Asian Journal of Chemistry Vol. 10, No.4 (1998), 651–689

REVIEW

Oligofurostanosides—Furostanol Saponins

S.C. SHARMA*, N.K. THAKUR and R. CHAND†
Chemistry Department
H.P. University, Summer-Hill, Shimla-171 005, India

Oligofurostanosides—the furostanol saponins with at least two sugar chains isolated till 1993 from various plants are reviewed along with their physical data. Latest chemical and spectroscopic techniques used for their isolation and characterisation have also been described.

Although a good number of reviews have appeared in various journals covering the spirostanol saponins,[1-13] but very little efforts have been made to compile the research work done on this new class of glycosides, the oligofurostanosides. The present work is an humble attempt to review all the chemical investigations carried out in this field.

In the recent past the chemistry of natural products has touched new horizons and is rapidly developing as a separate discipline in itself. The importance of this field lies in the fact that on one hand it is the organic chemistry associated with plants, animals, marine and on the other hand it is associated with plant biochemistry and the utility in pharmaceutical chemistry. Phytochemistry, as it is more popularly known, is concerned with enormous types of organic compounds which are not only synthesised by the plants, but are also preserved by them for their growth and protection. Due to this reason phytochemistry involves a study of the structures of chemicals compounds, their biosynthesis and biological functions. The plant kingdom contains enormous organic compounds of different classes, out of which the chemistry of glycosides has been the focal point of research of many modern chemists.

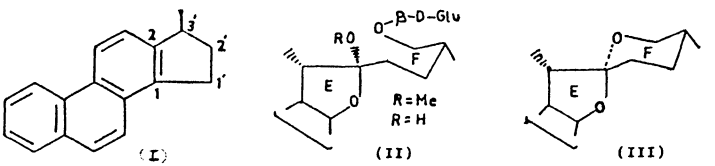
The O-glycosides, which produce copious foam on shaking with water, cause sneezing on inhalation, kill fishes and haemolyse red blood corpuscles are usually termed as 'Saponins' (Latin, *sapo* = soap) and have been classified as: Triterpenoid Saponins, Steroidal-Alkaloidal Saponins and Steroidal Saponins, out of which triterpenoid saponins have been reviewed most abundantly by many workers.

†Department of Forest Products, College of Forestry, Y.S. Parmar University of Horticulture and Forestry, Solan (Nauni)-173 230, India.

Steroidal Saponins

These saponins on acidic/enzymatic hydrolysis give C_{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[14–16] are degraded into Diels' hydrocarbon (3′-methyl 1,2-cyclo pentenophenanthrene, (I).

The C_{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_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[17–19] subclassified them as:



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 furostanosides.

2. Oligospirostanosides and Spirostanosides

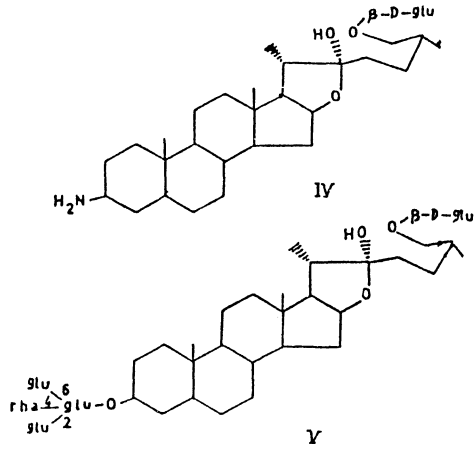
Parallelly, the spirostanolic saponins are classified as oligospirostanosides (≥ 3 sugars) and spirostanosides (< 3 sugars).

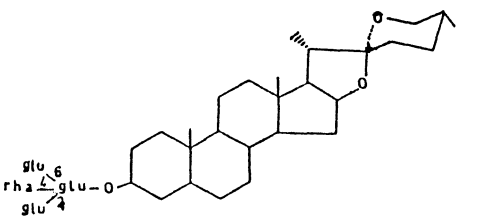
The first isolation and characterisation of this type of a compound, Jurubine (IV), a furostanolic-alkaloidal saponin, was reported by Schreiber and Ripperger[20, 21] from *Solanum paniculatum* L. and the very next year came the isolation and characterisation of first such saponin glycoside Sarsaparilloside (V) from *Smilax aristolochiae* Mill. roots by Tschesche *et al.*[22], which was termed as Bisdesmoside, with its corresponding oligospirostanoside, Parillin (VI).

