THEORETICAL
Glycosides are the organic compounds usually with a hemiacetal linkage between the reducing group of sugars and the hydroxyl group of the aglycones. This link when affected through oxygen, gives rise to most abundant glycosides called 'O-glycosides,' through nitrogen 'N-glycosides' and through carbon 'C-glycosides' etc. These O-glycosides, producing copious foam on shaking with water, causing sneezing on inhalation are termed as 'Saponins'. These compounds also possess the characteristic properties of killing fishes (fish index), haemolysing RBC (haemolytic index), forming precipitates with cholesterol in alcohol etc.

These glycosides occur abundantly in a number of species of higher plants as well as in some marine animals such as star-fish and sea-cucumber. Chemically, the saponins consist of two structural units:

(i) a sugar chain/s called glycone part, and
(ii) a sugar free unit called aglycone or sapogenin.

The common sugars of the glycone part of saponins have been found to be D-glucose, D-galactose, D-xylene, L-arabinose and L-rhamnose with a few exceptions. Depending upon the nature of the aglycone part the saponins are classified into: TRITERPENOID SAPONINS, STEROIDAL-ALKALOIDAL SAPONINS and STEROIDAL SAPONINS.
A. STEROIDAL SAPONINS

These saponins on acidic/enzymatic hydrolysis give C\textsubscript{27} sapogenins, which possess the carbon ring system of cholesterol along with the remaining 8-carbon atoms as a bicyclic ring system (rings 'E' and 'F'). These saponins on selenium dehydrogenation [1-3] are degraded into Diels' hydrocarbon (3' methyl 1, 2 cyclo pentenophenanthrene, (I).

\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}

(I)

The C\textsubscript{27} steroidal aglycones of steroidal saponins have been found to be oxygenated at carbon atoms 16, 22, 26 and carry a hydroxyl group at C\textsubscript{3}. Depending upon the nature of ring 'F', they are termed as Furostanolic saponins (Open ring 'F' (II) and Spirostanolic saponins (closed ring 'F', (III). Sharma et al. further [4-6] subclassified them as:

\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}

(II)  

(III)
1. OLIGOFUROSTANOSIDES AND FUROSTANOSIDES

Furostanolic saponins with >3 sugars are termed as oligofurostanosides because of their close relationship and resemblance with oligosaccharides on one hand and saponins on the other, whereas the furostanolic saponins with <3 sugars, not resembling with oligosaccharides, are called as furostanones.

2. OLIGOSPIROSTANOSIDES AND SPIROSTANOSIDES

Parallelly, the spirostanolic saponins are classified as oligospirostanosides (>3 sugars) and spirostanosides (<3 sugars).

The first isolation and characterisation of this type of a compound, Jurubine (IV), a furostanolic-alkaloidal saponin, was reported by Schreiber and Ripperger [7,8] from Solanum paniculatum L. and the very next year came the isolation and characterisation of first such saponin glycoside Sarsaparilloside (V) from Smilax aristolochiae Mill. roots by Tschesche et al. [9], which was termed as Bisdesmoside with its corresponding oligospirostanoside, Parillin (VI).
These findings were in contrast to Wall's claim [10] but supported Marker's classical suggestion [11] that a steroidal saponin is secondarily produced from a steroidal glycoside having an aliphatic chain at C₁₇ or via an oligofurostanoside. Oligofurostanosides are therefore, the real saponin glycosides present in nature and all others are the artefacts, which has been proved by the ageing of the plant material as well as thermal effects [4-7, 12-14].

DETECTION OF OLIGOFUROSTANOSIDES

Oligofurostanosides can be easily detected by:

1. **EHRlich REAGENT TEST [15-16]**

   The oligofurostanosides on spraying with a solution of p-dimethyl aminobenzaldehyde in HCl (Ehrlich Reagent) develop
a brilliant red colour. The test is specific for pseudocompounds (Δ^{20(22)} derivative) also. However, furostanolic saponins with 17-OH group are not detected by this reagent. [17]

2. Pt. IV OXIDE or NaBH₄ REDUCTION FOLLOWED BY ACID HYDROLYSIS [9, 18]

H₂/Pt oxide or NaBH₄ reduction of oligofurostanosides followed by acid hydrolysis leads mainly to the formation of a dihydroaglycone along with other minor products. Spirostanolic saponins are not affected by this reduction.

3. IR-SPECTRA [15, 19-21]

Oligospirostanosides give well defined bands around 860, 900, 920 and 980 cm⁻¹ in IR spectra which are fewer and broader or absent in oligofurostanosides.

4. TWO DIMENSIONAL TLC [19]

A spot of oligofurostanosides on two dimensional TLC turns into three diagonal spots because of their continuous conversion into a mixture of two products viz. C_{22}-OH and C_{22}-OMe/-OEt in MeOH/EtOH and vice-versa in aqueous medium.

5. NMR-SPECTRA [20,22]

The ¹H-NMR spectra of oligofurostanosides exhibit a characteristic singlet at about 3.25 ppm for 22-OMe group.
6. CRYSTALLISATION IN MeOH OR EtOH [9,19]

Oligofurostanosides on crystallisation in MeOH/EtOH yield a mixture of two products viz. C$_{22}$-OH and C$_{22}$-OMe/-OEt due to continuous transformation of the C$_{22}$-OH into C$_{22}$-OMe/-OEt derivatives and vice-versa. However, the oligofurostanosides on refluxing with water and acetone convert themselves exclusively into C$_{22}$-OH compounds and on refluxing with dry MeOH into C$_{22}$-OMe derivatives.

COMMON TESTS FOR STEROIDAL SAPONINS

Oligofurostanosides also show the following tests for spirostanosides and steroidal sapogenins:

1. **SANNE'S REAGENT TEST [23]**

   A spot of compound on a filter paper, on spraying with 1% ethanolic cinnamic aldehyde solution, drying and re-spraying with a mixture of acetic anhydride and H$_2$SO$_4$ (12:1) or alcohol : phosphoric acid : perchloric acid (30:50:0.5) develops yellow colour on heating.

2. **PARADIMETHYL AMINOBENZALDEHYDE REAGENT TEST [24]**

   These compounds give a brown-yellow colour on spraying with a mixture of p-dimethyl aminobenzaldehyde (0.25 g), ethanol (25 ml), phosphoric acid (10 ml) and perchloric acid (4 ml) on heating.
3. ANTIMONY TRICHLORIDE TEST [25]

This test is given by both the triterpenic and steroidal sapogenins possessing C₅-6 double bond. The spot of the compound on a filter paper soaked in a solution of antimony trichloride gives orange colour on treatment with sulphuric acid and acetic anhydride.

4. TETRANITROMETHANE TEST [56]

This test is specific for saponins possessing ethylenic double bond. A few milligrams of compound in CHCl₃ on treatment with 2-3 drops of tetranitromethane develop yellow colour.

5. CHLOROSULPHONIC ACID REAGENT TEST [27]

A brown coloured spot is developed on spraying the chromatogram of steroidal saponins with a mixture of chlorosulphonic acid : acetic acid (1:2) followed by heating for 5-10 minutes at 110°C. Fluorescence in long wave UV light is also observed.

6. LIEBERMANN-BURCHARD REAGENT TEST [28-29]

This test has been used with advantage in differentiating between the triterpenic and steroidal saponins. When to a hot solution of saponin in acetic anhydride a few drops of conc. sulphuric acid are added the resulting green to blue colour indicates triterpenoid
saponin, while a pink or purple colour indicates steroidal saponin.

7. CARBAZOLE TEST [30]

TLC plates on spraying with this reagent, prepared by adding 2 ml of concentrated $\text{H}_2\text{SO}_4$ in 10 ml of 1% solution of highly purified carbazole (crystallisation in benzene) in EtOH followed by heating (120°C for 5 min) develop reddish brown colour for triterpenoids and different colours with steroidal saponins.

8. ANISALDEHYDE REAGENT [15]

Steroidal saponins and sapogenins give yellow coloured spots on spraying the chromatogram with a solution of anisaldehyde (0.5 ml) in acetic acid (5 ml) containing concentrated $\text{H}_2\text{SO}_4$ (1 ml).

EXTRACTION, PURIFICATION AND CRYSTALLISATION

For the extraction of oligofurostanosides and oligospirostanosides, the air dried and powdered plant material is first extracted with pet. ether for 6 hrs usually 3 times to remove oily matter, chlorophyll and any neutral compounds and then with ethyl acetate thrice, 6 hrs each time, to remove colouring matters etc. Finally, the plant material is subjected to exhaustive methanol/ethanol extraction for 6 hrs, usually four times. The combined
alcoholic extract is concentrated under vacuum and examined for their contents with the help of TLC in suitable solvent systems.

The concentrated methanolic/ethanolic extract is dissolved in a minimum quantity of methanol and poured dropwise into large volumes of acetone with constant shaking to precipitate the oligofurostanosides and/or their artefacts. The purification is further achieved through column chromatography using different solvent systems and different adsorbents (Cf. TABLE-I).

Quantitative separation is generally achieved by column-chromatography, through elution in the order of increasing number of sugar molecules present in them. Thin layer (TLC) and Paper chromatographic (PC) techniques are generally employed to check the purity of these glycosides.

However, small quantities of saponins can also be separated through preparative TLC and PC. Generally, mixed solvents are used for the chromatographic separation of various saponin mixtures. Water saturated solvents afford better separation. The solvent systems containing chloroform, methanol and water in various proportions and silica gel as the adsorbent are most commonly employed.
TABLE - I

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>SOLVENT SYSTEM</th>
<th>NATURE OF STEROIDAL SAPONINS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Thin layer and Column chromatography:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica gel</td>
<td>CHCl$_3$:MeOH:H$_2$O 65:20-30:10</td>
<td>Non-polar [31-32]</td>
</tr>
<tr>
<td>Silica gel</td>
<td>CHCl$_3$:MeOH:H$_2$O 65:35:10</td>
<td>Neutral and non-polar [33]</td>
</tr>
<tr>
<td>Silica gel</td>
<td>EtAc:MeOH:H$_2$O 70:15:15</td>
<td>Acidic and neutral [34]</td>
</tr>
<tr>
<td>Silica gel</td>
<td>n-BuOH:EtOH:25% Ammonia sol. 60:13:30.5</td>
<td>Polar acidic [35]</td>
</tr>
<tr>
<td>Acidic silica</td>
<td>CHCl$_3$:MeOH:H$_2$O 65:35:10</td>
<td>Acidic [36]</td>
</tr>
<tr>
<td>Alumina (H$_2$O saturated)</td>
<td>Toluene:n-BuOH 2:1-1.4</td>
<td>Neutral [37]</td>
</tr>
<tr>
<td><strong>B. Paper and Column Chromatography:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paper (formamide impregnated, Whatman No.1)</td>
<td>CHCl$_3$:THF:C$_5$H$_5$N 10:10:2 (Formamide saturated)</td>
<td>Neutral [38-39]</td>
</tr>
<tr>
<td>Paper (Whatman No. 1)</td>
<td>Iso-BuOH:EtOH:Et$_2$NH:H$_2$O 5:5:1:4</td>
<td>Acidic [35]</td>
</tr>
<tr>
<td><strong>C. Gel Chromatography:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sephadex G-25 or G-50</td>
<td>Water</td>
<td>Saponins of different molecular sizes [40-41]</td>
</tr>
</tbody>
</table>
Two new techniques named as DCCC and HPLC are also frequently used now-a-days for these purposes.

