CHAPTER - 1

INTRODUCTION
The use of plants as source of medicine and food is as old as humanity. Herbals have occupied a significant place in the human life right from the dawn of its creation and this kind of systematised and analysed traditional knowledge of folk healing is known as 'Ethnic Medicine'. A careful scrutiny of our own pharmacopoeia places before us the 'foxglove' that has gained reputation in cardiology, 'red clover' that kept the blood freely flowing, 'euphorbia' used in respiratory problems, 'ranwolfa' in the treatment of hypertension, 'perwinkle' in the treatment of leukaemia, 'cinchona' in malaria and many more of ethno-medicinal origin.

Knowledge of diseases and ways of curing are available in the fabric of medical knowledge of yore of all the countries. Perhaps it is not incorrect to say that medical role and sociocultural aspects are interwoven and as such, one has to keep in view that these factors are great and important determinants in approach pattern in the field of medicine, despite of all advances.

The volume of dangerous signals that mankind has commenced to face in respect of his living habit, environment, and quality of life has compelled him to peep into traditional medical wisdom, which stood at the ravages of time and continued to shower its best for the benefit of mankind; with
socio-cultural milieu.

Today no country or society, however prosperous and generous it may be able to carry the economic load of providing sophisticated approaches, usable by a handful of remedies at exorbitant cost. Therefore, there is immediate need to realise the constraints upon the medical advances and put them to judicious use.

Thus there is an imperative need to exploit the resources of nature, which the climate has provided for the betterment of mankind and need to be used judiciously with discretion.

Attempts have therefore been on to bring to door step of the common man, simple remedies that are easily available from the natural resources and that could be used with no ill effects but with advantage. Herbs have thus been the mainstay in this process and as such there is an urgent need for their systematic investigations based on, modern scientific lines, which has already started last over thirty years and the investigations have revolutionized the Indian System of Medicine.

In several cases the bioactive constituents of these indigenous drugs have been isolated and identified and their physiological values have been recognised, thereby revitalising the Indian Pharmacopoeia. A good number of these compounds have been synthesised and even in few cases
Compounds of greater therapeutic values and those of analogous structures have also been synthesised, thus opening a separate field of research in the synthetic organic chemistry.

This revitalisation in the field of phytochemistry has been mainly due to the tremendous advancements made in modern analytical techniques and their immense applications which have proved to be a boon in the isolation and characterisation of complex organic molecules. Separation methods such as column, paper, thin and thick layer and gas chromatography, coupled with spectroscopic techniques of ultraviolet, infra-red, nuclear magnetic resonance, and mass spectroscopy are increasingly applied for the isolation and structural elucidation of various organic compounds in the field of chemistry of natural products.

A brief resume of each of these is given below:

**Chromatographic Techniques**

Chromatography is the most versatile tool recognised today for isolation, and purification of plant constituents. Some of them have been reviewed in standard works. The techniques of chromatography may conveniently be divided as follows:

1. **Adsorption chromatography;**
2. **Partition chromatography, including gas liquid chromatography;**
(iii) Thin layer chromatography;
(iv) Paper chromatography;
(v) Ion-exchange chromatography.

The utility of chromatography was known since
of Martin and Synge, who introduced this technique for the
separation of acetylated amino acids. During years following
1931, Sesse devised the fluorescent adsorbent methods and
Gillan and Ride, Karrer and Schoppe, observed the columns
under UV light. In this field, there has been a tendency to
use various columns e.g. starch columns were utilised by
Reichstein and cellulose columns by Hough.

Paper chromatography has proved to be a very important
technique for separation and characterisation of amino
acids in the field of protein analysis while circular
paper chromatography was used by Berry and Mitchell for
the separation of even micro quantities of sugars.

Martin and Garden used electrochromatographic
techniques by which Mangold and Sämmerck separated methyl
esters of unsaturated fatty acids. The technique has also
been successively utilized for the separation of fatty acids,
terpenes and coumarins.