These findings were in contrast to Wall's claim[23] but supported Marker's classical suggestion[24] that a steroidal saponin is secondarily produced from a steroidal glycoside having an aliphatic chain at C_{17} 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[17–20, 25–27].

Detection of Oligofurostanosides

Oligofurostanosides can be easily detected by:





Ehrlich reagent test[29]: 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 ($\Delta^{20(22)}$ derivative) also. However, furostanolic saponins with 17-OH group are not detected by this reagent.[30]

Pt. (IV) oxide or $NaBH_4$ ***reduction followed by acid hydrolysis***[22, 31]: H_2/Pt oxide or $NaBH_4$ 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.

IR-spectra[28, 32–34]: 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.

Two-dimensional TLC[32]: 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.

NMR-spectra[33, 35]: The ^{1}H-NMR spectra of oligofurostanosides exhibit a characteristic singlet at about δ 3.25 ppm for 22–OMe group.

Crystallisation in MeOH or EtOH[22, 32]: 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.

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 h usually 3 times to remove oily matter, chlorophyll and any neutral compounds and then with ethyl acetate thrice, 6 h each time, to remove colouring matters etc. Finally, the plant material is subjected to exhaustive methanol/ethanol extraction for 8 h 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-1).

TABLE-1

Adsorbent	Solvent system	Nature of steroidal saponins
A. *Thin layer and column chromatography*		
Silica gel	$CHCl_3$: MeOH : H_2O 65 : 20–30 : 10	Non-polar[36–37]
Silica gel	$CHCl_3$: MeOH : H_2O 65 : 35 : 10	Neutral and non-polar[38]
Silica gel	EtAc : MeOH : H_2O 70 : 15 : 15	Acidic and neutral[39]
Silica gel	*n*-BuOH : EtOH : 25% Ammonia sol. 60 : 13 : 30.5	Polar, acidic[40]
Acidic silica	$CHCl_3$: MeOH : H_2O 65 : 35 : 10	Acidic[41]
Alumina (H_2O saturated)	Toluene : *n*-BuOH 2 : 1–1.4	Natural[42]
B. *Paper and column chromatography*		
Paper (formamide impregnated, Whatman No. 1)	$CHCl_3$: THF : C_5H_5N 10 : 10 : 2 (Formamide saturated)	Neutral[43–44]
Paper (Whatman No. 1)	Iso-BuOH : EtOH : Et_2NH : H_2O 5 : 5 : 1 : 4	Acidic[40]
C. *Gel chromatography*		
Sephadex G-25 or G-50	Water	Saponins of different molecular sizes [45–46]

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.

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.*[47], 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 to 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 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.[48–50]

(ii) High Performance or High Pressure Liquid Chromatography[51–53]

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 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 the results obtained are essentially without errors.

The structure determination of oligofurostanosides involves the following methods:

Enzymatic hydrolysis[22, 32]: Enzymatic hydrolysis with β-glucosidase cleaves off the β-linked glucose at C_{26} (in almost all cases with only a few exceptions) leading to the cyclisation of the ring 'F' with C_{22}-OH and formation of oligospirostanoside. If β-D-glucose is the terminal sugar of the sugar chain

attached at C_3 of the aglycone, it will also be liberated leading to the formation of lower oligofurostanosides/furostanosides/oligospirostanosides etc.

Acid hydrolysis[54–56]: 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 concentration under vacuum at 40–50°C is subjected to descending paper chromatography[57–59] on Whatman filter paper No. 1 using the solvent systems, *n*-BuOH : AcOH : H_2O (4 : 1 : 5); EtAc : Py : H_2O (10 : 4 : 3); *n*-BuOH : Py : H_2O (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.

Kiliani hydrolysis[60]: In order to find out the sequence of sugars in the glycone moiety the oligofurostanoside is subjected to hydrolysis with Kiliani mixture (AcOH : H_2O : 35% HCl, 35 : 55 : 10) at room temperature. 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.