(i) **DROPLET COUNTER CURRENT CHROMATOGRAPHY**

It is a support free separation technique developed by Tumimura et al. [42], employing the passage of droplets of mobile phase through stationary liquid phase and the solute is continuously partitioned between two phases.

The columns are filled with stationary phase and sample after dissolution in selected solvent is charged in sample chamber. The mobile phase is pumped through sample chamber as a result of which a stream of droplets is formed in immiscible stationary phase. These droplets are then allowed to move through the column, where partitioning of solute occurs in stationary and solute phase, resulting to the separation of components. However, binary systems are not much useful, hence, tertiary and quaternary systems are usually taken up for the preparation of two phases.

This technique has great advantages of taking less time, no loss of sample, separation of small quantity of samples, less requirements for sample purification and easy separation of closely resembling compounds and hence, has achieved significant importance in the isolation, purification and separation of saponins [43-45].
(ii) HIGH PERFORMANCE OR HIGH PRESSURE LIQUID CHROMATOGRAPHY

A liquid which is a mobile phase in HPLC is propagated through the column by pumps and the sample is introduced at the head of a column through an injector without disturbing the flow of mobile phase as well as column packing. A device called as detector senses and measures the sample component from column effluent. The response of the detector is recorded by a recording device. Now-a-days, a number of recording devices like chromatographic data system, integrator, computers can be linked with the HPLC and results obtained are essentially without errors.

GENERAL PROPERTIES OF SAPONINS

A. PHYSICAL PROPERTIES

1. State Amorphous
2. Mol. Wt. High
3. Mp. High, generally with decomposition
4. Solubility
   (a) Water Very high, foam copiously on shaking
   (b) Organic solvents (i) Inhibit foaming
       (ii) Insoluble in acetone, ether and other less polar solvents
       (iii) Soluble in alcohol but sapinins with less number of
sugars dissolve poorly.

(iv) Saponins with less number of sugars are fairly soluble in CHCl₃: MeOH or CHCl₃: MeOH : H₂O system.

5. Characteristic affects

(i) Cause sneezing
(ii) Bitter in taste
(iii) Haemolyse red blood corpuscles
(iv) Kill fishes
(v) Lower the surface tension
(vi) Form suspension of few substances
(vii) Dialyse with difficulty or not at all
(viii) Prevent sedimentation of finely divided particles.

B. CHEMICAL PROPERTIES

1. Complete acid With mineral acids and enzymes yield hydrolysis aglycone and glycone.

2. Partial hydrolysis Yield prosaponins with lesser number of sugar molecules i.e. lower saponins

3. Precipitation Precipitated by Pb(OAc)₂[49] and Ba(OH)₂[50]
4. Addition compound  With sterols [8,11,51-52] they form addition compounds and can be separated and purified by:
   (i) Boiling in xylene [51]
   (ii) Dissolving in pyridine [11] and extracting with ether
   (iii) Oligofurostanosides do not form any complex with cholesterol [8, 52]

5. Oxidising agents  (i) Break down the carbon ring system [9, 17, 20-21, 53]

6. Dehydrogenation  With Zn-dust or Selenium
   (i) Steroidal saponins give Diels' hydrocarbon [1-3]
   (ii) Triterpenic saponins give naphthalene and picene derivatives

C. BIOLOGICAL PROPERTIES [39]
1. Pharmacological
   (i) Antitumour activity [55-56]
   (ii) Antinarcotic effect [57]
   (iii) Anticancer activity [58]
   (iv) Anti inflammatory activity [59-61]
   (v) Antiulcer activity [62]
   (vi) Antifatigue activity [63]
(vii) Antibiotic activity [64-65]
(viii) Antimiotic activity [66]
(ix) Anticoagulant effect [67]
(x) Antiexudative property [68]
(xi) Antifeedant activity [69]
(xii) Antihypertensive activity [70]
(xiii) Decrease cholesterial intestinal absorption [71]
(xiv) Detoxification effect on the liver [72]
(xv) Exhibit sedative and tranquillizing action in animals [173-74]
(xvi) Antiviral activity against influenza type virus [75]
(xvii) Tested against reticulifermes flavipes and strongly inhibited in verocity of termites [76]
(xviii) Lowers γ-globulin in blood serum [77]
(xix) Analgesic, anticonvulsent and antipyretic activities [78]
(xx) Possess cholenergic, histamin, atropin and papaverine like activities [79]
(xxi) Molluscicidal activity [68, 80-81]

(xxii) Steroidal saponins and cholesterol complex of these compounds show fungitoxicity [81-90]

(xxiii) Furostanosides show lesser fungicidal as well as haemolytic activity than spirostanosides [8-9, 19, 91]

(xxiv) Possess activity in vitro against many RNA and DNA viruses [92]

(xxv) Possess activity against JTC-26 (originating from human carcinoma) [93]

(xxvi) Inhibitory activity on cAMP phosphodiesterase [94-95]

USES OF SAPONINS

1. Foaming property, Manufacture of gloss and foam
   lowering surface producing substances viz. shaving
   tension and non- soaps, tooth pastes [96],
   alkaline nature shampoos, cosmetics [97], shoe
   and nail polishes, photographic films and in paper industry [98].
2. Therapeutic
Saponins are used as expectorants, diuretics and antisyphilitics [99]

3. Agricultural
Good fungicides as these are harmless to human beings and preferred over chlorine and nitrogen containing fungicides available in the market [81-90].

4. Other uses
(i) For the production of oral contraceptives [100]
(ii) For the manufacture of sex hormones, cortisones, pregnanes and many other related drugs.
(iii) Separation of hydrocarbons by liquid membrane extractions [101]
(iv) In anti incendiary emulsions [102]
(v) Concrete setting [103]
(vi) For poultry, production of eggs with low cholesterol contents [104]

STRUCTURE DETERMINATION

The structure determination of oligofurostanosides involves the following methods:
1. ENZYMATIC HYDROLYSIS [9, 19]

Enzymatic hydrolysis with β-glucosidase cleaves off the β-linked glucose at C26 (in almost all cases with only a few exceptions) leading to the cyclisation of the ring 'F' with C22-OH and formation of oligospirostanoside. If β-D-glucose is the terminal sugar of the sugar chain attached at C3 of the aglycone, it will also be liberated leading to the formation of lower oligofurostanosides/ furostanosides/ oligospirostanosides etc.

2. ACID HYDROLYSIS [105-107]

Oligofurostanosides on complete hydrolysis with 8-10% mineral acid yield a steroidal sapogenin and the monosaccharides (sugars) and/or their oxidation products. The genin is identified by mp, mmp, Co-TLC, IR, NMR, MS and also by converting it into acetate and its mp etc. Neutralised aqueous sugar solution after conc. under vac. at 40-50°C is subjected to descending paper chromatography [108-110] on Whatman filter paper No-1 using the solvent systems, n-BuOH AcOH : H2O (4:1:5); EtAc : Py : H2O (10:4:3); n-BuOH : Py : H2O (75:15:10) etc. to identify the sugars. The spots are visualised by spraying with reagents like aniline-hydrogen phthalate, p-aniline hydrochloride, ammonical silver nitrate solution etc.
3. KILIANI HYDROLYSIS [111]

In order to find out the sequence of sugars in the glycone moiety the oligofurostanoside is subjected to hydrolysis with Kiliani mixture (AcOH : H₂O : 35% HCl, 35:55:10) at room temp. The sugars liberated with the run of time are studied by PC. The sugars are liberated from the sugar chain(s) starting from the outermost sugar(s) of the chain(s) towards the aglycone. Further, if two or more than two spots are obtained with the run of time, at one particular moment, branching in the sugar moiety is indicated.

4. REDUCTION FOLLOWED BY HYDROLYSIS [9, 18]

Discussed under detection of oligofurostanosides (Sr. No.-2, page-9).

5. CrO₃ OXIDATION [9,20-21, 112]

The form of ring 'F' as well as the nature and number of sugars attached to C₂₆ of the oligofurostanoside can elegantly be proved by CrO₃ oxidation. The oligofurostanoside is converted to peracetate Δ²₀(22) through acetylation followed by the removal of a molecule of H₂O or MeOH by heating in AcOH, which on oxidation with CrO₃ in AcOH gives an oxidised product. The basic hydrolysis (t-BuOH/KOH) of this product affords 6-hydroxy-γ-methyl n-valeric acid glucoside, which contains the sugar unit glycosidated at C₂₆ of the sapogenin. A survey of literature showed that so far
\(\beta\)-linked D-glucose has only been found to be attached at \(C_26\) (a few exceptions). Another product obtained by alkaline hydrolysis is a glycoside containing the main sugar chain(s) of the parent glycoside intact, which on acid hydrolysis yields the corresponding pregnolone and sugars attached at \(C_3\).

6. **BAEYER-VILLIGER-OXIDATION [14, 20]**

Similar to \(CrO_3\) oxidation, the structure of the side chain in oligofurostanoside can also be confirmed by the Baeyer-Villiger oxidation using \(H_2O_2\)-formic acid/ acetic acid whereby, \(5\alpha, 5\beta, 6\alpha, 6\beta, 16\alpha, 20\alpha\) pentanol tetraacetate is obtained instead of pregnolone.

7. **PERMETHYLATION**

The positions of attachment of various sugars with each other as well as with the aglycone are determined by permethylation of oligofurostanoside and methanolysis/hydrolysis studies of the permethylated derivatives. Permethylation is generally carried out by Purdie [113] (\(Ag_2O\) and MeI), Kuhn [114] (\(BaO, Ba(OH)_2\) and MeI/DMSO) and Hakomori [115] (\(NaH, DMSO\) and MeI/N\(_2\) atm.) methods, out of which the latter yields better results.

