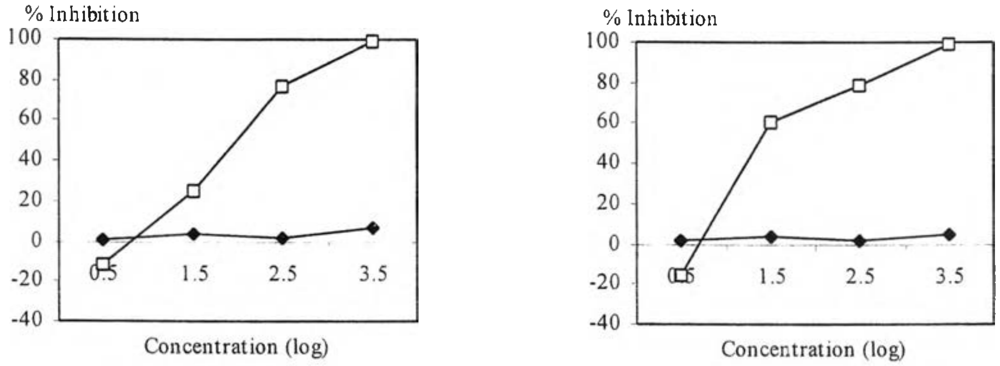
(C33) (C35)

Fig 3.24 Germination and root growth inhibition of 3,4-methylenedioxycinnamic (**C33**) and 3-nitrocinnamic (**C35**) acids against *E. crus-galli*



(C33) (C35)

Fig 3.25 Germination and root growth inhibition of 3,4-methylenedioxycinnamic (**C33**) and 3-nitrocinnamic (**C35**) acids against *E. geniculata*



(C33) (C35)

Fig 3.26 Germination and root growth inhibition of 3,4-methylenedioxycinnamic (**C33**) and 3-nitrocinnamic (**C35**) acids against *A. americana*

The germination of *M. pigra*, *E. crus-galli*, *E. geniculata* and *A. americana* was slightly decreased while the concentration of 3,4-methylenedioxycinnamic (**C33**) and 3-nitrocinnamic (**C35**) acids was increased. However, the germination of almost tested species was inhibited less than 40% even at the highest concentration, 3000 ppm. This might conclude that these compounds did not have germination inhibitory effect, but showed only root growth inhibition effect. This was confirmed by the root growth of the seedlings that germinate in this experiment, which yield the same trend as the previous study of giant mimosa. It might say that the herbicidal potential of these compounds (**C33** and **C35**) was post-emergence herbicidal potential.

3.7 Commercially Available Herbicides against *Mimosa pigra* Linn.

Three commercially available herbicides **H1-H3** were selected for comparing the degree of inhibition, **H1** and **H2** exhibited high growth inhibition activity of 85 and 80 %, respectively. When comparing the results derived from these commercially available herbicides with those obtained from the synthesized substituted *trans*-cinnamic acids, it was found that among those synthesized compounds, eight *trans*-cinnamic acids: 3-fluorocinnamic acid (**C1**), 3-chlorocinnamic acid (**C4**), 2,6-dichlorocinnamic acid (**C10**), 2-chloro-6-fluorocinnamic acid (**C12**), 3-methoxycinnamic acid (**C14**), 4-methoxycinnamic acid (**C15**), 3,4-methylenedioxycinnamic acid (**C33**) and 3-nitrocinnamic acid (**C35**) showed high activity (82-98 % inhibition) comparable to **H1** and **H2** (80-85 % inhibition). These synthesized compounds revealed promising tendency for the development as new herbicide for *Mimosa pigra*. Root growth inhibition of eight potent *trans*-cinnamic acids (**C1**, **C4**, **C10**, **C12**, **C14**, **C15**, **C33** and **C35**) and commercially herbicides (**H1** and **H2**) against *M. pigra* at 300 ppm were shown in Fig 3.27 and 3.28, respectively.