Reduction followed by hydrolysis[22, 31]: Discussed under detection of oligofurostanosides.

CrO_3 oxidation[22, 33–34, 61]: The form of ring 'F' as well as the nature and number of sugars attached to C_{26} of the oligofurostanoside can elegantly be proved by CrO_3 oxidation. The oligofurostanoside is converted to peracetate $\Delta^{20(22)}$ through acetylation followed by the removal of a molecule of H_2O or MeOH by heating in AcOH, which on oxidation with CrO_3 in AcOH gives an oxidised product. The basic hydrolysis (t-BuOH/KOH) of this product affords δ-hydroxy-γ-methyl n-valeric acid glucoside, which contains the sugar unit glycosidated at C_{26} of the sapogenin. A survey of literature showed that so far β-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.

Baeyer-Villiger oxidation[27, 33]: 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, 5α, pregnane-3β, 5α, 6β, 16β, 20α pentanol tetraacetate is obtained instead of pregnolone.

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[62] (Ag_2O and MeI), Kuhn[63] (BaO, $Ba(OH)_2$ and MeI/DMSO) and Hakomori[64] (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[34, 61] 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[65–67] and NMR[68] 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[32] 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_2O (5 : 1 : 4)[59], 2-butanone saturated with 2% NH_3[69] and Benzene : EtOH : H_2O : ammonia (200 : 47 : 14 : 1).[70] Aniline hydrogen phthalate is generally used as the developing reagent. Methylated sugars have also been studied by TLC[44, 71–72] on silica gel and cellulose.

Partial hydrolysis[73–75]: 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_2SO_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.

Molecular rotation: The α- and β-configurations of different sugars in the oligofurostanosides have been proved by molecular rotation values.[76–78] 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.

Methyl sugars	$[M]_D$
β-methyl-D-glucopyranoside	−66°
α-methyl-D-glucopyranoside	+309°
β-methyl-D-galactopyranoside	+10°
α-methyl-D-galactopyranoside	+380°
β-methyl-D-xylopyranoside	−108°
α-methyl-D-xylopyranoside	+253°
β-methyl-L-arabinopyranoside	+403°
α-methyl-L-arabinopyranoside	+28°
β-methyl-L-rhamnopyranoside	+170°
α-methyl-L-rhamnopyranoside	−111°

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 can be traced easily.[79–90] 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 C_3, C_{11}, C_{12} and C_{13} affects the –ve rotation by a strongly +ve one.
4. Change in the stereochemistry at C_8 and C_{14} does not appreciably affect the shapes of the curves.

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 (λ_{max} and ε_{max} values and the well defined additional band at approximately 280 nm) in steroidal compounds.[91–95]

IR spectroscopy: IR spectra have provided valuable information about the structural features, various functional groups and stereochemistry at various centres of oligofuro- and oligospirostanosides as well as their aglycones[28, 32–34, 96–105] *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 Δ^5 unsaturation.
5. The intensities of the typical spiroketal absorptions are reduced to a great extent by the presence of substitution in ring 'F'.

NMR spectroscopy[106]: (i) *^{1}H-NMR:* The ^{1}H-NMR study of steroidal sapogenins in deutero-chloroform is particularly of great help in stereochemical assignments[107], *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 become more distinct,[108] further supported by Tori and Aono[109], who also showed the validity of Zurcher's additivity rules[110] by studying the effect of substituents on the positions of the proton signals for the four methyl groups.

^{1}H-NMR study of oligofurostanosides etc. also throws much light on the structure of the glycoside molecule. The linkages (α- or β-)[33–35, 111–113] 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 (δ 4.0–6.30).
2. D-sugars generally occur with β-linkages and are characterised by their high coupling constants (J, 6–9 Hz).
3. The rarely occurring α-linkages of corresponding sugars have low coupling constants (J, 2–4 Hz).
4. The coupling constants of the commonly α-linked occurring sugars, L-rhamnose and L-arabinose are J, *ca.* 2 Hz and J, *ca.* 6–8 Hz respectively.
5. The furostanolic nature of oligofurostanosides is shown[33, 35] by 22-OMe signals at about δ 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.*[114] 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.[115] Characteristic chemical shifts are observed for α- and β-positions of the —OH group where glycosidation takes place.