The technique of thin layer chromatography has been
suitably applied in the field of alkaloids and sterols and
its applications have been reviewed by Mirini et al.,
while that of gas liquid chromatography has been extensively used for the study of essential and fixed oils and triterpenoidal alcohols\textsuperscript{20-24}.

The work of Martin\textsuperscript{25} and others has firmly established the gas chromatography as an investigative separation technique, although it was assumed that the technique was suited exclusively for the analysis of volatile substances, but Horgan and co-workers\textsuperscript{26} demonstrated that high molecular weight steroids could be separated successfully by this new technique. The use of the gas chromatography was then extended to a wide variety of high molecular weight, polar, nitrogenous substances such as phenolic amines\textsuperscript{27}, nucleosides\textsuperscript{28} barbiturates\textsuperscript{29} and carbohydrates\textsuperscript{30}. The investigations of Giddings\textsuperscript{31}, Horvath\textsuperscript{32}, Pretorius Smuts\textsuperscript{33}, Sco and Rowell\textsuperscript{34} and Huber\textsuperscript{35} have contributed much to the instrumental development of gas chromatography and now it has become not only the most widely used analytical tool, but also the subject of extensive theoretical investigations.

**SPECTROSCOPIC TECHNIQUES**

**ULTRA-VIOLET SPECTROSCOPY**

Molecular absorption in the U.V. and visible region of the spectrum is a function of the electronic structure of the molecule. Absorption of energy is quantized and results in the elevation of electrons from orbitals in the ground state to orbitals in the higher energy state
i.e. excited state. In practice, ultra violet spectrometry is for the most part limited to conjugated systems.

There is however, an advantage to the selectivity of ultra-violet absorptions since characteristic groups may be recognised in molecules of widely varying complexities. A large portion of a relatively complex molecule may be transparent in the ultra-violet regions so that we may obtain a spectrum similar to that of a much simpler molecule. Thus the spectrum of the male hormone, testosterone closely resembles the spectrum of mesityl oxide, which results mainly due to the conjugated enone structure of the two compounds.

The abundance of reference material relating to the theory and interpretation of ultra-violet spectra is available. Two of the most useful references for the organic chemist are the text by Stern and Timmons and by Scott. The latter is particularly useful for the natural products chemist. The text by Jaffe and Orchin is an excellent source of theory for both the spectroscopist and the organic chemist. Several compilations of U.V. spectra and absorption data are available which are of specific use to the organic chemist.

**INFRARED SPECTROSCOPY**

Infra-red radiations refer broadly to that part of the electromagnetic spectrum which lies between the visible and microwave regions, of which portion, between 4000 \( \text{cm}^{-1} \) to 666 \( \text{cm}^{-1} \) (2.5-15-0 μm) is of greatest use to the organic
chemists. Recently there has been an increasing interest in the near infra-red region \( \nu = 4000 \text{ cm}^{-1} \) (0.7 - 2.5 \( \mu m \)) and the far infra-red region \( \nu = 300 \text{ cm}^{-1} \) (14.3 \( \mu m \)) too.

Although the infrared spectrum is characteristic of the entire molecule, it may be mentioned that certain groups or atoms give rise to the bands at or near the same frequency, regardless of the structure of the rest of the molecule. It is persistence of these characteristic bands that permits the chemist to obtain useful structural information by simple inspection and reference to generalized charts of characteristic group frequencies.

The increased emphasis on infra-red spectrometry as a tool of the practicing organic chemist is readily apparent from the number of books devoted wholly or in part to discussions of applications of infra-red spectrometry. There is no lack of reference material covering all aspects of infra-red spectrometry.\(^{48-62}\) The text by Colthup, Daly and Wiberly\(^{55}\) presents a thorough coverage to the theory, practice and spectra structure correlations in the field of IR spectroscopy. The compact manuals by Gross\(^{56}\), Flett\(^{57}\), Szymaniski \(^{58}\) and Nakanishi \(^{59}\) are also the convenient sources of concise information. Several volumes by Potts\(^{51}\) and Miller \(^{62}\) are the available valuable references for instrumentation in the field of I.R. spectroscopy.
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectrometry which is the most powerful tool available in the hands of organic chemist engaged in the field of organic structural elucidation is basically another form of absorption spectrometry, akin to infra-red or ultra-violet. Under appropriate conditions, a sample can absorb electromagnetic radiations in the radio frequency region at frequencies, characteristics of the sample. Absorption is a function of certain nucleus in the molecule. A plot of the frequencies of the absorption peaks versus peak intensities constitutes a NMR spectrum.

