CHAPTER I
INTRODUCTION

Since Thailand is an agricultural country, there are many kinds of serious problems to cultivate crops, for examples, irrigation, weather, quality of soil or especially weed-derived problems. Weed is an undesirable plant which grows in the same planting area of crop. Weed can make huge damage to agriculture, such as diminishing quality and quantity of crops, blocking dam and irrigation system, causing forest fire, making main plant die, including water pollution and in some cases, irritation to human or animals. Therefore, weed problem is the most tedious and inevitable problem leading to the need for eradication. Nowadays, the farmer favorably uses herbicides to get rid of weeds. In the midst of pesticides, herbicides are extremely imported from foreign countries and the tendency of importation is annually increased. From this reason, Thailand must spend over two thousand-billion bahts per year to import herbicides. Therefore, the search for new agrochemical is fundamentally crucial project for agricultural country as Thailand. Even though the use of synthetic agrochemical was found to be more potent and effective than those derived from plant-original, many problems caused by synthetic chemicals such as safety to living organisms, cattle, human being and environmental concerns and so on are their drawbacks. The concept of trying to employ chemicals from plant sources or synthetic chemicals whose structures derived from natural products is still called for seriously extensive study. As mentioned above, the knowledge about allelopathy and allelopathic agents (or allelochemicals) is necessary.

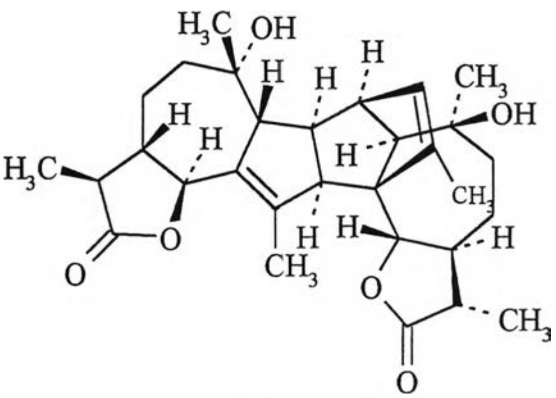
The term allelopathy was coined by Molish in 1937.[1] Presently, "allelopathy" generally refers to the detrimental effects of higher plants of one species (the donor) on the germination or development or growth of plants of another plants (the recipient). Allelopathy can be separated from other mechanisms of plant interference because the detrimental effect is exerted through release of chemical inhibitors (allelochemicals) by the donor species. In 1974, Rice[2] defines "allelopathy" as "any direct or indirect harmful effects of one plant (including microorganisms) on another through the production of chemicals that escape into the environment". The term "allelopathy" should be extended to include the manifold mutual effects of metabolic of both plants and animals.

The study of allelopathy has a long history. According to Rice[3], Lee and Monis[4] found a report by Banzan Kumazawa in a Japanese document some 300 years old that rain or dew washing of the leaves of red pine (*Pinus densiflora*) was harmful to crops growing under the pine. This was substantiated by these workers in a series of experiments. Historically, this is considered to be the first report on allelopathy. Besides, Bonner[5] found that the residue of guayule (*Parthenium argentatum*) produced *trans*-cinnamic acid, which is toxic to young guayule plants. He also found that cinnamic acid was slowly decomposed in soil, so that the effect disappeared with time.[6]

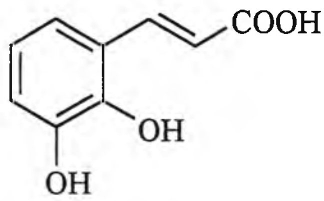
The following few examples illustrate the importance of allelopathy that affect the growth and development of agricultural crops.

The work demonstrated by Bode on the exudation of absinthin (**I**) from *Artemisia absinthium*[7] showed that the growth of neighboring plants such as *Foeniculum vulgare* and others were influenced by these toxins and so, for the first time, produced exact evidence that such metabolic products can in nature influence the development of nearby plants.