The permethylated saponins on methanolysis in dry MeOH:HCl (5-10% V/V) give a mixture of methyl methylated sugars, which can be identified and estimated by GLC [21, 112] by comparison of their retention times with authentic
samples. Position(s) of the free hydroxyl group(s) in the methyl methylated sugars show the attachment of different sugars with each other. The methyl methylated sugars can also be identified by their MS [116-118] and NMR[119] studies. The vicinal branching in the sugar moiety can also be determined alternatively through periodate oxidation studies of the methyl methylated sugars, whereby the corresponding methyl methylated sugars disappear. The PC and isolation studies [19] of the methylated sugars, obtained by the hydrolysis of the methyl methylated sugars confirm the linkages of different sugars with each other.

Most commonly employed solvent systems for better PC resolution of methylated sugars are: n-BuOH : EtOH : H$_2$O(5:1:4) [110], 2-butanone saturated with 2% NH$_3$ [120] and Benzene : EtOH : H$_2$O : Ammonia (200:47:14:1) [121]. Aniline hydrogen phthalate is generally used as the developing reagent. Methylated sugars have also been studied by TLC [39, 122-123] on silica gel and cellulose.

8. PARTIAL HYDROLYSIS[124-126]

An oligofurostanoside containing a large number of sugars is difficult to handle for its glycone moiety's structure determination, since it may involve a good number of branchings. In such cases, the oligofurostanoside is partially hydrolysed by refluxing it with 5% aq. H$_2$SO$_4$-MeOH on steam bath for 30 min. or 1N-HCl-MeOH on steam bath for
40 min. Usual work up yields the liberated sugars and a mixture of lower glycosides. These new glycosides are then permethylated and subjected to methanolysis followed by hydrolysis. The resulting methyl-methylated sugars/methylated sugars are identified by PC and compared with those obtained from the permethylated oligofurostanoside to fix up the exact linkages between the sugars themselves and with the aglycone.

9. MOLECULAR ROTATION

The α- and β-configurations of different sugars in the oligofurostanosides have been proved by molecular rotation values [127-129]. For calculating the theoretical values, the aglycone contribution is calculated from the known values of the corresponding methyl sugars. The best befitting theoretical and experimental molecular rotation values give the configuration of the particular sugar.

<table>
<thead>
<tr>
<th>Methyl Sugars</th>
<th>[M]_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-methyl-D-glucopyranoside</td>
<td>-66°</td>
</tr>
<tr>
<td>α-methyl-D-glucopyranoside</td>
<td>+309°</td>
</tr>
<tr>
<td>β-methyl-D-galactopyranoside</td>
<td>+10°</td>
</tr>
<tr>
<td>α-methyl-D-galactopyranoside</td>
<td>+380°</td>
</tr>
<tr>
<td>β-methyl-D-xylopyranoside</td>
<td>-108°</td>
</tr>
<tr>
<td>α-methyl-D-xylopyranoside</td>
<td>+253°</td>
</tr>
<tr>
<td>β-methyl-L-arabinopyranoside</td>
<td>+403°</td>
</tr>
<tr>
<td>α-methyl-L-arabinopyranoside</td>
<td>+28°</td>
</tr>
<tr>
<td>β-methyl-L-rhamnopyranoside</td>
<td>+170°</td>
</tr>
<tr>
<td>α-methyl-L-rhamnopyranoside</td>
<td>-111°</td>
</tr>
</tbody>
</table>
10. ORD AND CD

From the sign and shape of the ORD and CD curves, not only the carbonyl groups in the different positions in the steroidal aglycone can be located but also their chemical environment be traced easily [130-141]. Some of the generalisations provided by these studies are as follows:

1. Alternation of A/B ring junction does not affect the rotatory dispersion curve to any appreciable extent.

2. Sapogenins with 22α-configurations with weak chromophores (-OH, isolated >C=C<) give -ve plain curves and those having 22β -configuration give +ve plain curves.

3. Introduction of carbonyl group at C3, C11, C12 and C13 affects the -ve rotation by a strongly +ve one.

4. Change in the stereochemistry at C8 and C14 does not appreciably affect the shapes of the curves.

11. UV-SPECTROSCOPY

This technique has very successfully been used for the detection of ethylenic bond (193-205 nm, depending upon the position and environment of the double bond) and the carbonyl chromophores (λmax and εmax values and the well defined additional band at approximately 280 nm) in steroidal compounds [142-146].
12. IR SPECTROSCOPY

IR spectra has provided valuable informations about the structural features, various functional groups and stereochemistry at various centres of oligofuro- and oligospirostanosides as well as their aglycones [15,19-21, 147-156] e.g.

1. The presence of spiroketal system is visualised by the presence of four characteristic bands around 980, 920, 900 and 860 cm$^{-1}$. In case of (25S) 920 cm$^{-1}$ band is stronger than 900 cm$^{-1}$ and in case of (25R) 900 cm$^{-1}$ band is stronger than 920 cm$^{-1}$.

2. Open 'F' ring compounds have either no or broader and fewer above characteristic bands but also their bands below 2830 cm$^{-1}$ are shifted to lower frequency.

3. The absence of any one of the spiroketal band usually means the absence of ring 'F'.

4. A band at about 1240 cm$^{-1}$ indicates trans A/B ring junction or $\Delta^5$ unsaturation.

5. The intensities of the typical spiroketal absorptions are reduced to a great extent by the presence of substitution in ring 'F'.

13. NMR SPECTROSCOPY [157]

(i) $^1$H-NMR

The $^1$H-NMR study of steroidal sapogenins in deuterio-chloroform is particularly of great help in stereochemical assignments [158] e.g.
1. In (25R)-methyl series, the equatorial (25R)-methyl protons resonate at a higher field than the C_{20}-methyl protons.

2. The equatorial (25R)-methyl protons resonate at a higher field than the corresponding axial (25R)-methyl protons.

In pyridine solution the spectral differences between (25R)- and (25S)-methyl series became more distinct [159], further supported by Tori and Aono [160], who also showed the validity of Zürcher's additivity rules [161] by studying the effect of substituents on the positions of the proton signals for the four methyl groups.

In $^1$H-NMR study of oligofurostanosides etc. also throws much light on the structure of the glycoside molecule. The linkages ($^\alpha$-or-$^\beta$) [20-22, 162-164] of various sugars in saponins are very precisely given by the signals and coupling constants of the anomeric protons of sugars. The measurements are usually made indirectly, via the spectra of oligoglycoside permethylates which are soluble in CHCl$_3$. A few generalisations are summarised as follows:

1. The anomeric protons of various sugars give peaks in down field region ($^\delta$4.0-6.30).

2. D-sugars generally occur with $^\beta$-linkages and are characterised by their high coupling constants ($^\text{J}$, 6-9Hz).
3. The rarely occurring $\alpha$-linkages of corresponding sugars have low coupling constants ($J$, 2-4 Hz).
4. The coupling constants of the commonly $\alpha$-linked occurring sugars, L-rhamnose and L-arabinose are $J_{\alpha} \approx 2$ Hz and $J_{\alpha} \approx 6-8$ Hz respectively.
5. The furostanolic nature of oligofurostanosides is shown [20, 22] by 22-OMe signals at about $\delta 3.25$ ppm.

(ii) $^{13}$C-NMR

This technique provides a non-destructive way for the characterisation and identification of an oligofuro-and oligospirostanoside. For structure elucidation of new compounds by $^{13}$C-NMR studies, it is always desirable to compare the observed data with the recorded data for model and related compounds. Mahato et al. [165] utilised $^{13}$C-NMR for the structure elucidation of dioscin and gracillin by a comparison of their peaks with those of their aglycone diosgenin and the sugar moieties using known chemical shifts [166]. Characteristic chemical shifts are observed for $\alpha$- and $\beta$ positions of the -OH group where glycosidation takes place.

Thakur and Agrawal et al. [167] have compiled the $^{13}$C-NMR chemical shifts of naturally occurring oligofuro-and oligospirostanosides. In general, $^{13}$C-NMR spectra are recorded under proton-noise (broad band) decoupling [168] in order to avoid signal overlapping. Usually, $^{13}$C-NMR shielding
is not very sensitive to solvent but as solute-solvent interactions occur, hence change in chemical shifts can be observed. To avoid this change mainly chloroform and pyridine solvents are used [169].

$^{13}$C-NMR spectral data of the oligofurostanosides differs significantly from that of the oligospirostanosides, particularly in the chemical shifts for carbon atoms of ring 'E' and 'F'. Oligofurostanosides exhibit C$_{22}$ peaks at 110.8 ppm and at 113.5 ppm for C$_{22}$-OH and C$_{22}$-OMe derivative respectively. The C$_{22}$-OMe signals usually occur at 47.2±0.2 [170-171] though in a few cases at 56.5 ppm [172]. TABLE-II shows the chemical shifts for the parent steroidal skeleton [173]. These values show that the chemical shifts for the ring 'A' and 'B' carbon atoms are markedly affected, hence helpful for differentiating 5$\alpha$, 5$\beta$ and $\Delta^5$ steroidal sapogenins because the signals for C$_5$ and C$_{19}$ exhibit more variation.

The number of anomeric signals determine the number of sugars. The matching values of these signals in the same solvent lead to their identification [174-176] as solvents alter the chemical shift markedly [177-178]. Furanose sugars are distinguished by chemical shifts for C$_1$, C$_2$ and C$_4$ by 4-14 ppm down field where as C$_5$ by 4-7 ppm upfield as compared to the pyranose form [177, 179].
### TABLE -II

**$^{13}$C-NMR Chemical shifts**

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* Values derived by comparisons of the data in various references.
A close resemblance of the chemical shifts due to a terminal sugar with respect to a methyl-0-glycoside leads to its characterisation, whereas chemical shifts of inner sugars differ significantly in comparison to methyl-0-glycoside due to $\alpha$-$\beta$ effects of the glycosidation [180]. The glycosidation causes a down field shifts of 4.2-8.5 ppm of the $\alpha$-carbon, the hydroxyl of which has been directly involved in the glycosidation while neighbouring $\beta$-carbon atom shows an upfield shift of 0.05-2.0 ppm in oligoglycosides. The upfield shifts of the $\beta$-carbon atoms are quite informative but less consistent, whereas the down field shift of the $\alpha$-carbon is characteristic enough for the establishment of inter-glycosidic ($\alpha, \beta$) linkages.