Several lucid non-mathematical introductions to nuclear magnetic resonance are available for greater depth, e.g. the classic treatise of Pople, the work of Esley Peeney and Sutchi, and the book by Carrington and Mohachlan. Two volumes of N.M.R. spectra have been published by Varian Associates, which are indexed by an unique code that shows the type of proton, nearest and the next nearest neighbour functional group. The well known Sadtler catalogue of IR and UV are supplemented by NMR spectra.

Sets of spectra are also issued by the American Petroleum Institute. Indexes to the NMR literature have been published by Jackman and Sternhell's book which contains over 2600 papers. NMR spectroscopy has been
very successfully employed for the detection of functional group and structural elucidation of even complex organic molecules. It has also found very extensive applications in polymer 70-72 and pharmaceutical 73 industry.

The details of its various applications have been reviewed in several standard works 74-77.

\textbf{\textsuperscript{13}C- NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY :}

\textsuperscript{13}C has a nuclear spin of 1/2 and can be observed by NMR at a frequency of 10.705 MHz at a field of 10 kilogauss. The analysis is limited because the relative abundance of \textsuperscript{13}C is only 1.1\% (compared to \textsuperscript{12}C), the \textsuperscript{13}C resonance has only 1.6\% the sensitivity of the \textsuperscript{1}H resonance, and the relaxation time for \textsuperscript{13}C is longer than for \textsuperscript{1}H. These limitations have been overcome by using relatively large samples and pulsed instrumentation. Since the spin number of \textsuperscript{13}C is the same as for \textsuperscript{1}H, the same rules apply for predicting the multiplicity of these absorption. The coupling constant for \textsuperscript{13}C-\textsuperscript{1}H are large (100-250\% Hz) and the interpretation of \textsuperscript{13}C spectra can be difficult because of overlapping \textsuperscript{13}C-\textsuperscript{1}H multiplets. To simplify the spectrum, \textsuperscript{13}C nuclei are usually completely decoupled from all of the \textsuperscript{1}H nuclei by use of double resonance. The spectrum is then simply a series of singlets corresponding
to each variety of carbon atom present. A textbook of $^{13}$C spectrometry\textsuperscript{78} and a catalogue of $^{13}$C spectra\textsuperscript{79} are available. Recently a book oriented towards organic chemists have also been published\textsuperscript{80} on $^{13}$C NMR spectroscopy.

**Mass Spectrometry:**

A mass spectrometer bombards an organic molecule under investigation with an electron beam and quantitatively records the results as a spectrum of positive ion fragments which is a mass spectrum. Separation of the positive ion fragments depends on the basis of mass/charge ratio, because the majority of ions are singly charged.

A number of good general texts are available in the field of mass spectrometry, which include the books by Biemann\textsuperscript{81}, Mayeon\textsuperscript{82} the more recent work of Hamming and Foster\textsuperscript{83} and the extensive volumes by Buzikiewicz, Djerassi, and Williams\textsuperscript{84-85}. Brief introductions to the field by McLafferty\textsuperscript{86} and Sharda\textsuperscript{87} are available where as pertinent journals in the field are: Organic mass spectrometry; the journal of mass spectrometry, ion physics, and the archives of mass spectral data, and several other compilations of spectra are available, e.g. the atlas of mass spectral data\textsuperscript{86} and the eight peak index\textsuperscript{89}, the chemical compound index of the journal of organic mass spectra and the Grenoble compilation\textsuperscript{90}. The details of the use of mass spectrometry in characterization
of plant constituents have been extensively dealt in the work of Peach and Tracey\textsuperscript{91}, Rakhash\textsuperscript{92} and Methieson\textsuperscript{93} and several other works\textsuperscript{94-96}.