Several aromatic compounds, such as caffeic acid (**II**), chlorogenic acid (**III**), *trans*-cinnamic acid (**IV**), *p*-coumaric acid (**V**), ferulic acid (**VI**), gallic acid (**VII**), vanillic acid (**VIII**), vanillin (**IX**) and *p*-hydroxybenzaldehyde (**X**) have been found in crop residues and many of them have been isolated from field soil.[3,7] Guenzi and McCalla[8] also isolated those compounds from residues of corn (*Zea mays* L.), wheat (*Triticum aestivum* L.), oats (*Avena sativa* L.) and sorghum (*Sorghum bicolor* L.). The same chemicals were found to inhibit the growth of sorghum, soybeans (*Glycine max*), sunflower (*Helianthus annuus* L.) and tobacco (*Nicotiana tabacum* L.).[9]



I



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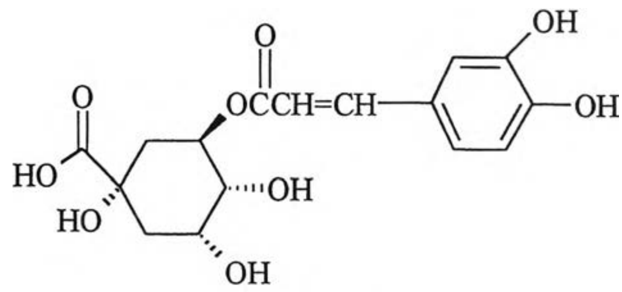

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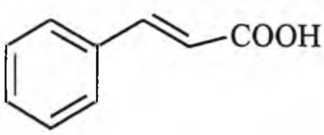

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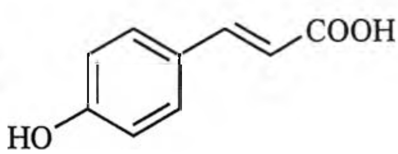

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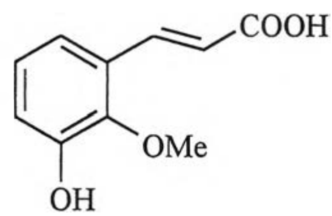

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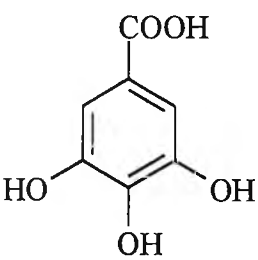

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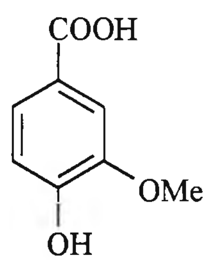

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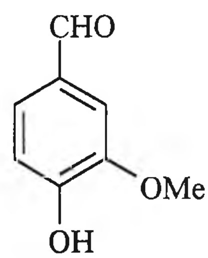

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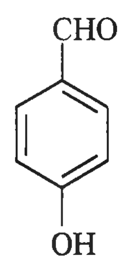


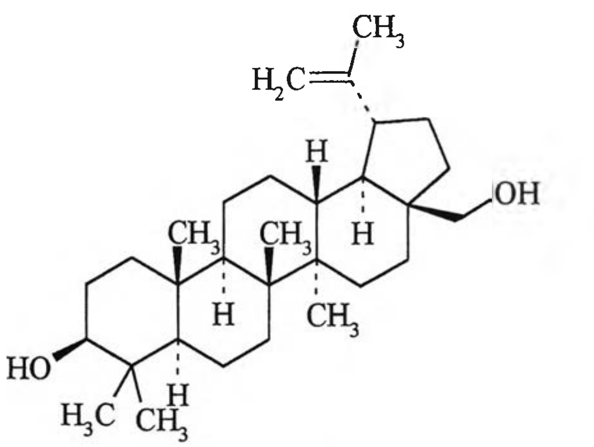
X

According to Robinson[10], Whittaker and Feany[11], and Rice[3], a great majority of secondary plant products have been implicated as allelopathic agents. Main groups of compounds could be described as:

1. Aliphatic compounds
2. Unsaturated lactones
3. Fatty acids and lipids
4. Cyanogenic glycosides
5. Terpenoids
6. Aromatic compounds

Chemicals with allelopathic potential are present in virtually all plant tissue, including leaves, stems, roots, rhizomes, flowers, fruits and seeds. Whether these compounds are released from plant to the environment in quantities sufficient to elicit a response, remains the critical question in field studies of allelopathy. Allelochemics may be released from plant tissues in a variety of ways, including volatilization, root exudation, leaching and decomposition of the plant residues.

