CHAPTER I

INTRODUCTION
The moment Adam and Eve appeared on this planet, they were plagued with diseases, decay and death and compelled them to search for those substances which could potentially be exploited to save the threatening of their existence. In his attempt to do so, he looked for the vast resources of plant kingdom which the omnipotent has been kind enough to bestow on human being.

With the enormous development in the field of medical sciences, still no system of medicine in the world can claim to have obtained complete expertise in solving all the problems of health and diseases as there still remain innumerable unconquered fields.

The mankind has been lucky to be bestowed with vegetable kingdom. Vegetables have provided large variety of potent drugs to minimise sufferings from diseases. Inspite of immense advances in the manufacture of synthetic drugs, the plant originated drugs have still retained their reputation. Although it is interesting to record that the use of plant based drugs in advanced countries is increasing.

Our country has the richest flora of plants and knowledge on plant based drugs is used in preventive and curative medicine. Ancient Indian scholars, Charak, Sushruta, Vagvatta and several others have given remarkable description of Indian medicinal plants in the Atharvaveda. The plant
preparation are still held in high reputation in the medical profession.

The medicinal value of plants depends on the presence of their tissues of chemical compound or compounds that have biological activity in men and animals. The active principles may accumulate in the storage organs, particularly in the roots or in seeds and sometimes in leaves, flowers, bark or other parts of the plants. So the impetus behind the study of medicinal plants lies on the biodynamic compounds which are present in their different tissues. There is no working principle which can tell us about plants products with certain specific predetermined kinds of activity. The active principles are isolated empirically by practical research based on experience which have a limited validity.

The folklore of plants may sometimes point out the type of pharmacological action; for example the use of garlic and onion by common people for heart ailments. Recent chemical investigations has showed that garlic and onion oils contain 5-methyl cysteine sulphoxide along with other sulfer containing substances. This compound has a prophylactic value in Coronary heart diseases because 'Escherichia Coli' in the digestive tract converts this compound into dimethyl cystine disulphide which reduces cholesterol content of the blood.
Catharanthus roseus\textsuperscript{1} (Vincarosae) which is known as a folk medicine in the treatment of diabetes in India. It is used as a vermifuge and for treatment of dysentery in malagasy. Recent research has shown that the plant contains both monomeric and dimeric indole alkaloids having hypoglycemic (Vindolinine), anticancer (Leurocristine) and other types of biological properties.

So far several flavanoidal glycosides are known to occur in plants and recent years reports of new flavanoidal compounds appeared.

The Crotalaria genera\textsuperscript{2-4} belongs to family Leguminosae and consists of the various species:


These plants are of great medicinal importance because of the reports about their utility in various forms for the treatment of infantile diarrhoea, antiinflammatory of the mouth, scabies, impetigo. Many of the species are also reported to be used as fodder, but some of them are toxic to cattle. \textit{Crotalaria mucronata} has been tried as a cover crop in tea, rubber and coconut plantations. \textit{Crotalaria albida} root is used as a purgative, \textit{Crotalaria verucosa} leaves are used as bitter expectorant, emetic, cure "Kapha"
biliousness, dyspœnea, fever, blood impurities throat and mouth diseases, heart complaints (Ayurveda). The juice of its leaves is used in medicine, it is reported to be efficacious in diminishing salivation. It is prescribed by Tamil doctors both internally and externally in cases of scabies and impetigo.

Ye-Shili and Yong-Long Liu$^5$ isolated an flavanol glycoside, 8-prenyl kaempferol 3-O-α-L rhamnopyranosyl (4→1) glucopyranosyl 7-O-β-D-glucopyranosyl from *Epimedium pubescens* (Berberidaceae).

It is useful as toxic, aphrodisiacs and anti-rheumatics in Chinese herbal medicine.

![Chemical Structure]

$R_1 = \text{Rha (4→1) Glu.}$

$R_2 = \text{Glc,}$

$R_3 = \text{H}$

$\text{Glc} = \beta-D$-glucopyranosyl.

$\text{Rha} = \alpha-L$-rhamnopyranosyl.

([1])
Biologically active flavones 5, 4' dihydroxy 3,6,7,8,3' pentamethoxy flavone and 5,3',4' trihydroxy 3,6,7,8 tetramethoxy flavone were isolated from the ariel parts of *Gutierrezia resinosa* (Compositae). A

These flavones showed significant inhibition in vitro against the cells derived from human epidermoid carcinoma of the nasopharynx (KB).

![Chemical structure](image)

[I] $R = \text{Me}$

[II] $R = \text{H}$

(II)

Recently some new flavanoids have been isolated from the roots of *Muntingia calabura* roots which have been found to be very much cytotoxic in nature are as given below:

![Chemical structure](image)

1 $k1 = R^2 = \text{H}, k3 = \text{OH}$

(III)
(2S) 5'-hydroxy 7, 3', 4' trimethoxy flavan.