CLASSIFICATION OF THE PLANT CONSTITUENTS AND THEIR RECENT STUDIES:

The organic compounds which are responsible for attributing therapeutic values to the plants may be correlated by the study of the nature and quantity of all the organic components of which the plants are made of. Seasonal changes, habitat differences and varying composition of the soil and artificial interference by man during cultivation, produces changes in the qualitative and quantitative composition of the plant constituents.

Some of the important plant ingredients fall under the following categories:

1. Glycosides
2. Terpenoids
3. Steroids
4. Saponins
5. Colouring matters
6. Alkaloids
7. Coumarins
8. Gums and mucilages
9. Proteins
10. Carbohydrates etc.

A brief description of few of those investigated by the author is unmentioned.
GLYCOSIDES:

Glucosides\(^{97-99}\) are the class of compounds which generally occur in leaves, seeds and parts of the plants and on hydrolysis yield one, two or more sugars and an aglycone. They are generally colourless, crystalline solids having bitter taste, poisonous nature, laevo-rotation and possess reputation of exerting great physiological action.

On the basis of the occurrence of sugars, the glucosides, may be grouped into two groups:

(1) GROUP-A-GLYCOSIDES:

In this group of glycosides following, eight sugars are predominant:

<table>
<thead>
<tr>
<th>Number</th>
<th>Sugar</th>
<th>Sugar</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>D-glucose</td>
<td>(ii) D-glucuronic acid</td>
</tr>
<tr>
<td>(iii)</td>
<td>L-xylose</td>
<td>(iv) L-fucose</td>
</tr>
<tr>
<td>(v)</td>
<td>L-galactose</td>
<td>(vi) L-galacto uronic acid</td>
</tr>
<tr>
<td>(vii)</td>
<td>L-arabinose</td>
<td>(viii) L-rhamnose.</td>
</tr>
</tbody>
</table>

The actual glycosides of this group are 0-glycosides. Except 0-glycosides, N-glycosides, S-glycosides and C-glycosyl compounds are also found in nature and are discussed in brief.

0-GLYCOSIDES:

This class of substances, which is very abundant
in nature can be subdivided into phenolic, aliphatic and alicyclic glycosides depending on the nature of the aglycone. Only rarely are sugars found that are not listed in Table (I), e.g. glucomethylglose in and 1-chinovin, and in purgic acid, L-Fucose in Convolvulus and Jalepin[100].

**PHENOLIC GLYCOSES:**

These glycosides are very abundant in the plant kingdom (flavones, anthocyanines, antaragulose and derivatives).

Two simple examples of this class are rutin (I) and Primaverin (II)

![Structural formulas]

The compounds of this class of plant origin are described in several standard works [101-104].

**N-GLYCOSES:**

N-glycosides play a significant role as nucleosides in the cell function. So far only the sugars L-rucose and 2-deoxy L-rucose have been found in this class of substance e.g. adenosine (III)
S-Glycosides:

Mustard oil glycosides belong to this class of substances e.g. Sinigrin (IV)

C-Glycosyl compounds:

Bergenin (from Bergenia cernua) Honoacetoin, Vitexin, Barcaclin (V) and Carminic acid (VI) belongs to this group of substances.
GROUP B-GLYCOSIDES:

This group includes:

1) Cardenolides or Cardiac glycosides
2) Bufanolides
3) Ligtanoglycosides
4) Ester glycosides of C-nor-D-homosteroid

1) CARDENOLIDES:

Cardenolides are steroid derivatives found in many higher plants. They derive their name on account of their specific 'digitalis like' action on cardiac muscle.
They have 6-23 genins and characterized by their 14-\(\beta\)-hydroxyl group (Cis-fusion of nine C and 6) and their \(\chi\)-unsaturated \(\gamma\) -lactone ring.