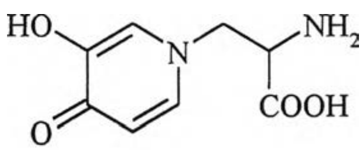
Nowadays, there are many reports to affirm that some weeds constituted substances, which affected the growth of side-growing plant or their creatures. For instance, *Sphenoclea zeylanica* Gaerth., weed growing in rice field, contained betulinic acid **(XI)** which can inhibit the growth of rice and has piscicidal activity. *Imperata cylindrica* can emit substance that controls the growth of *Stylosanthes*.[12]



XI

Many natural plant growth regulators, such as agrostemin, can be used to control weeds.[13] Agrostemin is obtained from the corn cockle, *Agrostemma githago* L., a common weed in fields of wheat and other cereals. The compound has been widely used in eastern European countries and is harmful neither to animal nor humans. In addition, natural products from neem plants (*Azadiraehta indica* A.) have also been used extensively in India as herbicides, fungicides, and nematoticides.[14]

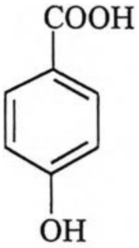
In Leguminous plantations *Leucaena leucocephala*, there is an absence of understory growth other than itself. This is due primarily to the phytotoxins, including eight phenolic acids, flavonoids, and mimosine **(XII)**, released from its leaves and litter. Those compounds can suppress the growth of many weeds and forest species, such as *Acacia confusa*, *Ageratum conzoides*, *Liquidambar formosana*, *Casuarina glauca*, *Mimosa pudica*, and *Alnus formosana*.[15] It is notable that *M. pudica* was suppressed by *Leucaena* leaf leachate even though the leaves of *M. pudica* contain relatively high levels of mimosine. Of eighty-four *M. pudica* seedlings tested, only two seedlings survived, showing that mimosine and other compounds, such as phenolics, can be of practical use in the control of field weeds.



XII

1.1 Literature Review

There are many reports to affirm that some plants constituted substances, which affected the growth of side-growing plant or their creatures. For example, in 1987 C.H. Chou[16] reported that rice (*Oryza sativa*), the most important crop in Taiwan, is planted twice a year by a continuous monoculture system. The yield of the second crop has been generally lower by 25% than that of the first crop (a reduction of about 1000 kg/ha). The phytotoxins present in the rice straw-soil mixture with different intervals of decomposition were identified by chromatography. The compounds isolated were identified as *p*-coumaric acid (**V**), *p*-hydroxybenzoic acid (**XIII**), syringic acid (**XIV**), vanillic acid (**VIII**), *o*-hydroxyphenylacetic acid (**XV**), ferulic acid (**VI**), propionic acid, acetic acid and butyric acid. These compounds affected to toxic that the roots of retarded plants were dark brown and the root cells were abnormal and enlarged. Further experimental results showed that the amount of rice straw mixed was increased, the phytotoxicity increased with the increase of straw added. In 1993 H.H. Li, M. Inoue, J. Nishimura and E. Tsuzuki[17] reported that phenolic compounds have been identified as the most common allelochemicals produced by higher plants and found that *trans*- cinnamic acid (**IV**) and abscisic acid (ABA, **XVI**) inhibited on seed growth and seed germination of lettuce. Moreover, in nature *trans*-cinnamic acid (**IV**), *o*-, *m*-, *p*-coumaric acids (**XVII**, **XVIII**, **V**), coumarin (**XIX**) and chlorogenic acid (**III**) and ferulic acid (**VI**) can either promote or inhibit plant growth depending on their concentrations. Moreover, in 1995 C.H. Chou[13] reported that the extracts of many dominant plants, such as *Delonix regia*, *Digitaria decumbens*, *Leucaena leucocephala*, and *Vitex negundo* contained allelopathic compounds, including phenoilc acids, alkaloids, and flavonoids. These can be used as natural herbicides, fungicides, etc. which were less disruptive of the global ecosystem than synthetic agrochemicals.



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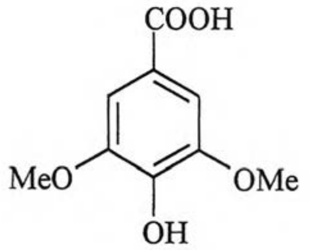

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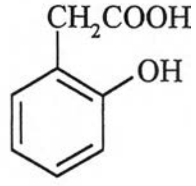

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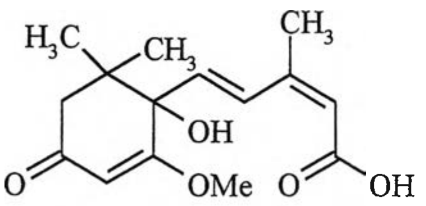

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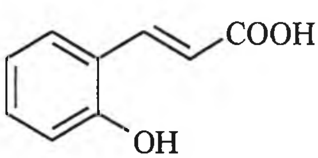