(IV)

\[ R_1 = R_3 = \text{O}Me, \quad R_2 = H \]

(2S) 7,8,3',4',5'-Pentamethoxy flavan

(h1 = R3 = OMe, \( R_2 = H \))

7,8,3',4',5' Pentamethoxy flavone

(V)
\[ R_1 = \text{OMe}, \quad R_2 = \text{H}, \quad R_3 = \text{OH} \]

5'-hydroxy 7,8,3',4' tetramethoxy-flavone

\[ (\text{VI}) \]

\[ k = \text{OMe} \]

\[ [M], \quad (2S), \quad (2''S)-P, \quad (2S), \quad (2''S)-8, \quad 8''-5''-\text{Trihydroxy}-7,7'', \quad 3',3''', \quad 4', \quad 4''', \quad 5''''-\text{hepta methoxy}-5', \quad 5''''-\text{biflavan}. \]

Some recent studies of flavonoidal constituents and application of separation and modern spectroscopic techniques in the isolation and structural elucidation also led to the
discovery of a large number of novel and rare flavanoidal glycosides.

Some such recently investigated flavanoidal glycosides are:

1. Two new flavanol glycosides isolated from the underground parts of *Epimedium kereanum* (N).\(^8\)

2. Reassessment of the structure of a flavanol glycoside from the nutt of *Rutbeckia bicolar*.\(^9\)

3. Senegalensein p\(\text{p}\)renylated flavanone isolated from the stem-bark of *Erythrina senegalensis*.\(^10\)

4. Puddumin \(\text{\textregistered}\) novel flavonone glucoside from the stem of *Prunus cerasoides*.\(^11\)

5. A flavanol glucoside 3, 3'-di-O-methyl quercitin 4'-O-glucoside known iso-rhamnetin 3-O-glucoside and 3-O-neohesperidoside from the leaves of *Typha latifolia*.\(^12\)

6. Two iso-vitexin 2'-O-glycosides; C-glycosyl flavone O-glycosides from the primary leaves of *scale cercale*.\(^13\)

7. Flavone glycoside from the leaves and stem of the same *Launaea* species.\(^14\)

8. Two flavone glycosides isolated from the whole plant of *Sideritis leucantha*.\(^15\)
9. Leaf flavanoids flavanol glycosides from the leaves of *Ziziphus spinachristi*.16

10. 2'-P-coumaroyl vitexin 7-glucosides C-glycosyl flavones from the aerial parts of *Mollugo oppositifolia*.17

11. A flavanone glycosides from the Fern fronds of *Caterach officinarum* (roots).18

12. Flavanol 3-glycosides isolated from the leaves of *Flemingia stricta*.19

13. Trisubstituted flavanol glycosides from the flowers of *Coronilla ennerus*.20

14. Two acylated flavone glycosides from the aerial parts of *Anisomeles ovata*.21

15. Flavanol glycosides from the whole plant of *Humata pectinata*.22

16. A flavanol glycosides and sesquiterpene cellulobioside from the fresh aerial parts of *Trillium tschonoskii*.23

17. Flavanoid glycosides isolated from the needles of *Pinus massioniana*.24

18. Acylated flavanols quercetin (3''-benzoil-2'' glucosyl 3-glucoside; acylated flavanol glycosides from the leaves of *Delphnium carolinianum*.25

In view of the medicinal importance of *Crotalaria*
species and on the basis of several reports about the occurrence of heterocyclic physiologically active constituents by earlier workers (as tabulated in Table - I).

The authoress was fascinated, and felt that there is still adequate scope for further phytochemical investigations of Crotalaria lapurnifolia Linn. and Crotalaria prostrata hottl. and therefore she took up the challenging task of further investigating them phytochemically and her findings are summarised below:
<table>
<thead>
<tr>
<th>PLANT</th>
<th>PART</th>
<th>FAMILY</th>
<th>COMPOUND ISOLATED</th>
<th>STRUCTURE</th>
<th>REFERENCE</th>
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<tr>
<td>C. laburnifolia Linn.</td>
<td>Seeds</td>
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<td>Iso-orientin (luteolin-6-C-glucoside)</td>
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<td>Orientin (luteolin-8-C-glucoside)</td>
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<td>Quercitin-3-galactoside</td>
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<td>β-sitosterol</td>
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<td>C. laburnifolia Linn.</td>
<td>Seeds</td>
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<td>Crotalaburnine</td>
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<td>β-sitosterol; flavonoids C-glycosides</td>
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<td>C. laburnifolia Linn.</td>
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<td>Alkaloids acetycholine, histamine, 5-hydroxytryptamine, nicotine and barium crotalaburnine</td>
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<td>C. laburnifolia Linn.</td>
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<td>Major alkaloid</td>
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<td>Senikirine, anacrotine, madurensis</td>
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<td>C. striata</td>
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<td>Apigenin and its glycoside</td>
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<td>C. mucronata</td>
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<td>C. paniculata</td>
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<td>C. anagyroides</td>
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<td>C. inzcania</td>
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<td>Anacrotine</td>
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<td><em>C. medicaginea</em></td>
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<td>D-glucuronic</td>
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<td>Insectisides compounds 2-methoxy-3,5, dimethyl pyrazine and 2, methoxy 3, iso-propyl prazine and major (2) 2 Ocetanol</td>
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<td>Chemical composition nutritive value 3.02, 18.97 and 14.42% protein</td>
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<td><em>C. walkeri</em></td>
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<td>Monocrotaline 0.9%</td>
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<td><em>C. madurensis</em></td>
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<td>Secopyrrolizidine alkaloids, β-sitosterol</td>
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<td><em>C. grahamiana</em></td>
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<td>Pyrrolizidine alkaloids</td>
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<td>Peri-carps</td>
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<td>Grahamine 3'-(−)-2-methyl butsyl I ester of monocrotaline</td>
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<td><em>C. axillaris</em></td>
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<td>Cropodine</td>
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<td>axillaroline and axillaridine novel pyrrolizidine alkaloid</td>
<td>XXIV</td>
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PROBLEM TAKEN AND WORK DONE
PROBLEM TAKEN AND WORK DONE