Here the aglycone or genin (the steroid moiety) is coupled with one or more sugars by a glycosidic linkage. The cardiac glycosides therefore differ from other glycosides only in the special structure of the genin component, and from other steroid glycosides, only in the side chain which in this case is present as a lactone ring.

The cardiac glycosides which contain some sugars as mentioned in (Table II, III & IV) occur in about dozen plants families and in certain insects, such as Grasshopper, roskilocerus cauponius and the Monarch butterfly (Vanessa plexippus). The insects obtain them from the diet, being presumable, unable to synthesize them.

**Table - II**

<table>
<thead>
<tr>
<th>6-glucose</th>
<th>6-gulomethyllose</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-allomethylase</td>
<td>L-rhamnose</td>
</tr>
<tr>
<td>L-glucomethylase</td>
<td>L-fucrose</td>
</tr>
<tr>
<td>L-fucose</td>
<td>L-fucrose</td>
</tr>
</tbody>
</table>
Table - III:

Methyl ethers of hexoses and D-deoxy methyllose:

- 3-O-Methyl-D-glucose
- 2:3 Di-O-methyl-D-glucose
- D-Thevetose (3-O-Methyl-D-glucosethylose)
- L-Acoriose (3-O-Methyl-D-ribofuranose)
- L-Acorovose (3-O-Methyl-D-talomethylose)
- L-Digitaiose (3-O-Methyl-D-fructose)
- 2,3-Di-O-methyl-D-fructose
- 2-O-Methyl-D-fructose
- 3-O-Methyl-altromethyllose
- L-Thevetose

Table - IV:

2-O-deoxy sugars:

- D-Arabo-2-deoxyhexose (2-Deoxy-D-glucose)
- L-Arabinose (L-rino-2,6-bisdeoxyhexose).
- L-Sorbinose (L-rino-2,6-bisdeoxyhexose).
- D-Camarose (Probably 5-Arabo-2,6-bisdeoxy hexose)
- L-Gumarose (3-O-Methyl-D-rino-2,6-bisdeoxy hexose)
- L-Oleanose (3-O-Methyl-D-arabo-2,6-bisdeoxy hexose)
- D-Garmsenose (3-O-Methyl-D-xylo-2,6 bisdeoxy hexose)
- D-Licinose (3-O-Methyl-D-lyxo-2,6 bisdeoxy hexose)
- L-Licinose.
- L-Cumarose.
The pharmacological activity of cardiac glycosides depends on their structural features e.g., an unsaturated lactone ring, C/D cis juncture, and β-orientation of the side chain. The most active steroids have rings A and B as fused and the 3-hydroxyl group in β-orientation. The aldehyde group at C-10 increases the toxicity as does acetylation or formylation of the 16-hydroxyl group.

Cardiac glycosides, in purified form are used in medicine under a variety of trade names e.g., 'Digitalis' has been one of the most popular drugs for treatment of congestive heart failure. Injectable tinctures are used for prompt initial digitalization and powdered leaf tablets for maintenance doses.

Some recently investigated compounds of this class of plant origin are:

Syriose (VII)\textsuperscript{111} from Asclepias syriaca, and Strophanthidin diglycosid\textsuperscript{112} (VIII)
Study of cardenolides are described in several standard works\textsuperscript{113-121}.

(2) \textbf{BUFANOLIDES}:

Bufanolides derived from C-24 genin are much less widely distributed in the plant kingdom than the cardenolides. So far they have been discovered in Liliaceae and Ranunculaceae. The sugars found in them are:

- D-glucose
- L-rhamnose
- L-thevetose.