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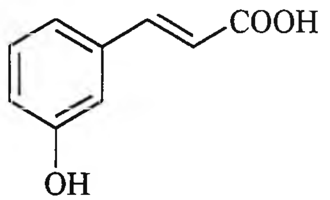
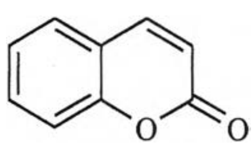


XVIII

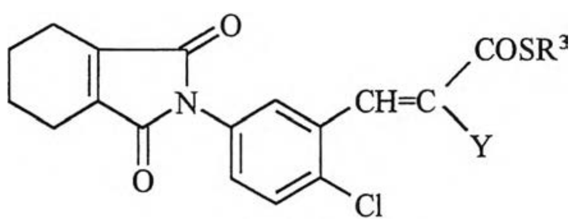


XIX

As mentioned above, *trans*-cinnamic acid, its derivatives and related compounds were interesting to study as the herbicides especially weeds, which made some problems for the farmers in Thailand.

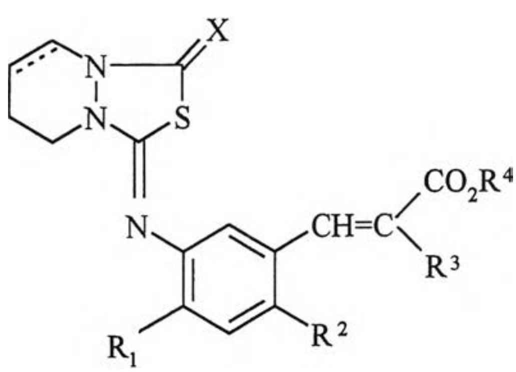
Many reports about cinnamic acid and its derivative as herbicide have been reported. For example, 5-(*N*-3,4,5,6-tetrahydrophthalimido)cinnamic acid derivatives of the formula **XX** and **XXI**[18] where the substituents were defined as follows: Y was chlorine, bromine or C_1-C_4-alkyl, R^1 was hydrogen, C_1-C_8-alkyl, substituted or unsubstituted C_2-C_4-alkyl, C_3-C_6-alkenyl, C_3-C_6-alkynyl, or substituted or unsubstituted phenyl or benzyl, R^2 was C_5-C_8-alkyl, substituted or unsubstituted C_2-

C_4-alkyl, C_3-C_6-alkoxy, C_3-C_6-alkenyl, C_3-C_6-alkenyloxy, C_3-C_6-alkynyl, C_3-C_6-alkynyloxy, or substituted or unsubstituted phenyl, phenoxy, benzyl or benzyloxy, R^3 was C_1-C_6-alkyl or substituted or unsubstituted C_2-C_6-alkyl. 5-(*N*-3,4,5,6-tetrahydrophthalimido)cinnamic acid derivatives of the formula **XX** and **XXI** defined previously, which have an advantageous herbicidal effect particularly in post-emergence and which were selective with respects to a number of crop plants.



XXI

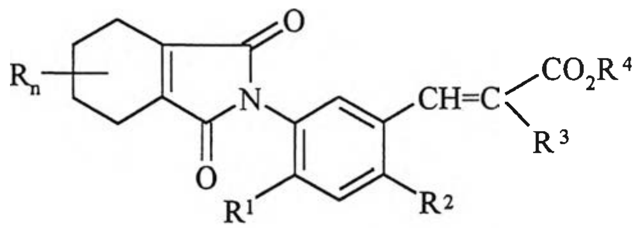
In addition, a report of cinnamic ester of formula **XXII**[19] where the dotted bond was a single or double bond, R^1 was hydrogen or fluorine, R^2 was halogen, R^3 was hydrogen, halogen or C_1-C_4-alkyl, R^4 was hydrogen, substituted or unsubstituted C_1-C_6-alkyl, or was C_3-C_6-alkenyl, C_3-C_6-alkynyl or benzyl, and X was oxygen or sulfur was recently reviewed.



XXII

Moreover, 3-(*N*-3,4,5,6-tetrahydrophthalimido)cinnamic ester of the general formula **XXIII**[20] was posted where R^1 was hydrogen or fluorine, R^2 was halogen, R^3 was hydrogen, halogen or C_1-C_4-alkyl, R^4 was hydrogen, C_1-C_4-alkyl which can be substituted by one or two C_1-C_4-alkoxy or C_1-C_4-alkylthio groups, or C_3-C_7-

cycloalkyl, C_3-C_6-alkenyl, C_3-C_6-alkynyl or benzyl, R was C_1-C_4-alkyl and n was 1 or 2.