In view of co-occurrence of diseases, death and decay from the time of appearance of Adam and Eve on this planet it become imperative for him to search for those substances which possessed curative values and due to easily availability of plant kingdom and because of the rich flora of the plants in our country, the authorress took a deep sweep in the available literature or medicinal plant and was fascinated by the significantly important therapeutic values of Crotalaria species, because the reports by various earlier worker's were of adequate importance to warrant further inspiration to her, so she selected Crotalaria prostrata Rottl. and Crotalaria laburnifolia Linn. for further phytochemical investigation and her work is summarised below:

II. ISOLATION AND STUDY OF A NOVEL ACYLATED FLAVANONE GLYCOSIDE; 4'-O-METHYL CARThAMIDIN 7-O-P-(2"-O-P-CouMaroyL) GLUCOPYRANOSIDE FROM THE SEEDS OF CROTALARIA PROSTRATA ROTT.
(N.G. LEGUMINOSAE)

This chapter incorporates the study of a novel acylated flavanone glycoside yield (c.050%) molecular formula \(C_{31}H_{30}O_{13}\), m.p. 184-86\(^{0}\)C and \([M]^{+}\) 610 (\(\epsilon\)IMS), obtained from the acetic soluble fraction of the concentrated water soluble fraction of 95% ethanolic extract of the seeds of Crotalaria prostrata Rottl. It was identify as; 4'-O-methyl carthamidin
7-O-β-D-(2''-O-β-Coumaroyl) glucopyranoside by various colour reactions, chemical degradations and spectral data.

III. ISOLATION AND STUDY OF A NOVEL FLAVONE GLYCOSIDE; KAEMPFEROL 7-O-β-D-GLUCOPYRANOSYL (1→4)-O-β-D-XYLOPYRANOSIDE FROM THE SEEDS OF CROTALARIA LABURNIFOLIA LINN. (N.O. LEGUMINOSAE)

The chloroform soluble fraction of 95% ethanolic extract from the seeds of Crotalaria laburnifolia Linn. has been described in this chapter. The study of a novel flavone glycoside yielded (0.040%) when worked up, gave a novel flavone glycosides molecular formula C_{26}H_{28}O_{15}, m.p. 237-38°C, [α]D'' 980 (L1MS). It was identified by different colour reaction, chemical degradation and spectroscopic analysis as; kaempferol 7-O-β-D-glucopyranosyl (1→4)-O-β-D-xylopyranoside.
IV. ISOLATION AND STUDY OF A NOVEL FLAVANONE GLYCOSIDE; ARUMADENDRIN 7-O-α-L-RHAMNOPYRANOSYL (1→4)-O-β-D-
GLUCOPYRANOSIDE FROM THE SEEDS OF CROTALARIA LABURNIFOLIA LINN. (N.O. LEGUMINOSAE)

This chapter deals the study of a novel flavanone glycoside yield (c. 48%) molecular formula C_{27}H_{32}O_{15},
m.p. 190-91°C, [M]^+ 596 (εIMS), obtained from the methanol soluble part of the concentrated water soluble fraction of 95% ethanolic extract of the seeds of Crotalaria laburnifolia Linn., which was identified as; Arumadendrin 7-O-α-L-rhamnopranosyl (1 → 4)-O-β-D-galactopyranoside, by various colour reactions, chemical degradations and spectral analysis.
V. ISOLATION AND STUDY OF A NOVEL FLAVANOL GLYCOSIDE: 
TAXIFOLIN 3-O-B-D-GALACTOPYRANOSYL (1→6)-O-B-D-
GLUCOPYRANOSIDE FROM THE SEEDS OF CROTALEARIA PROSTRATA 
HOTT. (N.O. LEGUMINOSAE)

The isolation and identification of a novel flavanol glycosides yield (0.05%) from the methanolic extract of the concentrated water soluble part of 95% ethanolic extract of the seeds of *Crotalaria prostrata* Hott., molecular formula C_{27}H_{32}O_{17}, m.p. 200-201°C, [M]^+ 628, which was identified as; Taxifolin 3-O-B-D-galactopyranosyl (1→6)-O-B-D-glucopyranoside. On the basis of different colour reactions, chemical degradations and UV, IR, $^1$H NMR and Mass spectroscopy has been described in this chapter.
REFERENCES


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