$^{13}$C-NMR of pyranoside reveals that the coupling constant for the anomeric carbon atom strictly depends upon the orientation of anomeric hydrogen. The one bond coupling constants for $C_2$ to $C_6$ of sugars vary in the range of 142-148 Hz while the anomeric carbon exhibits a larger value of 160-175 Hz [181-182]. For pyranose with a axial $H_1$ ($\beta$-anomer, 160 Hz) the value is about 10 Hz lower than the corresponding value in equatorial $H_1$ ($\alpha$-anomer, 170 Hz).

The point of attachment of sugar with the aglycone leads to the down field shift of the $\alpha$-carbon atom and upfield shift of adjacent carbon atom [183-187]. In most of the cases ($C_3$-sugar chain) it is 6.6+1.0 ppm down field
shift with lower shielding of $C_2 (1.1-3.0 \text{ ppm})$ than $C_4 (1.8-4.6 \text{ ppm})$. In oligofurostanosides, in most of the cases having D-glucose at $C_{26}$, a $6.8 \pm 0.3 \text{ ppm}$ down field shift along with usual $1.8 \pm 0.4 \text{ ppm}$ upfield shift of $C_{25}$ has been observed. TABLE-III shows the $^{13}$C-NMR chemical shifts and $J_{CH}$ values (in parentheses) of methyl glycopyranosides which commonly occur in oligofurostanosides (D$_2$O as a solvent).

The application and utility of this technique can be exemplified by the structure elucidation of Chloromaloside-A and Chloromaloside-B [188].
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### $^{13}$C NMR Chemical shifts of sugar moieties in Py.

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13C-NMR chemical shifts of aglycone moieties in Py

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<td>24</td>
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<td>28.2</td>
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<tr>
<td>OMe</td>
<td>--</td>
<td>47.4</td>
</tr>
</tbody>
</table>

(iii) 2D-NMR [157]

Two dimensional NMR, now-a-days has become a major tool, to determine the sequence of different sugar molecules in various glycosides by the following two techniques:

(a) COSY : Homonuclear correlation spectroscopy

(b) NOESY : Heteronuclear correlation spectroscopy
COSY [189-192) reveals to interpretation connectivities and hence, identifies the location of the branching points of each sugar in the glycoside molecule. Counting of protons and determining the coupling constants reveal the nature of individual sugars. Usually, 1-D-normal spectrum, 2-D-COSY and 2-D long range COSY are sufficient to identify the sequence of the sugars in reasonably complex steroidal saponins [193]. The observation of typical splitting patterns for characteristic protons H(5) of glucose, rhamnose, arabinose and xylose provides a short cut for the identification of sugars.

NOESY spectrum [194] reveals the Nuclear Over-hauser Effect [NOE] between intra- and inter-protons of sugar molecules, which makes the identification of monosaccharides and their sequencing even more easy.

14. MASS SPECTROMETRY

Mass spectrometry is an important technique for establishing the structure of sapogenins and their glycosides. All techniques i.e. EIMS, FDMS, D/CIMS, FABMS and Unimolecular MIKE have been utilised for this purpose with great success.

(a) EIMS

EIMS not only furnishes the correct molecular weight but also indicates the positions of certain substituents in
sapogenins by comparing the characteristic ion peaks with those of unsubstituted standard sapogenins [195-202]. The characteristic fragmentation pattern of these compounds differentiates them from other classes of compounds. Substituents in the molecule induce a shift in the ion peaks according to their molecular weights. Stereochemical changes in the skeleton cause significant changes in mass fragmentation.

EIMS of permethylated oligofurostanosides and oligospirostanoid s [22, 202] also impart invaluable information about the sequence of sugars in the glycone part through the characteristic ion peaks as:

<table>
<thead>
<tr>
<th>m/z</th>
<th>sugars</th>
</tr>
</thead>
<tbody>
<tr>
<td>219,187</td>
<td>D-Glucose</td>
</tr>
<tr>
<td>189,157</td>
<td>L-Rhamnose</td>
</tr>
<tr>
<td>175,143</td>
<td>L-Arabinose or D-Xylose</td>
</tr>
<tr>
<td>331</td>
<td>D-Glucose peracetate</td>
</tr>
<tr>
<td>273</td>
<td>L-Rhamnose peracetate</td>
</tr>
<tr>
<td>259</td>
<td>D-Xylose peracetate</td>
</tr>
</tbody>
</table>

(b) FDMS

To overcome the difficulties in EIMS like, derivatisation of glycoside, evaporation, thermal excitation and unsuitability for substances of low volatility, extensive fragmentation with small or undetectable molecule
ion abundances and no molecular ion peaks from oligofuro- and oligospirostanosides, modern techniques like CI (Chemical Ionisation) [203-205] and FI (Field Ionisation) [206] have been used. However, the thermal stress required for evaporation can't be avoided with these methods which may cause complete decomposition of the sample prior to ionisation.

FDMS [207], although only a recent offspring of Field Ionisation mass spectrometry has been found to be highly useful for the structure elucidation of non-volatile and thermally labile substances. In this method, the sample is absorbed on the emitter in a solid layer and is then ionised in the absorbed state. FDMS gives important informations about the sequence of the sugar moities present in the glycoside with only a few peaks in comparison to those present in the EIMS spectrum and hence, it is easy to interpret.

Inorganic impurities mostly alkali halides, present in the plant glycosides, play an important role in the formation of ions. After a detailed study of FDMS of a series of oligofuro- and oligospirostanosides [208-213] following generalisations have been drawn:

(i) Alkali metal ions cationisation leads to the formation of most intense [M+Na]+ and less intense [M+K]+ peaks.
(ii) Sometimes less intense \([M+2Na]^{++}\) ions are also recorded.

(iii) \([M]^+\) and \([M+H]^+\) ion, though formed, are very uncommon.

(iv) The molecular ion peak for the loss of terminal sugar is also observed.

(v) Simultaneous losses of two sugars from different positions of branched glycone moiety of oligofuro- and oligospirostanosides are observed as less intense peaks.

(vi) Cleavage of sugar units at glycosidic oxygen has been explained by analogy with well established mechanism of solvolysis in solution chemistry. The \([H]^+\) ion may be generated by chemically induced reactions.

(vii) The cleavage of O-glycoside bond between the aglycone and the sugar attached to it is observed \([208, 210]\)

The application and utility of this technique can easily be exemplified by the structure elucidation of Sprengeroside-B \([6]\) as follows:
Sprengeroside-B

(a) m/z 1069 [(M+K)-MeOH]⁺, 1053 [(M+Na)-MeOH]⁺ (base peak) and 538[(M-MeOH)+2Na]++ not only confirm the purity but also prove the presence of C₁₂ methoxy group.

(b) The molecular ion peak at m/z 1062 is also observed.

(c) The peaks at m/z 939[(M+Na)-146]⁺ and 793 [(M+Na)-(146+146)]⁺ confirm the presence of two terminal rhamnose units.

(d) The peaks at m/z 923 [(M+Na)-162]⁺ and 777[(M+Na)-(162+146)]⁺ prove the presence of terminal glucose and a terminal rhamnose unit.

(e) The peaks displayed at m/z 613[(M+Na+H₂O)-454]⁺ confirm the complete sugar chain at C₃ of aglycone.

(f) The results clearly establish the structure as:

\[
\text{rha} \rightarrow \text{glu-(C₃)} \rightarrow \text{diosgenin-glu(C₂₆)}, \ C₂₂-\text{OMe}
\]
(C) D/CIMS

As compared to few informations obtained from FDMS the new technique D/CIMS [214-215] is more informative. The measurements are carried out on a quadrupole MS equipment with ammonia feedline. The emitter is a coiled tungsten wire where the solubilised sample is applied. Ammonia is generally used as the reactant gas since, it provides a softer ionisation than methane or isobutane and thus gives invaluable informations. The main advantages of this technique over FDMS and EIMS are:

(i) Exact molecular weight of glycoside is obtained.
(ii) No derivatisation of glycoside is required.
(iii) Sequence of sugars is also established.
(iv) The characteristic fragmentations of sapogenins are also obtained which are not predominantly present in FDMS.

(D) FABMS

Barber et al. [216] invented the technique of FABMS in 1981 to overcome some of the problems of FDMS as it was difficult in practice and the ions providing molecular weight information were produced only transiently. In FABMS an ion surface is developed to accommodate the solid materials and the phenomenon of ion sputtering employing a beam of fast neutral atom, especially of Ar of 2-8 KeV as the primary particles is used. The sample is normally
dissolved in glycerol/m-nitrobenzyl alcohol (matrix) to facilitate the production of sample ions in high abundance for relatively long periods. Molecular weight information is usually obtained from \([\text{M+H}]^+\) ions in +ve ion spectrum and from \([\text{M-H}]^-\) ion in -ve ion spectrum. Odd-electrons molecular ions are not normally produced in abundance which give structural informations. Barber et al. believed that the \([\text{M+H}]^+\) and \([\text{M-H}]^-\) ions are either formed by proton transfer reactions which may occur as the molecules are bombarded and pass into gas phase or those already existing in matrix.

FABMS exhibit protonated or sodium adduct \([217]\) molecular ions, which gave a series of characteristic fragment ions promising to give a clear picture for defining the sequence of constituents of sugar moieties of the glycosides and also for identifying the glycone (sugars).

Sharma et al. [6], have for the first time successfully used this technique for structure elucidation of oligofurostanosides. FABMS has been found to have some specific advantages viz:

(i) Mass spectra of molecules with relatively high molecular weight can easily be obtained.

(ii) Volatilisation of sample is not required and so no thermal effects are observed.
(iii) No sample derivatisation is required.
(iv) The method works in either polarity and gives pseudomolecular ion sensitivity with structurally significant fragmentation.
(v) Ionisation occurs from the solid at room temperature.

The application and utility of this technique can be explained by the structure determination of Sprengeroside-E
[6]

\[
\text{Sprengeroside-E}
\]

(a) Molecular ion peak m/z 595\([M+H]^+\) was observed.
(b) The peak at m/z 397\([M+H]-(162+2H_2O)]^+\) suggested the presence of one terminal glucose and two free-OH groups.
(c) The peak at m/z 577\([(M+H)-H_2O]^+\) seems to be observed due to the formation of the following fragment.
All these results clearly established the structure of Sprengeroside-E as given above.

