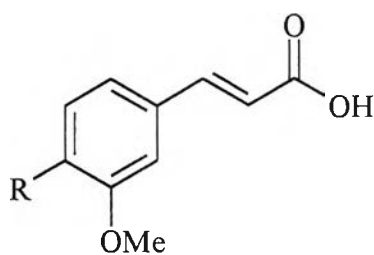


CHAPTER IV

CONCLUSION

During the course of this research, the synthesis of substituted *trans*-cinnamic acids was carried out with the aim to comprehend the structure-activity relationship (SAR) of these analogue compounds and its weed growth and germination inhibition *Mimosa pigra* Linn. as the main bioassay species. Synthesis of the desired compounds was accomplished by employing the condensation between malonic acid and selected aromatic aldehydes in anhydrous pyridine and in the presence of piperidine. Forty-seven substituted *trans*-cinnamic acids were synthesized in medium to very high yield. Six sodium cinnamate derivatives were obtained in high yield by employing the preparation between selected *trans*-cinnamic acids and sodium hydroxide in toluene. Three calcium cinnamate derivatives were also achieved in medium to high yield. Twelve cinnamamides were attained in medium to high yield by using nucleophilic substitution of acid chlorides and amines in tetrahydrofuran. Fifteen cinnamate esters were acquired in medium to high yield by using esterification of selected *trans*-cinnamic acids and alcohol in benzene and in the presence of conc sulfuric acid. All synthesized compounds were well-confirmed their identifies by their physical properties and spectroscopic techniques such as IR, ¹H-NMR and ¹³C-NMR and in some cases MS were also performed. There are two compounds, namely 4-octyloxy-3-methoxycinnamic acid (**C24**) and 4-dodecyloxy-3-methoxycinnamic acid (**C25**) that have not been reported in chemical literatures. The structure of new compounds are shown below:



Cpds	R
C24	OC ₈ H ₁₇
C25	OC ₁₂ H ₂₅

The evaluation of herbicide activity of *trans*-cinnamic acids and related compounds against *M. pigra* L. and *E. crus-galli* B. have also never been reported in chemical literature. Therefore, all synthesized *trans*-cinnamic acids were subjected to examine for weed growth inhibition. Considering in the weed growth of 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-methylenedioxcinnamic acid (C33) and 3-nitrocinnamic acid (C35) showed very high activity in the range of 80-100 % at 300 ppm concentration. *trans*-Cinnamic acids bearing NO₂ and OCH₃ substituents on a benzene ring at *meta*- position showed the highest activity. *trans*-Cinnamic acids with fluoro and chloro groups on a benzene ring at *meta*- position illustrated higher activity than that at *para*- position. *trans*-Cinnamic acids with bromo group on a benzene ring at *meta*- position showed higher activity than that at *ortho*- position. In the case of compounds bearing chloro and nitro groups on a benzene ring, the activity was lower than that of only chloro or nitro group on a benzene ring. When a number of methoxy substituents on a benzene ring increased, the activity was decreased. The optimization of the numbers of carbon atoms in an alkoxy chain at *para*- position on a benzene ring was deduced that one carbon atom exhibited the highest activity when a benzene ring bearing either a methoxy group at *meta*- position or none. In addition increasing the branch chain of carbon atom at *para*- position on a benzene ring provided the diminishing of growing inhibition activity.

Weed growth inhibition against *E. crus-galli* of 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) exhibited very high activity inhibition range of 80-100. *trans*-Cinnamic acids bearing bromo substituent on a benzene ring at *meta*- position illustrated the highest activity, *para*- position observed the middle and *ortho*- position provided the lowest activity. *trans*-Cinnamic acid with a chloro group on a benzene ring at *para*- position showed higher activity than that of *ortho*- position. When a number of chlorine substituted on a benzene ring increased, the activity was increased. The addition of a Cl atom at *para*- position of a benzene ring bearing 3-NO₂ substituted group provided less activity than that containing only 3-NO₂ substituted group on a benzene ring. Moreover, the addition of

three methoxy groups on a benzene ring displayed lower activity than that with only one methoxy group. Furthermore, considering the variation of the numbers of carbon atoms of alkoxy group on a benzene ring at *para*- position exhibited the highest activity when the number of carbon atoms in chain hold only one carbon atom.

Derivatives of selected *trans*-cinnamic acids against *M. pigra*, calcium 3,4-methylenedioxy-cinnamate (**CS3**) exhibited the highest activity compared with its parent compound; 3,4-methylenedioxy-cinnamic acid. 3,4-Methylenedioxy-cinnamic acid showed almost the same activity as that of sodium 3,4-methylenedioxy-cinnamate (**S6**) and more than those of *N*-(2,4-dichlorophenyl)-3,4-methylenedioxy-cinnamide (**D10**) and (2,4-dichlorophenyl) 3,4-methylenedioxy cinnamate (**E15**), which showed almost the same activity as ethyl 3,4-methylenedioxy-cinnamate (**E5**), respectively. When 3-nitrocinnamic acid was a parent compound, it illustrated the highest activity and higher than sodium 3-nitrocinnamate (**S5**) and calcium 3-nitrocinnamate (**CS2**), respectively. Calcium 3-nitrocinnamate (**CS2**) showed almost the same activity as 2,4-dichlorophenyl 3-nitrocinnamate (**E14**) and more than ethyl 3-nitrocinnamate (**E4**) and *N*-(2,4-dichlorophenyl)-3-nitrocinnamide (**D9**), respectively.

Taking into an account in the case of germination of 3,4-methylenedioxy-cinnamic and 3-nitrocinnamic acids against various weeds, the concentration used was not related with percent germination inhibition but related with percent root growing inhibition. These results could surely be utilized for further development as the application for post-emergence herbicide for *M. pigra*, *E. crus-galli*, *E. geniculata* and *A. americana*.

Focussing in the case of weed growth inhibition against *M. pigra*, almost substituted *trans*-cinnamic acids did not show any noticeably eminent activity, except for 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-methylenedioxy-cinnamic acid (**C33**) and 3-nitrocinnamic acid (**C35**). These compounds exhibited the activity comparable with selected commercial herbicide.

Finally, it was clearly disclosed that substituted *trans*-cinnamic acids possess herbicidal activity. These informative results could surely be utilized for further development as the applications for agrochemicals in the future.

Proposal for the Future Work

From this study, the results of weed growth inhibition against giant mimosa of *trans*-cinnamic acid disclosed the relationship of these studied activities and *trans*-cinnamic acid structures. The possibly further work related to this research would be the study of *trans*-cinnamic acid structure and other weeds that caused problems in Thai agriculture (e.g., *Leptochloa chinensis* (L.) Nees., *Ageratum conyzoides* L., *Cyperus imbricatus* Retz., *Fimbristylis miliacea* (L.) Vahl.). In addition, other function groups substituted on these structures should be attractive to be searched for more active compounds and to attain the relationship between structures and activities. Besides, the molecular modeling studies of these compounds should be performed in order to find out the real active-site in the compound. Moreover, the investigation of herbicidal activity was well-known as a preliminary indicator which could be used for further study on other bioassays such as antifungal and antimutagenic etc. The SAR study of other natural herbicide molecules such as benzofuran, chromene or etc. might be the next generation-researchers.