CHAPTER ONE

INTRODUCTION
Phytochemistry has come to be recognised as the most advancing branch of science and much of the fascination in the subject is due to its ever increasing utility. Man right from the dawn of civilisation has been trying to find out means to ward off diseases and to find cures for them. In his search for substances having curative value, he made an elaborate study of plants and was able to recognise the curative value of various plants for different ailments.

In a country like India, such a study is all the more important because of the varied climatic conditions due to which it is bestowed with a rich medicinal flora of the world. The national flora is not only rich but also highly cosmopolitan in nature and is reported to be associated with great medicinal properties,¹ and a large number of plants find use as household remedies. The systematic phytochemical and pharmacological investigations of these medicinal plants have led to the development of what is known as modern pharmacopoeia. Still a large number of plants are left which have not so far been investigated phytochemically completely.

The medicinal use of plants may be traced to the remote past and the earliest mention about the same
is found in Rigveda which is the oldest repository of
human knowledge having been written between 4500–4600
B.C. The Ayurveda which is the oldest document on
medicine throws light on the early scientific
accomplishments of the Aryans and also Charaka and
Rigveda. However, a systematic investigation of
indigenous drugs on modern scientific basis was started
more than thirty years ago and since then a number of
important medicinal plants prescribed by 'Kavirajas'
and 'Hakims' have been investigated. The phyto-
chemical investigations not only lead to the isolation
and structural elucidation of new constituents, but
also open a new chapter for the synthesis of analogous
active principles.

MODERN TECHNIQUES OF ANALYSIS:

The enormous development in the field of
chemistry of natural products has been due to the
development of micro and semi-micro methods of analysis
and also due to the advancements in a number of modern
physical methods like:

1. Chromatography, including Gas chromatography
2. Infra red and Ultra violet Spectroscopy.

4. Mass spectroscopy etc. 61-66

These techniques are reviewed in standard works.

CLASSIFICATION OF THE PLANT CONSTITUENTS AND THEIR RECENT STUDIES;

Plant constituents generally provide materials of biological activity. The chemical composition of a plant can be completely studied only when the nature and quantity of all the organic compounds of which it is made of, are known. Seasonal changes and differences in habitat and chemical nature of the soil and artificial interferences brought about due to cultivation generally produce far reaching changes in the qualitative as well as quantitative composition of the plants.

The physiological activity of the plants has been shown due to the active principles present in them. These physiologically active principles fall under the following groups:

1. Saponins
2. Alkaloids
3. Glycosides
4. Fixed oil
5. Proteins
6. Sterols
7. Colouring matters
8. Enzymes
9. Coumarins
10. Inorganic plant constituents.

ALKALOIDS:

Ladenburg has defined alkaloids as natural plant constituents having basic character and physiological action having at least one nitrogen atom in the heterocyclic ring. Alkaloids may be regarded as the basic nitrogenous plant constituents with a powerful physiological action. These are widely distributed in plant families viz. Apocynaceae, Rubiaceae and Solonaceae. The chemistry of plant alkaloids has been very extensively reviewed in a number of standard works.

GLYCOSIDES:

The glycosides are laevorotatory, crystalline, poisonous solids, generally found in leaves and seeds of the plant. Glycosides are present in plants in combination with polyhydric alcohols and sugars and are always accompanied by enzymes which hydrolyse them into sugars and non-sugars (aglycone). The glycosides give rise to one, two or more sugars and an
aglycone on hydrolysis. Glycosides mostly possess marked therapeutic properties and find extensive use in medicines. A good number of terpenoids and steroids are present in nature as glycosides of various types, viz. cardiac glycosides, sterolins, saponins and glycosyl alkaloids. Gupta\textsuperscript{75} and Dehmen\textsuperscript{76} have recently investigated some glycosides.

**SAPONINS:**

Saponins are plant glycosides and are of two types:

(a) Steroidal saponins
(b) Triterpenoidal saponins.

**STEROIDAL SAPONINS:**

Steroidal saponins are amorphous in nature but form colloidal solution in water and on hydrolysis gives steroids and sugars. Recently Tiwari\textsuperscript{77} and Tschesche\textsuperscript{78} studied some saponins.