(E) UNIMOLECULAR-MIKE METHOD [218]

The distinction between A/B and C/D cis and trans isomers is usually not possible by normal EIMS, which consists of reaction products formed in ion source from high energy reactions in a few microseconds or less. However, the possibility of more stereochemical information might be forthcoming for lower energy reactions, occurring in Unimolecular Mass Analyzed Ion Kinetic Energy (MIKE) Spectrometry. This is because

(i) The spectra are simpler being only the reaction products of one ion e.g. molecular ion.

(ii) The occurrence of unimolecular reactions of metastable ion is very sensitive to change in the critical energies of these reactions.

By the study of MIKE spectra of various steroidal compounds, the following generalisation have been carried out:
(a) For cis A/B ring junction ($5^\beta$) the change in critical energy for reaction involving $C_{19}$ methyl group loss is less as compared to trans A/B ring junction ($5^\alpha$).

(b) For cis C/D ring junction ($14^\beta$) the change in critical energy for the reaction involving $C_{18}$ methyl group loss is greater as compared to trans C/D ring junction ($14^\alpha$).

A list of the furostanol saponins reported till 1993, from various plants is tabulated below:
Structure of aglycone (FUROSTANOL)

1. (25S)-5α-furostan-3β-amino-22α, 26-diol
2. (25S)-5α-furostan-12-on-3β, 22α, 26-triol
3. (25R)-5α-furostan-3β, 22α, 26-tetrol
4. (25R)-5α-furostan-2β, 3β, 22α, 26-teratol
5. (25R)-5α-furostan-12-on-3β, 22α, 26-triol
6. (25R)-5α-furostan-2β, 3β, 6β, 22α, 26-pentaol
7. (25S)-5α-furostan-2α, 3β, 6β, 22α, 26-pentaol
8. (25R)-5α-furostan-3β, 22α, 26-tetatol
9. (25R)-5α-furostan-2α-OBZ, 3β, 5α, 6β, 22α, 26-pentaol
10. (25S)-5α-furostan-3β, 22α, 26-triol
11. (25R)-5α-furostan-6-on-3β, 22α, 26-triol
12. (25S)-5β-furostan-3β, 22α, 26-triol
13. (25R)-5β-furostan-1β, 2β, 3α, 22α, 26-pentaol
14. (25R)-5β-furostan-2β, 3α, 22α, 26-tetrol
15. (25S)-5β-furostan-2β, 3α, 22α, 26-tetrol
16. (25R)-5β-furostan-2β, 3β, 11α, 22α, 26-pentaol
17. (25S)-5β-furostan-1β, 3α, 4β, 5β, 22α, 26-hexaol
18. (25S)-5β-furostan-1β, 2β, 3α, 4β, 5β, 22α, 26-heptaol
19. (25R) -furost-5-en-3β, 22α, 26-triol
20. (25S) -furost-5-en-3β, 22α, 26-triol

Corresponding spirostanol (F Ring closed)

Jurubidine
Neohecogenin
Tigogenin
Gitogenin
Hecogenin
Agigenin
Neaagigenin
β-Chlorogenin
Karatavegenin
Neotigogenin
Laxogenin
Sarsasapogenin
Tokorogenin
Yonogenin
Neoyonogenin
Metagenin
Convellagenin-B
Neopentologenin
Diosgenin
Yamogenin
21 (25R) -furost-5-en-2\(\alpha\),3\(\beta\),22\(\alpha\),26-tetraol  Yuccagenin
22 (25R) -furost-5-en-3\(\beta\),17\(\alpha\),22\(\alpha\),26-tetraol  Pennogenin
23 (25R) -furost-5-en-1\(\beta\),3\(\beta\),22\(\alpha\),26-tetraol  Rescogenin
24 (25S) -furost-5-en-1\(\beta\),3\(\beta\),22\(\alpha\),26-tetraol  Neorescogenin
25 (25R) -furost-5-en-3\(\beta\),17\(\alpha\),22\(\alpha\),26-tetraol  Gentrogenin
26 (25R) -furost-5-en-3\(\beta\),14\(\alpha\),22\(\alpha\),26-tetraol  Prazerigenin-A
27 (25S) -furost-5-en-3\(\beta\),14\(\alpha\),22\(\alpha\),26-tetraol  Neoprazerigenin-A
28 5\(\beta\)-furost-25(27)-en-3\(\beta\),22\(\alpha\),26-triol  Macranthogenin
29 5\(\beta\)-furost-25(27)-en-1\(\beta\),3\(\beta\),22\(\alpha\),26-tetraol  Convallamarogenin
30 furost-5,25(27)-dien-1\(\beta\),3\(\beta\),22\(\alpha\),26-tetraol  \(\Delta\)Convallamarogenin
31 (25R)-5\(\alpha\)-furostan-26-O-acetyl-3\(\beta\),14\(\alpha\),17\(\alpha\),22\(\alpha\),26-pentaol --
32 (25R)-5\(\alpha\)-furostan-26-O-acetyl-3\(\beta\),17\(\alpha\),22\(\alpha\),26-pentaol --
33 (25S)-5\(\beta\)-furostan-4\(\beta\)-acetoxy-2\(\beta\),3\(\alpha\),22\(\alpha\),26-tetraol  Diotigenin-4-acetate

34 17(20)Dehydrocryptogenin
35 Pseudodosgenin(25R)
<table>
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<tr>
<th>S.No.</th>
<th>SOURCE (Part)</th>
<th>SAPONIN (m.p.°C; [α]D&lt;sup&gt;0&lt;/sup&gt;)</th>
<th>STRUCTURE</th>
<th>REFERENCE</th>
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<tbody>
<tr>
<td>1.</td>
<td><em>Agave americana</em> (Lf)</td>
<td>Agavoside-C</td>
<td>rha&lt;sub&gt;3&lt;/sub&gt;glu&lt;sup&gt;4&lt;/sup&gt;glu-gal-O-&lt;sup&gt;3&lt;/sup&gt;[5]; R=H</td>
<td>219-220</td>
</tr>
<tr>
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<td></td>
<td>Agavoside-H 228-30;-113(MeOH)</td>
<td>rha&lt;sub&gt;4&lt;/sub&gt;rha&lt;sub&gt;3&lt;/sub&gt;glu&lt;sup&gt;4&lt;/sup&gt;glu-gal-O-&lt;sup&gt;3&lt;/sup&gt;[5]; R=H</td>
<td>219-221</td>
</tr>
<tr>
<td>2.</td>
<td><em>Allium ampeloprasus</em></td>
<td>Ampeloside-BF&lt;sub&gt;1&lt;/sub&gt;</td>
<td>glu&lt;sup&gt;3&lt;/sup&gt;glu&lt;sup&gt;4&lt;/sup&gt;glu-gal-O-&lt;sup&gt;3&lt;/sup&gt;[6]; R=H</td>
<td>222</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ampeloside-BF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>glu&lt;sup&gt;4&lt;/sup&gt;gal-O-&lt;sup&gt;3&lt;/sup&gt;[6]; R=H</td>
<td>222</td>
</tr>
<tr>
<td>3.</td>
<td><em>Allium karataviense</em> (Lf)</td>
<td>Karatavioside-C</td>
<td>xyl&lt;sub&gt;3&lt;/sub&gt;glu&lt;sup&gt;4&lt;/sup&gt;glu-gal-O-&lt;sup&gt;3&lt;/sup&gt;[21]; R=H</td>
<td>223</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Karatavegenin-&lt;sub&gt;-glucoside&lt;/sub&gt; 294-98</td>
<td>glu-O-&lt;sup&gt;3&lt;/sup&gt;[9]; R=H</td>
<td>224</td>
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<td><em>Allium narcissiflorum</em></td>
<td>Alliumoside-B</td>
<td>glu&lt;sup&gt;3&lt;/sup&gt;glu&lt;sup&gt;3&lt;/sup&gt;glu-O-&lt;sup&gt;3&lt;/sup&gt;[19]; R=H</td>
<td>225</td>
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<td></td>
<td></td>
<td>Alliumoside-C</td>
<td>rha-rha-rha-gal-O-&lt;sup&gt;3&lt;/sup&gt;[19]; R=H</td>
<td>225</td>
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<td>Alliumoside-D</td>
<td>glu&lt;sup&gt;3&lt;/sup&gt;rha-rha-glu&lt;sup&gt;2&lt;/sup&gt;O-&lt;sup&gt;3&lt;/sup&gt;[19]; R=H</td>
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<td>Alliumoside-E</td>
<td>glu&lt;sup&gt;4&lt;/sup&gt;rha-rha-glu&lt;sup&gt;2&lt;/sup&gt;O-&lt;sup&gt;3&lt;/sup&gt;[19]; R=H</td>
<td>225</td>
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<td>5.</td>
<td>Allium ostowskianum</td>
<td>Glycoside-B</td>
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<td>(Blb)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>glu&lt;sub&gt;3&lt;/sub&gt;glu&lt;sub&gt;6&lt;/sub&gt;glu&lt;sub&gt;-0&lt;/sub&gt;-3[19]; R=H 226</td>
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<tr>
<th>6.</th>
<th>Allium sativum</th>
<th>Protoeruboside-B</th>
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<tr>
<td></td>
<td>(Blb)</td>
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<td>glu&lt;sub&gt;2&lt;/sub&gt;glu&lt;sub&gt;2&lt;/sub&gt;glu&lt;sub&gt;4&lt;/sub&gt;gal-0-3[6,7]; R=Me 227</td>
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<th>7.</th>
<th>Allium schubertii</th>
<th>Aginoside &amp; Turcoside-A</th>
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<tbody>
<tr>
<td></td>
<td>(Blb)</td>
<td>-34.5(Py)</td>
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<td></td>
<td></td>
<td>xyl&lt;sub&gt;3&lt;/sub&gt;glu&lt;sub&gt;4&lt;/sub&gt;gal-0-3[6,7]; R=H 229</td>
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<tr>
<th>8.</th>
<th>Allium turcomanicum</th>
<th>Turoside-C</th>
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<tbody>
<tr>
<td></td>
<td>(Blb)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>glu&lt;sub&gt;2&lt;/sub&gt;glu&lt;sub&gt;2&lt;/sub&gt;glu&lt;sub&gt;4&lt;/sub&gt;gal-0-3[7]; R=H 230</td>
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<thead>
<tr>
<th>9.</th>
<th>Anemarrhena asphodeloides</th>
<th>Anemarsaponin-B</th>
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<tbody>
<tr>
<td></td>
<td>(Rh)</td>
<td>226</td>
</tr>
<tr>
<td></td>
<td></td>
<td>glu&lt;sub&gt;2&lt;/sub&gt;gal-0-3[35]; 231</td>
</tr>
</tbody>
</table>