XXIII

It was also reported that it was useful to apply novel compounds **XX**, **XXI**, **XXII** and **XXIII**, either alone or in combination with other herbicides, in admixture with other crop protection agents e.g., agents for combating pests or phytopathogenic fungi or bacteria. The compounds may also be mixed with solutions of mineral salts used to remedy nutritional or trace element deficiencies.

The above data showed that herbicidal activity of *trans*-cinnamic acid derivatives was promising. However, the studies on the relationship of *trans*-cinnamic acid derivatives and antigrowth activity of *Mimosa pigra* Linn. and *Echinochloa crus-galli* (L.) Beauv. have never been reported in chemical literature. Thereby, it is worth considering for increasing potential knowledge, understanding and utilizing of these compounds in agricultural purposes.

1.2 Synthesis of *trans*-Cinnamic Acid

Many methods were reported to apply for the synthesis of *trans*-cinnamic acid. Utilizing benzaldehyde as a substrate, the synthesis of *trans*-cinnamic acid could be accomplished by various well-known reactions; for instance, [21]:

Perkin reaction: condensation between benzaldehyde and acid anhydride in the presence of sodium salt functioning as a catalyst

Knoevenagel reaction: condensation between benzaldehyde and malonic acid, and ammonia, piperidine or diethylamine with alcohol as solvent

Doebner rection: condensation between benzaldehyde and malonic acid with pyridine as solvent and trace of piperidine as catalyst

Claisen reaction: condensation between benzaldehyde and ethyl acetate with metallic sodium and trace of alcohol

Reformatsky reaction: condensation between benzaldehyde and ethyl bromoacetate with metallic zinc and benzene as solvent

1.3 Knowledge about Studied Weeds

In this research *Mimosa pigra* Linn. and *Echinochloa crus-galli* (L.) Beauv. were selected for bioassay.

1.3.1 *Mimosa pigra* Linn.

Mimosa pigra Linn., a perennial woody shrub of family Mimosaceae, known as Giant Sensitive Plant, or in Thai as Maiyarap Yak. It is a noxious broad leaves weed through out the country. It infests both agricultural or non agricultural area, causes serious problem for irrigation and transportation.[22] The plant has strong stem with spine, 2-4 meters height. It is less sensitive than that of *Mimosa pudica*. Flower is inflorescence with pink head. Pods is hairy and slightly curved 5-10 centimeters long. Seed is green to brown with thick waxy coat, so the seed is seed-coat dormancy. The seed dormancy can be broke with hot-water.

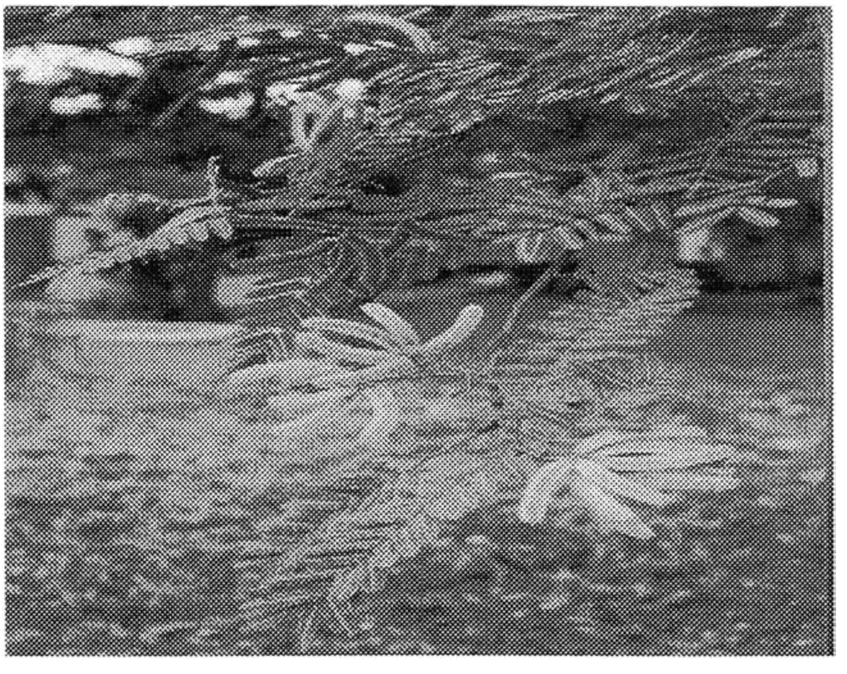


Fig 1.1 *Mimosa pigra* Linn. (Giant mimosa)