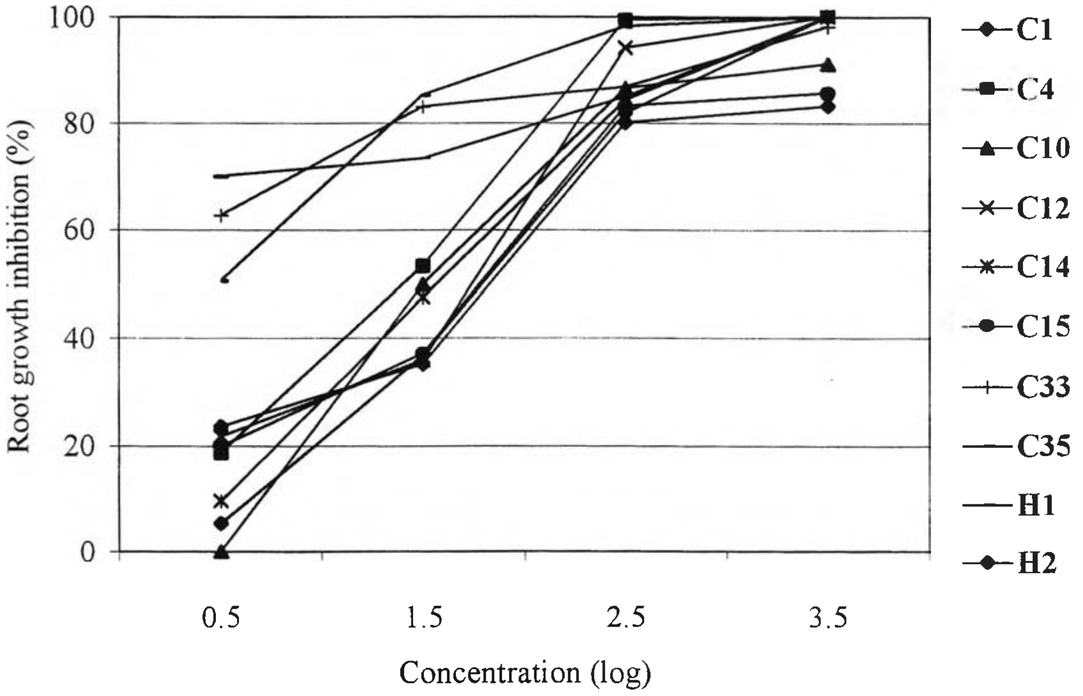


Fig 3.27 Inhibitory effect of eight potent *trans*-cinnamic acids (**C1**, **C4**, **C10**, **C12**, **C14**, **C15**, **C33** and **C35**) and commercially herbicides (**H1** and **H2**) on root growth of *M. pigra* (%)

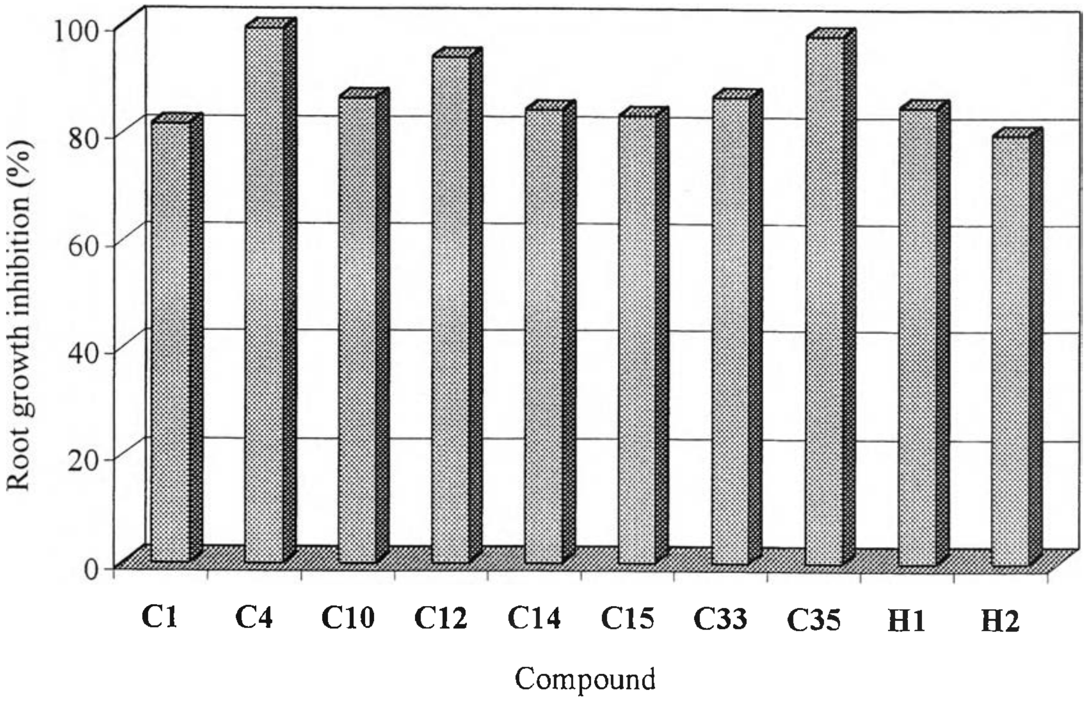


Fig 3.28 Inhibitory effect of eight potent *trans*-cinnamic acids and commercially herbicides (**H1** and **H2**) on root growth of *M. pigra* at 300 ppm (%)