<table>
<thead>
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<th>10.</th>
<th>Arecastrum romanoffianum</th>
<th>Methyl proto Pb</th>
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<tbody>
<tr>
<td></td>
<td>(Lf)</td>
<td>192-5; -91.8(Py)</td>
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<tr>
<td></td>
<td></td>
<td>rha&lt;sub&gt;2&lt;/sub&gt;rha&lt;sub&gt;4&lt;/sub&gt;glu&lt;sub&gt;-3&lt;/sub&gt;[19]; R=Me 232</td>
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<th>11.</th>
<th>Asparagus ascndens</th>
<th>Asparoside-A</th>
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<tr>
<td></td>
<td>(Pt)</td>
<td>180-84; -53(MeOH)</td>
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<td>Asparoside-B</td>
<td>170-78; -58(Py)</td>
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<td>Asparoside-C</td>
<td>167-72; 75(MeOH)</td>
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<td>Asparoside-D</td>
<td>161-66; -66(Py)</td>
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<td></td>
<td>rha&lt;sub&gt;4&lt;/sub&gt;glu&lt;sub&gt;-3&lt;/sub&gt;[12]; R=Me 5</td>
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<td></td>
<td>glu&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-do-; R=H 5</td>
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<td></td>
<td>rha&lt;sub&gt;4&lt;/sub&gt;</td>
<td>ar&lt;sub&gt;2&lt;/sub&gt;glu&lt;sub&gt;-3&lt;/sub&gt;[12]; R=Me 4</td>
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<tr>
<td></td>
<td>ar&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-do-; R=H 4</td>
</tr>
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Adscendoside-A
-89(MeOH)

Adscendoside-B
-92(H2O)

12. Asparagus cochinchenensis

(Re)

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<thead>
<tr>
<th>Compound</th>
<th>Rha&lt;sup&gt;6&lt;/sup&gt;Glu-&lt;sup&gt;3&lt;/sup&gt;[20]; R=Me</th>
<th>Rha&lt;sup&gt;4&lt;/sup&gt;Glu-&lt;sup&gt;3&lt;/sup&gt;[20]; R=Me</th>
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</thead>
<tbody>
<tr>
<td>Adscendoside-A</td>
<td>233</td>
<td>233</td>
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<tr>
<td>Adscendoside-B</td>
<td>233</td>
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<table>
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<tr>
<th>Compound</th>
<th>Xyl&lt;sup&gt;4&lt;/sup&gt;Glu-&lt;sup&gt;3&lt;/sup&gt;[12]; R=Me</th>
<th>Xyl&lt;sup&gt;4&lt;/sup&gt;Glu-&lt;sup&gt;3&lt;/sup&gt;[12]; R=Me</th>
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<tbody>
<tr>
<td>ASP-IV</td>
<td>165-7; -22.9(MeOH)</td>
<td>165-7; -22.9(MeOH)</td>
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<td>ASP-V</td>
<td>146-49; -30.9(Py)</td>
<td>146-49; -30.9(Py)</td>
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<td>ASP-V</td>
<td>150-56; -45.5(MeOH)</td>
<td>150-56; -45.5(MeOH)</td>
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<td>ASP-V</td>
<td>270-75; -45.5(Py)</td>
<td>270-75; -45.5(Py)</td>
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<td>ASP-VI</td>
<td>165-68; -50(MeOH)</td>
<td>165-68; -50(MeOH)</td>
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<td>ASP-VI</td>
<td>169-72; -49.5(Py)</td>
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<td>ASP-VII</td>
<td>179-81; -27(MeOH)</td>
<td>179-81; -27(MeOH)</td>
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<td>ASP-VII</td>
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<td>ASP-VIII</td>
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<tr>
<td>Methylprotodioscin</td>
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<td>Methylprotodioscin</td>
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</table>
13. *Asparagus curillus*  

(Ft)  
Curilloside-A  
180-84; -53 (MeOH)  

Curilloside-B  
170-74; -58 (Py)  

(Rt)  
Curilloside-E  
-47 (MeOH)  

Curilloside-F  
-51 (H₂O)  

Curilloside  
-78  

Curilloside  
-66  

Curilloside-G  
173-75; -50  

Curilloside-H  
181-83; -53  

---  

14. *Asparagus filicinus*  

(Rt)  
Aspafiloside-C  

---  

---
15. **Asparagus officinalis**

*(Re)*

- Officinalisnins-I
  162-68; -23.8 (MeOH)
- Officinalisnins-II
  175-82; -41.6 (MeOH)
- Asparagusoside-B
- Asparagusoside-E
  254-60; -38 (H₂O)
- Asparagusoside-G
- Asparagusoside-H

*(Sh)*

- Furostanol Saponin-1
  192-95; -92.5 (CHCl₃:MeOH)
- Furostanol Saponin-2
  188-92; -74.6 (CHCl₃:MeOH)

16. **Asparagus plumosus**

- Furostanol glycoside-I
  171-3; -78 (MeOH)
- Furostanol glycoside-II
  183-5; -81 (H₂O)

<table>
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<tr>
<th>Compound</th>
<th>Structure</th>
<th>R</th>
<th>Molar Mass</th>
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<td>Officinalisnins-I</td>
<td>glu⁻²glu⁻⁰⁻³[12]; R=H</td>
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<td>Officinalisnins-II</td>
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<td>glu⁻²glu⁻⁰⁻³[12]; R=H</td>
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<td>Asparagusoside-B</td>
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<td>Asparagusoside-E</td>
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<td>Asparagusoside-G</td>
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<td>Asparagusoside-H</td>
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<tr>
<td>Furostanol Saponin-1</td>
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<td>Furostanol Saponin-2</td>
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<tr>
<td>Furostanol glycoside-I</td>
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<tr>
<td>Furostanol glycoside-II</td>
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</table>
17. **Asparagus racemosus**

(Rt) Asparacemoside-A
213-14

Asparacemoside-B
180-83

18. **Asparagus sprengeri**

(Rt) Sprengeroside-A
180-84; -100.3(MeOH)

Sprengeroside-B
187-92; -99.5(MeOH)

Sprengeroside-C
186-90; -84.5(Py)

Sprengeroside-D
192-98; -83.4(Py)

Sprengeroside-I
186-90; -95.5(Py)

Sprengeroside-J
195-98; -79.5(Py)

19. **Aspidistra elatior**

---
235-6; -34.8(MeOH)

---
195-8; -60.4

rha$_6$glu-0$^3$[12]; R=H 241

xyl$_2$glu-0$^3$[12]; R=H 241

rha$_2$glu-0$^3$[20]; R=Me 6

rha$_2$glu-0$^3$[20]; R=Me 6

rha$_2$glu-0$^3$[20]; R=H 6

rha$_2$glu-0$^3$[20]; R=Me 242

rha$_2$glu-0$^3$[20]; R=H 242

 glu-0$^5$[17]; R=Me 243

 glu-0$^5$[17]; R=H 243
Methylprotoaspidistrin 202-7663.4(Py)
Protoaspidistrin 64(Py)

20. **Balanites aegyptica**
(Ft)
Balanitoside-A
Balanitoside-B

21. **Balanites roxburghii**
(Sbk)
Protodeltonin

22. **Beshorneria yuccoides**
(Lf)
Beshornoside 219-21; 25(Py)

23. **Capsicum annum**
(Sd)
Capsicoside 295; 35(CHCl₃:MeOH)

24. **Chamaerops humilis**
(Wp)
Methylprotodioscin [Cst₄,Cu₃] 185-89; 102.9(Py)
Methylproto Pb. [Cl₂,Cst₂,Cu₃] 189890; 86.4(Py)

\[ xy^1 \text{glu}^2 \text{gal-0-3}[19]; R=Me 171 \]
\[ -do-; R=H 171 \]
\[ rha^2 \text{glu}^4 \text{gal-0-3}[19]; R=Me 244 \]
\[ -do-; R=H 244 \]
\[ \text{glu}^4 \text{gal-0-3}[19]; R=H 69 \]
\[ rha^4 \text{glu}^4 \text{gal-0-3}[3]; R=H 245 \]
\[ \text{glu}^3 \text{glu}^4 \text{gal-0-3}[4]; R=H 246 \]
\[ rha^4 \text{glu}^4 \text{gal-0-3}[19]; R=Me 247 \]
\[ rha^2 \text{glu}^4 \text{gal-0-3}[19]; R=Me 247 \]
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<th>R Value</th>
<th>M.W.</th>
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<td>Methylprotorhapissaponin</td>
<td>glu^4-rha^4-rha^2 glu-0-^3[19]; R=Me</td>
<td>196299; -92.4(Py)</td>
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<td>[Cus]</td>
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<td>Chlorophyllum malayense</td>
<td>xyl^3-glu-gal-0-^3[2]; R=Me</td>
<td>295-98; -48.3(Py)</td>
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<td>Chloromaloside-B</td>
<td>glu^2 rha^2-qui-0^1 glu^4-rha-0^3</td>
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<td>Convallaria majalis</td>
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<td>(Rt)</td>
<td>Convallamaroside</td>
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<td>Costus speciosus</td>
<td>Costusoside-I</td>
<td>220-24; -76.5(Py)</td>
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<tr>
<td>(Sd)</td>
<td>Costusoside-J</td>
<td>248-50; -79.1(Py)</td>
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<td>194-7; -70.4(Py)</td>
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<td>Methyl protodioscin</td>
<td>185-7; -102.9(Py)</td>
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<td></td>
<td>Protodioscin</td>
<td>190-6; -57.8(Py)</td>
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<td>Digitalis lanata</td>
<td>Lanagitoside</td>
<td>260-83; -18.6(CHCl_3:MeOH)</td>
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<td>(Lf)</td>
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<td>xyl^3-glu-gal-0-^3[4]; R=Me</td>
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<td>glu^2-gal-0-^3[4]; R=Me</td>
<td>-do- ; R=H</td>
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<tr>
<td>29.</td>
<td>Digitalis purpurea (Lf)</td>
<td>Purpureogitoside</td>
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<td>xyl&lt;sub&gt;3&lt;/sub&gt;glu&lt;sub&gt;1&lt;/sub&gt;gal-O-{3; 4}; R=Me 19</td>
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<td>-do-; R=H 19</td>
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<td>30.</td>
<td>Dioscorea colletii (Rh)</td>
<td>Saponin-C 183-5; -81(H&lt;sub&gt;2&lt;/sub&gt;O)</td>
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<td>rha&lt;sub&gt;3&lt;/sub&gt;glu&lt;sub&gt;1&lt;/sub&gt;-O-{3; 20}; R=H 252</td>
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<td>Dioscorea deltoidea (Rh)</td>
<td>Deltoside-II</td>
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<td>glu&lt;sub&gt;3&lt;/sub&gt;-O-{19}; R=H 253</td>
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<td>32.</td>
<td>Dioscorea floribunda (Rh)</td>
<td>Methylprotodioscin</td>
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<td>rha&lt;sub&gt;3&lt;/sub&gt; [19]; R=Me 22</td>
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<td>Floribundasaponin-E 226-29; -66(Py)</td>
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<td>-do-; R=H 254</td>
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<td>33.</td>
<td>Dioscorea gracillima (Rh)</td>
<td>Methylprotodioscin</td>
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<td>rha&lt;sub&gt;4&lt;/sub&gt;glu&lt;sub&gt;3&lt;/sub&gt;-O-{19}; R=Me 20</td>
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</table>
34. **Dioscorea tenuipes** (Ap)