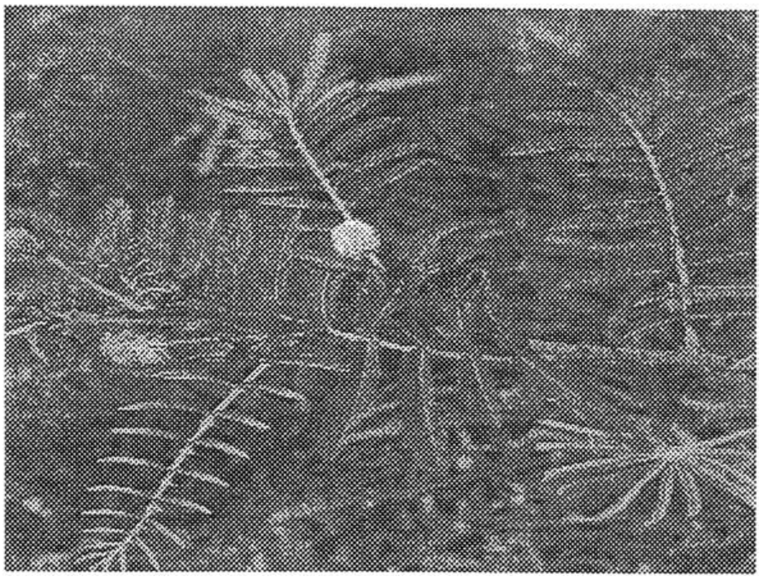


Fig 1.1 (cont.)

CLASSIFICATION[23]

Kingdom	Plantae (Metaphyta)
Division	Tracheophyta
Subdivision	Gymnospermae
Class	Angiospermae
Subclass	Dicotyledoneae
Family	Leguminosae
Genus	*Mimosa*
Species	*Mimosa pigra* Linn.

1.3.2 *Echinochloa crus-galli* (L.) Beauv.

Echinochloa crus-galli (L.) Beauv., is an annual noxious narrow leaves weed of Family Poaceae, which common name as barnyard grass, water grass, or baronet grass.[24] This weed known as Yha Khownok in Thai. Barnyard grass is a damaging weed in the paddy-field and other crops.[25] Leaves are linear and acuminate with 10-30 centimeters long. Flowers are inflorescence, panicle 10-20 centimeters long, compose of 9-12 branches (spikes). It is a vigorous, worm season annual grass reaching 1 to 5 feet in high with bases of many stems reddish to dark purple.[26] This weed is not noxious weed in Thailand but also of the world. Holm[25] reported it as a top-ten world worst weed, distribute both in tropical and temperate zone of the world, both in paddy and upland field. This weed cause harmful effect to crop especially to rice.[27]

Fig 1.2 *Echinoloa crus-galli* (L.) Beauv. (Barnyard grass)

CLASSIFICATION[23]

Kingdom	Plantae(Metaphyta)
Division	Tracheophyta
Subdivision	Gymnospermae
Class	Angiospermae
Subclass	Monocotyledoneae
Family	Poaceae (Gramineae)
Genus	*Echinochloa*
Species	*Echinochloa crus-galli* (L.) Beauv.

Method of Controlling *Mimosa pigra* L. and *Echinochloa crus-galli* (L.) Beauv.

The methods for giant mimosa and barnyard grass growing control could be classified into many types for example[28, 29]:

1. Chemical controlling method: chemical control includes all control techniques involving the use of chemical agents (herbicides) to kill *M. pigra* and *E. crus-galli.*

2. Biological controlling method: biological control is defined as "the action of parasites, predators and pathogens in maintaining another organism's density at a lower level than would occur in their absence" and "the action of fungus and insects."

1.4 Goal of Research

This research is designed to utilize *trans*-cinnamic acid derivatives in reverting behaviors of plants. The approach is based upon the assumption that structure-activity relationship (SAR) study is not merely a knowledge of how much activities of them has, but also match structures and activities of studied compounds. In addition, the SAR study will permit a logical opportunity to predict relationship of other molecules (analogues of *trans*-cinnamic acid) and these activities. Therefore, the goal of this research can be summarized as follows:

1. To synthesize *trans*-cinnamic acid and related compounds
2. To study the relationship between *trans*-cinnamic acid and related compounds and weed growth inhibition against *Mimosa pigra* Linn and *Echinochloa crus-galli* (L.) Beauv.