Some recently investigated compounds of this class of plant origin are: \textit{helleurigenin glucoside (IX)} and \textit{helleurigenol glucoside (X)} from \textit{Urena depressa}\textsuperscript{122-125}.
(3) DIGITANOL GLYCOSIDES

Digitanol glycosides have so far been isolated only from digitalis species. Biologically, they do not exhibit any digitalis-like effect e.g., diginin (XI)\textsuperscript{124} and digacetinin\textsuperscript{125} (XII)

\[ Z = D\text{-d-glucose} \]
The glycosides are found in Asclepiadaceae, family and are derived from C-21 genins and presumably possess the C-Nor-5-homosteroid skeleton. Biologically, the substances of this group do not have any digitalis like action e.g. sarcostin$^{126}$ (XIII) and linonolin$^{127}$(XIV)
In plants these glycosides are present in combination with various sugars and as esters of different acids.

The sugars which have been found to occur are: \(\alpha\)-digitoxose, \(\beta\)-cymarose (cleumarose), \(\gamma\)-thevetose (digitalone) and \(\delta\)-glucose.

SAPONINS:

Saponins are high molecular weight plant glycosides which are cytotoxic, antimicrobial and powerful emulsifier and derive their name due to this
property and their glycosides are known as sapogenins. They are characterized by foaming in aqueous solution. These solutions are haemolysic when injected into the blood stream of animals and therefore are highly toxic intravenously. They are also highly toxic to cold blood animals and toxicity appears to be related to their marked activity in lowering surface tension. Another characteristic of this class is the formation of molecular compounds with cholesterol and other 3β-hydroxy steroids which can be used both for isolation of sapogenins and for separation and purification of 3β-hydroxy steroids. Digitonin surpasses all other sapogenins in yielding steroid complexes of great insolubility and its 1:1 molecular compound with amyl alcohol may be used for its purification, whilst its complexes with (+) α-terpineol and (+) α-tetrahydro-β-naphthol have been used for resolution of these substances. Sapogenins are commonly isolated by extraction of the plant material with hot water and or ethanol followed by evaporation of the extract usually in vacuum; alternatively, they may be extracted with ethanol and precipitated by addition of ether.

The sapogenins are of two types:

(1) Triterpeneoidal sapogenins,

(2) Steroidal sapogenins
(1) **Tetracyclic Saponins**:

These are the group of plant constituents having 
C\textsubscript{30} carbon system and occur as free triterpenes or combined 
with sugars in glycosidic linkage to form saponins\textsuperscript{123-130}. 
They are divided into five groups according to their basic structure.

The first is squalene which is the only member 
of the acyclic group while the second is \(\beta\)-amyrin group, 
consisting of oleanolic acid, and \(\alpha\)-boswellic acid. The third is of \(\alpha\)-amyrin group which includes ursoic 
and \(\beta\)-boswellic acid\textsuperscript{131} while the fourth group consists of 
elastic acid, cryptol, and xenol. The last (fifth) is of 
mono-hydrate terpene, lupeol\textsuperscript{132-133}. The \(\alpha\) and \(\beta\) amyrin 
and lupeol groups are of pentacyclic group whereas elastic 
acid is of tetracyclic group.

Some recently studied saponins are described 
in several standard works\textsuperscript{130-133}.

(2) **Steroidal Saponins**:

Steroids when present as glycosides in plants 
are known as saponins in which generally the sugars are 
attached to 3-hydroxyl group. They are extensively used 
as the starting materials for the synthesis of allopamin, 
corticosterone and \(\Delta^2\)oxycorticosterone.
The chemistry of steroidal saponins and their use as intermediates in the synthesis of steroidal drugs have been extensively reviewed in several standard works. 139-142.

A few recently investigated compounds of this class are described in several works. 143-144.

**Colouring Matters**

Colouring matters are the class of compounds which are phenolic in nature, possess a pyrone ring, and have marked physiological actions. They occur free or as glycosides in the plants and from which the true colouring matter may be obtained in the form of aglycone after their hydrolysis. The various types of colouring matters may be distinguished from each other by simple colour tests.

The aqueous extract of these pigments when made alkaline is found to produce colour changes as following:

(a) Anthocyanins  $\rightarrow$ purple to blue.

(b) Flavones  $\rightarrow$ blue to purple.