- Protodioscin
  - 190-96; -57.8 (Py)
- Diotigenin-4-acetate
- furastanol-26-O-glucoside
  - 172-74; +134.4

[33]; R=Me 255

35. **Dioscorea tokoro** (Tc)

- Prototokorin
  - 177-78; -31.8 (MeOH)
- --
- [14]; R=H 257
- [15]; R=H 257

36. **Dioscorea septemloba**

- Methylprotogracillin
  - 249-51; -76.9 (MeOH)
- Protogracillin
  - 235-38; -57.8 (Py)
- Methylprotodioscin
- Protodioscin

- glu-O-[12]; R=H 256
- -do-; R=H 20

37. **Dioscorea zingiberensis**

- Zingiberenin-C
- Zingiberenin-D

- rha<sub>3</sub>glu-O-[19]; R=Me 20
- glu<sub>2</sub>rha<sub>2</sub>glu-O-[19]; R=Me 20
- rha<sub>3</sub>glu-O-[19]; R=H 258
- glu<sub>2</sub>rha<sub>2</sub>glu-O-[20]; R=H 258
38. **Dracaena afrormontana**
   (Twg) Afrmontoside
   >300; -69.3(Py)
   rha\(^4\)glu-0-3[19]; R=H
   But 26-O-rha.

39. **Funkia ovata**
   (Lf) Funkioside-B
   258-66; -135(MeOH)
   Funkioside-I
   rha\(^4\)rha\(^4\)glu\(^3\)glu\(^4\)gal-0-3[19]; R=H
   xyl\(^3\)

40. **Helleborus macranthus**
   (Rt+Rh) Macranthoside-I
   228-31
   Macranthoside-I
   263-66
   glu\(^6\)glu-0-3[28]; R=H
   -do-; R=Me

41. **Heloniopsis orientalis**
   (Wp) Hb(Methylprotodioscin)
   189-92; -98.2
   Hd(III) -92.1
   Hd(III) -100.2
   rha\(^4\)rha\(^4\)glu-0-3[22]; R=H
   -do-; R=Me

42. **Kallstroemia pubescens**
   (Wp) Kallstroemin-A
   235-38; -82(Py)
   rha\(^2\)rha\(^2\)rha\(^6\)glu-0-3[19]; R=H
   264
<table>
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<tr>
<th>Lf</th>
<th>Methyl proto dioscin</th>
<th>Rha&lt;sub&gt;2&lt;/sub&gt;Glu-0-3&lt;sup&gt;[19]&lt;/sup&gt;; R=Me</th>
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<td>Pt</td>
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<td>Rha&lt;sub&gt;2&lt;/sub&gt;Glu-0-3&lt;sup&gt;[19]&lt;/sup&gt;; R=Me</td>
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<td>-47.1(MeOH)</td>
<td>rha-(6-O-acetyl)-Glu-0-3&lt;sup&gt;[19]&lt;/sup&gt;; R=Me</td>
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<td>Compound-II</td>
<td>Glu&lt;sub&gt;3&lt;/sub&gt;Glu-0-3&lt;sup&gt;[3]&lt;/sup&gt;; R=H</td>
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<td>-75.8(MeOH)</td>
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<td>Compound-9</td>
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<td>-48.8(MeOH)</td>
<td>But 26-O-Ac.</td>
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<td>Pardarinoside-A</td>
<td>Rha&lt;sub&gt;2&lt;/sub&gt;Glu-0-3&lt;sup&gt;[32]&lt;/sup&gt;; R=Me</td>
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<td>-56.4(MeOH)</td>
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<td>Pardarinoside-B</td>
<td>Glu&lt;sub&gt;3&lt;/sub&gt;Glu-0-3&lt;sup&gt;[31]&lt;/sup&gt;; R=Me</td>
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<td>Pardarinoside-C</td>
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<td>-50.5(MeOH)</td>
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<td>B1b</td>
<td>Pardarinoside-D</td>
<td>Glu&lt;sub&gt;3&lt;/sub&gt;Glu-0-3&lt;sup&gt;[31]&lt;/sup&gt;; R=Me</td>
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<td>-59.7(MeOH)</td>
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</table>
Pardarinoside-F
-32.8(MeOH)

Pardarinoside-G
-40.8(MeOH)

47. **Lilium regale**
(B1b)  

48. **Liriope platyphilla**  
Methyl proto dioscin  
185-7; -102.9(Py)  
Proto dioscin  
190-6; -57.8(Py)

49. **Liriope spicata**  
Spicatoside-A  

50. **Lycopersicum esculentum**  
(Sd)  
Furastanol saponin  
217-20; -24(MeOH+CHCl₃)  
TFI  
217-18; -24(MeOH+CHCl₃)

51. **Mettanarthecium uteoviride**  
166-68; -73(Py)  
ara₁ʳha₂glu-0⁻³[31]; R=Me 268

ara₁ʳha₂glu-0⁻³[32]; R=Me 268

glu₁rha₂glu-0⁻³[20], R=Me 269

rha₁glu-0⁻³[19]; R=Me 270

rha₂ -do--; R=H 270

xylo₁fuc-0⁻¹[23]; R=Me 271

glu₁ -do--; R=H 271

glu₂glu-4gal-0⁻³[10]; R=Me 272

- do--; R=H 272

ara-0⁻¹¹[16]; R=Me 273
52. **Ophiopogon jaburan**  
(Rh) Glycoside-J$_5$  
165-68  
Glycoside-J$_6$  
201-3

53. **Ophiopogon ohwii**  
(Rh) Glycoside-O$_0$  
183-85; -50.8(Py)

54. **Ophiopogon planiscapus**  
Glycoside-D  
194-7; -70.4(Py)

Glycoside-F

Glycoside-G  
212-5; -55.2(Py)

55. **Paris formosana**

56. **Paris polyphylla**  
(Tb) Polyphyllin-G  
177-81; -76.9(Py)

Polyphyllin-H
57. **Paris teraphylla**
   Dehydrocryptogenin tetraglycoside
   rha_rha
   glu-0-3[34]; R=H
   17,267

58. **Phoenix canariensis**
    (Lf)
    Methyl (25S) Proto Pb
    255-8; -84.8(MeOH)
    rha_rha
    glu-0-3[20]; R=Me
    265

59. * **Phoenix dactylifera**
    (Lf)
    Methyl proto prosapogenin-A of dioscin
    173-77-87.6(Py)
    rha_ara
    glu-0-3[19]; R=Me
    265
    Methyl proto rectinatoside
    150-2; -86.7(Py)
    rha_rha
    glu-0-3[19]; R=Me
    265
    Methyl proto Pb
    176-9; -83.1(Py)
    rha_rha
    glu-0-3[19]; R=Me
    265

60. * **Phoenix humilis**
    (Lf)
    Methyl (25S) Proto Pb
    255-58; -84.8(MeOH)
    rha_rha
    glu-0-3[20]; R=Me
    265
    Methyl (25S) Proto louderiroside
    185-87; -78.3(Py)
    rha_ara
    glu-0-3[20]; R=Me
    265

61. * **Phoenix loureiri**
    (Lf)
    Methyl proto Pb
    192-95; -91.8(Py)
    rha_rha
    glu-0-3[19]; R=Me
    232
62. **Phoenix reclinata**  
(Lf)

Methyl proto Pb  
192-95; -91.8(Py)

Methyl proto rupicolaside  
195-99; -82.6(Py)

Methyl proto reclinata  
165-68; -44.2(Py)

63. **Phoenix rupicola**  
(Lf)

Methyl proto taccaoside  
180-83; -77.2(Py)

Methyl proto Pb  
192-95; -91.8(Py)