**TRITERPENOIDAL SAPONINS:**

Triterpenoids are found in free state as well as in the form of glycosides in plants and on
hydrolysis gives triterpenes and sugars. Several new saponins have been recently reported in the literature. 80-84

STEROLS:

Sterols are complex organic compounds of wide occurrence in animals and plants. Sterols are crystalline compounds and occur free as well as in the form of esters of the higher fatty acids. Recently many scientists made investigation on steroids. 85-89

COLOURING MATTERS:

A large number of colouring matters occur in the form of glycosides. The flavonoid water soluble ones generally occur in the aqueous cell sap and are responsible for the variety of colours in flowers. These anthocyanins contain similar nuclei with slight alternation in constitution. All these compounds are phenolic in nature containing a pyran ring linked with a benzene nucleus. The work of some scientists 90-96 is of valuable contribution in this field.
The chemistry of plant products is a dynamic branch of science, and much of the fascination in the subject is due to its ever increasing utility in the discovery of more potent drugs, useful against diseases which have been and are still the biggest threat to the survival of mankind. A study of the active constituents of plants would therefore revitalise the Indian System of Medicine, which still forms a potential source of alleviation of human sufferings to a large number of countryside people of the Indian Sub-Continent and at the same time add new and more potent drugs to the Modern Pharmacopoeia.

The enormous development in the field of phytochemistry has been due to advances made in the modern techniques of chromatography and spectroscopy (UV, IR, NMR and Mass). These techniques have been taken recourse to by the author during the present investigations, to find newer constituents from medicinal flora of hitherto uninvestigated plants. The findings are briefly described below:
1. ISOLATION AND STUDY OF THREE NEW FLAVONE GLYCOSIDES FROM THE SEEDS OF KIGELIA PINNATA.

PART I:

The hexane : ethyl acetate (1:1) extract of the rectified spirit extract of the dried, powdered and defatted seeds of *Kigelia pinnata* on purification yielded a light golden-yellow compound in needle shaped crystals, having m.p. 201-204°C, with the molecular formula C_{31}H_{36}O_{16}; M^+ = 664.

The compound responded to all the tests of flavonoidal glycoside and was identified as 6,7,3',4'-tetramethoxy flavone-5-O-β-D-glucopyranosyl-(1→4)-O-α-L-rhamnopyranoside (I) by classical degradative reactions and spectroscopic studies.
PART II:

The rectified spirit extract of the dried, powdered and defatted seeds of *Kigelia pinnata* yielded a brown viscous mass whose methanol soluble fraction yielded a saponin (separated by adding excess of ether). The filtrate when worked up by lead-lake procedure yielded a brown viscous mass having m.p. 286°C, with molecular formula \( \text{C}_{27}\text{H}_{28}\text{O}_{16} \); \( M^+ = 608 \).

The compound responded to characteristic colour reactions of a flavonoid glycoside. The glycoside on structural elucidation was identified as Kaempferol-5-O-\(\beta\)-D-glucopyranosyl - (1→4) -O-\(\alpha\)-D-xylopyranoside (II); Kaempferol being a well known flavone.

The structure (II) has been confirmed by degradative and spectral studies.
PART III:

The ethyl acetate extract on being subjected to column chromatography over neutral alumina, gave on elution with ethylacetate : carbon tetra-chloride (1:1), pink coloured needle shaped crystals, m.p. 228°C, with molecular formula \( \text{C}_{30}\text{H}_{34}\text{O}_{17} \); \( M^+ = 666 \).

It responded to positive Molisch's test after hydrolysis and gave all the colour reactions of a flavone glycoside. The compound has been identified as 7-3'-dihydroxy-6-8-4'-trimethoxy flavone -5-O-\(\beta\)-D-glucopyranosyl-(1\(\rightarrow\)4)-O-\(\alpha\)-L-rhamnopyranoside. (III)
2. **ISOLATION AND STUDY OF A NEW ANTHRAQUINONE GLYCOSIDE FROM THE FRUITS OF LEEA-AEQUATA.**

The dried, powdered and defatted fruits of *Leea aequata* on extraction with rectified spirit have yielded a brown coloured mass, which when poured into water gave a precipitate which crystallised to a pure compound m.p. 186°C (d), molecular formula $C_{29}H_{32}O_{16}$; $M^+ = 636$.

The compound gave positive Molisch's test and responded to all the colour tests characteristic of anthraquinone glycoside. The usual chemical degradative reactions along with well known colour reactions and spectral studies have confirmed its structure as 1,5-dihydroxy-2-methyl-6,7-dimethoxy-anthraquinone-3-O-β-D-glucopyranosyl-(1→4)-O-α-L-rhamnopyranoside. (IV)
As the two plants investigated by the author have been attributed to have a good number of medicinal properties, it is possible that pharmacological testing may reveal these properties to the presence of some of the constituents isolated and chemically examined in the present work. This would add a utilitarian aspect also to the present findings apart from the academic value and may thus lead to the alleviation of human sufferings in a small measure.
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