Some recently investigated compounds of this class of plant origin are described in several standard works. 145-146.
Ethnic medicine which is a systematised and analysed traditional knowledge has been the subject of fascinating study both from medicinal and clinical point of view.

For a country like India such a study is more important because of the exorbitant cost of various imported drugs, hardly affordable by large number of peoples of the subcontinent, due to their poor economic conditions. So there is an imperative need to exploit the resources of nature which the Omnipotent has been kind enough to bestow to this nation for the betterment of humanity.

Attempts have therefore been on to bring remedies at the doorstep of common man that could be used without any ill effects. As such a systematic phytochemical and pharmacological investigations of the available national flora is certainly on the one hand going to enrich the modern pharmacopoeia and on the other hand, revitalise the Indian System of Medicine.

Although during the last few years, a large number of new drugs of plant origin have been discovered, yet a deep sweep into the available literature about phytochemical studies of various medicinal plants still concludes that a
good number of them have not been investigated so far systematically.

This enormous development in the field of phytochemistry has been because of tremendous advances made in the development of chromatographic techniques of isolation and purification along with the applications of spectroscopic techniques which when applied together have proved to be of greater advantage to the organic chemist engaged in the field of isolation and structural elucidation of natural products and have been taken recourse to by the author during the course of his investigations.

The author was fascinated, because of the so important cardiotonic activity associated with *Streptus asper* (Lour) and significant antianaemia activity of *Anogeissus latifolia* (WALL) and therefore took up the challenging task of revealing the secret of their therapeutic values by carrying out their systematic phytochemical investigations by the aid of both classical degradative methods and modern spectroscopic techniques and his findings are described below:

(1) STUDIES ON CARDIAC GLYCOIDES FROM THE ROOTS OF STREPTUS ASPER (LOUR)

This chapter consists of two parts.
PART (I): ISOLATION AND STUDY OF A NEW CARDIAC GLYCOSIDE 'VJALOSID' FROM THE ROOTS OF STREBLUS ASPER (LOUR)¹

The 50% aqueous ethanolic extract of air-dried, powdered and defatted roots of *Streblus asper* (LOUR) was concentrated and treated with chloroform:methanol (2:1), and filtered. The filtrate on removal of the solvent gave a brown viscous mass which showed the presence of two spots on TLC examination, therefore it was subjected to column chromatography and eluted with chloroform:methanol in the ratios 3:4 and 4:7.

The chloroform:methanol (3:4) soluble part when worked up, yielded a new cardiac glycoside, molecular formula C₃₄H₅₂O₁₄, m.p. 171-72°C identified Periplocaenin-3-O-β-D-glucopyranosyl (1→5)-O-β-D-xylofuranoside (I) by usual degradation, several colour reactions and UV, IR, ¹H NMR and Mass spectroscopic studies.

![Chemical Structure of I](image)
PART (II): ISOLATION AND STUDY OF A CARDENOLIDE 'ASPEROSIL'
FROM THE ROOTS OF SCHRIBLUAS ASPER (L.) H.:

The chloroform: methanol (4:7) soluble part (obtained as described in Part I, Chapter II, Page 37) when worked up yielded another cardenolide, molecular formula C_{31}H_{46}O_{9}, m.p. 190-203°C identified as; Digitoxigenin-3-O-β-2-3-αl-0-methyl-D-glucopyranoside (II) with the help of degradation enzymatic, various chemical and spectral studies.

(2) ISOLATION AND STUDY OF A NEW ACYLATED LUTEOLIN GLYCOCOIDE FROM THE ROOTS OF ANGOISSUS LATIFOLIA (WALL):

The air dried, powdered and defatted roots of Anoehissus latifolia (Wall) were extracted with 95% ethanol. The
95% ethanolic extract was concentrated under reduced pressure to a brown viscous mass and resolved into water soluble and water insoluble parts. The water soluble part was concentrated and successively extracted with benzene, chloroform, ethyl acetate and acetone (the study of chloroform and ethyl acetate soluble part is reported in Chapter VI of the Thesis).