Methyl proto rupicolaside  
195-99; -82.6(Py)

\[\text{glu}^2 \text{rha}^4 \text{rha}^4 \text{glu-}O-^3[19]; R=\text{Me} \]

\[\text{rha}^5 \text{ara}^4 \text{glu-}O-^3[19]; R=\text{Me} \]

\[\text{rha}^4 \text{rha}^4 \text{glu-}O-^3[19]; R=\text{Me} \]

\[\text{rha}^5 \text{ara}^4 \text{glu-}O-^3[19]; R=\text{Me} \]

\[\text{rha}^4 \text{rha}^4 \text{glu-}O-^3[19]; R=\text{Me} \]

\[\text{rha}^2 \text{rha}^2 \text{glu-}O-^3[19]; R=\text{Me} \]

\[\text{rha}^2 \text{rha}^2 \text{glu-}O-^3[19]; R=\text{Me} \]
<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>Description</th>
<th>Formula</th>
<th>Comments</th>
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<tr>
<td>64</td>
<td><em>Polygonatum kingianum</em></td>
<td>(Rh)</td>
<td>Kingianoside-C</td>
<td>glu-4gal-0-3[25]; R=Me 278</td>
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<td>Kingianoside-C</td>
<td>gal-4fuc-0-3[25]; R=H 278</td>
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<td>(25R) epimer of PO-8</td>
<td>glu-4gal-0-3[19]; R=Me 278</td>
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<tr>
<td>65</td>
<td><em>Polygonatum latifolium</em></td>
<td>(Lf) Protopolygonatoside-E</td>
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<td>glu-3glu-4gal-3glu-4gal-0-3[19]; R=H 279</td>
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<td>66</td>
<td><em>Polygonatum odoratum</em></td>
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<td>PO-C</td>
<td>glu-3glu-4gal-0-3[27]; R=Me 280</td>
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<td></td>
<td>208-10; -49(Py)</td>
<td>glu-3glu-4gal-0-3[26+27]; R=Me 280</td>
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<td></td>
<td>PO-d</td>
<td>glu-3glu-4gal-0-3[19]; R=H 281</td>
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<tr>
<td>67</td>
<td><em>Polygonatum pratii</em></td>
<td>(RE) Pratioside-B</td>
<td></td>
<td>glu-2glu-4gal-0-3[25]; R=H 282</td>
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<td>-52.5(H₂O)</td>
<td>glu-2glu-4gal-0-3[19]; R=H 282</td>
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<td>68</td>
<td><em>Polygonatum officinale</em></td>
<td>(Rh) Polyfurosides</td>
<td></td>
<td>glu-4gal-0-3[19]; R=H 282</td>
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<td>252-58; -68(Py)</td>
<td>rha-4glu-0-3[19]; R=Me 283</td>
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<td>69</td>
<td><em>Polygonatum verticillatum</em></td>
<td>Methyl protodioscin</td>
<td></td>
<td>rha-2glu-3[19]; R=H 283</td>
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<tr>
<td>No.</td>
<td>Plant Name</td>
<td>Chemical Name</td>
<td>Molecular Formula</td>
<td>Condensation</td>
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<td>70</td>
<td><strong>Radix sarsaparilla</strong></td>
<td>Sarsaparilloside</td>
<td>-44(H$_2$O)</td>
<td></td>
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<tr>
<td>71</td>
<td><strong>Rhapis exelsa (Wp)</strong></td>
<td>Methylprotodioscin</td>
<td>[Est$_3$, El$_1$, Eu$_2$]</td>
<td>185.90; -102.9(Py)</td>
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<td>Methylprotodeltonin</td>
<td>[Est],</td>
<td>196-95; -59.8(Py)</td>
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<td></td>
<td>Methylproto Pb</td>
<td>[El$_2$, Est$_4$, Eu$_4$]</td>
<td>1892-90; -86.4(Py)</td>
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<td>72</td>
<td><strong>Rhapis humilis (Wp)</strong></td>
<td>Methylprotoprosapogenin-A of dioscin</td>
<td>[Hst$_4$, Hl$_1$, Hu$_2$]</td>
<td>178-80; -81.2(Py)</td>
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<td></td>
<td>Methylprotodioscin</td>
<td>[Hl$_2$, Hst$_6$, Hu$_2$]</td>
<td>1852-89; 102.9(Py)</td>
</tr>
</tbody>
</table>
Methyl protodeltonin 
[Hst.] 196-99; -59.8(Py)

Methylproto Pb 
[Hi₃, H₂4] 189-90; 86.4(Py)

73. **Ruscus aculeatus**
(Rh) Deglucoruscoside
Ruscoside

74. **Smilax aristolochiaceefolia**
(Rt) Sarsaparilloside
-44(H₂O)

75. **Smilax aspera**
(Lf) Asperoside

76. **Smilax chinae**
(Rh & Rt) Pseudoprotodioscin
-72(MeOH)
Methyl protodioscin
-86(MeOH)

\[ \text{glu}_4 \text{glu-0-3}[19]; R=Me \]
\[ \text{rha}_2 \]
\[ \text{rha}_4 \text{glu-0-3}[19]; R=Me \]
\[ \text{rha}_2 \]
\[ \text{rha}_2 \text{ara-0-1}[30]; R=H \]
\[ \text{glu}_3 \text{rha}_2 \text{ara-0-1}[30]; R=H \]
\[ \text{glu}_6 \text{rha}_4 \text{glu-0-3}[12]; R=H \]
\[ \text{glu}_2 \]
\[ \text{rha}_4 \text{glu-0-3}[20]; R=H \]
\[ \text{rha}_2 \]
\[ \text{rha}_4 \text{glu-0-3}[19]; R=Me \]
\[ \text{rha}_2 \]
\[ \text{rha}_4 \text{glu-0-3}[35]; R=Me \]
\[ \text{rha}_4 \text{glu-0-3}[19]; R=Me \]
\[ \text{rha}_2 \]
| 77. Smilax sieboldi (Rh) | Compound-4  
-44.8 (EtOH)  
Compound-5  
-46.3 (EtOH) |
|-------------------------|------------------|
| 78. Solanum lyratum (Ber) | Methylprotoaspidistrin  
202-7; -63.4 (Py)  
Aspidistrin  
210-14; -64 (Py)  
Furastanol glucuronoside  
-61.4 (H2O) |
| 79. Solanum melangena (Sd) | Melongoside-N  
187-89; -15 (MeOH)  
Melongoside-O  
183-84; -19 (MeOH)  
Melongoside-P  
179-80; -75 (H2O) |
| 80. Solanum nigrum (Wp) | Uttroside-A  
220-25; -49 (MeOH)  
Uttroside-B  
210-15; -46 (Py) |

|  | ara-glu-O-3[11]; R=H  
ara-glu-O-3[11], R=H  
| 6  |
|  | rha-gluc-O-3[19]; R=Me  
- do-; R=H  
| 2  |
|  | glu-gluc-O-3[3]; R=H  
gru-gluc-O-3[19]; R=H  
| 2  |
|  | rha-gluc-O-3[3]; R=H  
gru-gluc-O-3[3]; R=Me  
- do-; R=H  
| 3  |
|  | xy-gluc-gal-O-3[3]; R=Me  
- do-; R=H  
| 2  |
81. **Solanum paniculatum**  
(Rt) Jurubine  
212-14; -31(Py)

82. **Trachycarpus fortune**  
Methylprotodioscin  
Protodioscin

--  
174-7; -87

83. **Trachycarpus wagnerianus**  
(Wp) Methylprotodioscin  
[Tst.] 185-89; -102.9(Py)

Methylproto Pb  
[Tl3;Tu3] 189±90; ±86.4(Py)

Pseudoprotodioscin  
[Tst.] 174-76; -80.4(Py)

Pseudoproporubin Pb  
[Tl4;Tu4] 181-83; -84.4(Py)

84. **Tribulus terrestris**  
Methylprotodioscin  
189-93

\[ \text{[1]}; R=H \quad 7-8 \]

\[ \text{rha-} \text{gul-0-3[19]; R=Me} \quad 292 \]

\[ \text{rha-} \text{gul-0-3[19]; R=Me} \quad 292 \]

\[ \text{rha-} \text{gul-0-3[19]; R=Me} \quad 247 \]

\[ \text{rha-} \text{gul-0-3[19]; R=Me} \quad 247 \]

\[ \text{rha-} \text{gul-0-3[19]; R=Me} \quad 247 \]

\[ \text{rha-} \text{gul-0-3[19]; R=Me} \quad 247 \]
85. **Trigonella coerulescens**

*(Sd)* Methylprotodioscin 189-93

Protodioscin

86. **Trigonella foenum-graecum**

*(Sd)* Trigonelloside-B

Trigonelloside-C

Furostanol glycoside 242-46

Trigofoenoside-A-1 219-21; -90.1(Py)

Trigofoenoside-A 210-13

Trigofoenoside-B 198-200; -62.1(Py)

Trigofoenoside-C 210-12; -64.1(Py)

Protodioscin

Methylprotogracillin

Protodioscin

--do--; *R* = H 293-295

--do--; *R* = H 293-295

*glu*$_{3}$ *glu*-0-3[19]; *R* = Me 293-295

*rha*$_{2}$

*glu*$_{3}$ *glu*-0-3[19]; *R* = Me 293-295

*rha*$_{2}$

*glu*$_{4}$ *glu*-0-3[20]; *R* = Me 295-297

*rha*$_{2}$

*glu*$_{4}$ *glu*-0-3[10]; *R* = Me 298

*rha*$_{2}$

*glu*$_{4}$ *glu*-0-3[20]; *R* = Me 43

*do--; *R* = H 43

*do--; *R* = H 43

*do--; *R* = H 299

*do--; *R* = H 299
Trigofoenoside-D-1
246-48; -73.2 (Py)

Trigofoenoside-D

Trigofoenoside-F-1
256-58; -78.9 (Py)

Trigofoenoside-F
233-36

Trigofoenoside-G-1
270-74; -79.2 (Py)

Trigofoenoside-G
275-8

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glu atmospheric use.

87. **Trillium kamtschaticum**
(Ugp)

Furastanol bisglycoside
265-71; -83.1 (Py)

Protopennogenin, 3-O-
rhamnosyl glucoside
275-80; -84.6 (Py)

Dehydrocryptogenin-
diglycoside
265-68; -80.1 (Py)

Tj
205-12; -66.5
Tk
194-200; 90(Py)

88. **Trillium tschonoskii**
(Rt) Methylprotodioscin

89. **Yucca filamentosa**
(Rt) Protoyuccoside-C
182-84; 30(MeOH)
Protoyuccoside-E
150-52; 29(MeOH)

90. **Yucca gloriosa**
(F1) YG-4
+21(Py)

The following abbreviations have been used:

1. glu = D-Glucose; ara = L-Arabinose; xyl = D-Xylose; gal = D-Galactose; rha = L-Rhamnose.
qui = D-Quinovose; fuc = D-Fucose; Rt = Root; Rh = Rhizome; Lf = Leaf; Sd = Seed; Ugp = Under ground part; Wp = Whole part; B1b = Bulb; Ap = Aerial part; Ft = Fruit; Sh = Shoot;
Sbk = Stem bark; Tc = Tissue culture; Twg = Twigs; Tb = Tuber; Ber = Berry; Fl = Flower; Pt = petals.

2. All the sugars reported in the above saponins appear in the pyranose form except * marked,
where the sugars reported are in the furanose form.

3. The number in the brackets refer to the structure of aglycone part.

4. The linkages of sugars with each other, and with aglycone are *. 

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rha 4*rha *glu-0-3[22]; R=Me 302
rha 2

rha 4*glu-0-3[19]; R=Me 303
gal 2

rha 4*glu-0-3[12]; R=H 21
rha 2

gal 4*glu-0-3[12]; R=H 304
gal 2

xyl 4*glu-0-3[4]; R=H 305
xyl-gluc
BIBLIOGRAPHY