The acetone soluble part on working up yielded a new acylated flavone glycoside, molecular formula C_{31}H_{28}O_{14} m.p. 258-60°C and identification of the degraded products, coupled with its spectral studies, showed it as 6-methoxy-Luteolin (2'-O-p-coumaroyl)-7-O-β-D-glucopyranoside (III).
(3) **Isolation and Study of a New Steroidal Saponin from the Roots of Stereolus Asper (Lour):**

The 95% ethanol extract of the roots of Stereolus asper (Lour) was concentrated under reduced pressure to a dark brown viscous mass and successively extracted with benzene, chloroform, acetone and methanol. The benzene, chloroform, and acetone soluble parts resulted in very small amounts of various residues which were insufficient for any substantive study.

The methanol soluble part on concentration under reduced pressure yielded a brown viscous mass which on addition of excess of solvent ether gave a precipitate which on TLC examination showed two spots. The precipitate was therefore subjected to column chromatography and eluted with acetone : methanol in ratio 2:1 and 4:1 and studied separately. (The study of acetone : methanol (4:1) is reported in the Chapter V of the thesis).

The acetone : methanol (2:1) soluble part when worked up, yielded a saponin, molecular formula C_{48}H_{76}O_{14}, m.p 247-50\degree C which was identified as 1β-sitosterol-3-O-β-D-arabinofuranosyl (1→4)-O-α-L-rhamnopyranosyl (1→4)-O-β-D-glycopyranoside (IV).
(4)  **ISOLATION AND STUDY OF A NEW TRITERPENOID Saponin**

**FROM THE ROOTS OF STREUHLUS ASPER (LOUR)**:

The acetone : methanol (4:1) soluble part
(obtained as described in Chapter IV on Page 175), when
worked up yielded a saponin, molecular formula, \( C_{41}H_{70}O_{10} \),
m.p. 170-72°C, which on systematic degradations and
spectroscopic and enzymatic study was found to be Lupanol-3-
0-\( \beta \)-D-glucopyranosyl (1\( \rightarrow \) 5)-0-\( \beta \)-D-xylofuranoside (V).
(5) **STUDIES ON FLAVONE GLYCOSIDES FROM THE ROOTS OF ANGELISSUS LUTIFOLIA (VALL)**

This Chapter consists of two parts:

**PART (I): ISOLATION AND STUDY OF A NEW FLAVONE GLYCOSIDE FROM THE ROOTS OF ANGELISSUS LUTIFOLIA (VALL)**

The chloroform soluble part (obtained as described in Chapter III, page 128) when worked up yielded a flavone glycoside, molecular formula C_{27}H_{30}O_{16}, m.p. 272-72°C, identified as quercetin-3-0-β-D-galactopyranosyl (1→4)-0-α-L-rhamnopyranoside (VI) by usual degradation; and UV, IR, ^1H-NMR and Mass spectroscopic studies.
PART (II) : ISOLATION AND STUDY OF A FLAVONE GLYCOSIDE
FROM THE ROOTS OF ANOGAISSUS LAMIFOLIA (MALI)

The ethyl acetate soluble part (obtained as described in Chapter, III, Page 128) when worked up also yielded another flavone glycoside, molecular formula C_{27}H_{30}O_{16}, m.p. 190-92°C identified as: Luteolin-7-O-β-D-galactopyranosyl- (1→6) -O-β-D-galactopyranoside (VII) by usual degradation and spectroscopic studies.
References


43. Ultra-violet reference spectra, Sadler Research Laboratories (1972), 32000 spectra in 74 volumes.


47. Woodward, R.B. Ibid (1942), No. 64, page 72-76.


Vol. 1 Molecular weight 16.313 to 142.0089
Vol. 2 Molecular weight 142.0105 to 213.456.
Vol. 3 Molecular weight 213.4629 to 702.7961.


90. Compilations of Mass Spectral Data Centre d'Etudes Nucleaires de Grenoble, France, this compilation is an Index to some 6000 spectra.


112. Habermayer, E.; Dissertation, University, Munich, west Germany, (1980).