Thakur and Agrawal *et al.*[116] 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[117] 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.[118]

^{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 for C_{22}-OH and C_{22}-OMe derivative respectively. The C_{22}-OMe signals usually occur at 47.2 ± 0.2[119, 120] though in a few cases at 56.5 ppm.[121] Table-2 shows the chemical shifts for the parent steroidal skeleton.[122] These values show that the chemical shifts for the ring 'A' and 'B' carbon atoms are markedly affected, hence helpful for differentiating 5α, 5β and Δ^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[123–125] as solvents alter the chemical shift markedly[126, 127]. Furanose sugars are distinguished by chemical shifts for C_1, C_2 and C_4 by 4–14 ppm downfield whereas C_5 by 4–7 ppm upfield as compared to the pyranose form[126, 128].

A close resemblance of the chemical shifts due to a terminal sugar with respect to a methyl-O-glycoside leads to its characterisation, whereas chemical shifts of inner sugars differ significantly in comparison to methyl-O-glycoside due to α-β effects of the glycosidation[129]. The glycosidation causes a downfield shift of

4.2–8.5 ppm of the α-carbon, the hydroxyl of which has been directly involved in the glycosidation while neighbouring β-carbon atom shows an upfield shift of 0.05–2.0 ppm in oligoglycosides. The upfield shifts of the β-carbon atoms are quite informative but less consistent, whereas the downfield shift of the α-carbon is characteristic enough for the establishment of inter-glycosidic (α, β) linkages.

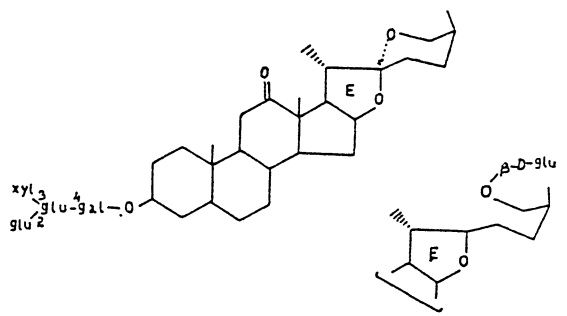
TABLE-2
^{13}C-NMR CHEMICAL SHIFTS

C Atom No.	Furostanosides						Spirostanosides					
	5α		5β*		Δ^5		5α		5β		Δ^5	
	22OH	22OMe	22OH	22OMe	22OH	22OMe	25R	25S	25R	25S	25R	25S
1.	38.5	38.5	37.4	37.4	39.9	39.9	38.7	38.7	37.6	37.6	39.9	40.5
2.	22.2	22.2	21.3	21.3	22.4	22.4	22.2	22.2	21.3	21.3	22.4	23.3
3.	27.1	27.1	27.3	27.3	28.0	28.0	26.8	26.8	27.0	27.0	28.0	27.7
4.	29.2	29.2	27.5	27.5	33.0	33.0	29.0	29.0	27.2	27.2	33.0	34.2
5.	47.1	47.1	43.7	43.7	143.7	143.7	47.1	47.1	43.7	43.7	143.7	144.7
6.	29.2	29.2	27.6	27.6	119.0	119.0	29.0	29.0	27.4	27.4	119.0	118.7
7.	32.4	32.4	26.8	26.8	32.0	32.0	32.4	32.4	26.8	26.8	32.0	32.3
8.	35.4	35.4	35.7	35.7	31.4	31.4	35.2	35.2	35.5	35.2	31.4	31.8
9.	54.8	54.8	40.6	40.6	50.1	50.1	54.8	54.8	40.6	40.6	50.1	50.5
10	36.4	36.4	35.6	35.6	36.6	36.6	36.3	36.3	35.5	35.5	36.6	37.0
11.	21.1	21.1	21.0	21.0	20.9	20.9	20.7	20.7	20.6	20.6	20.9	21.2
12.	40.2	40.2	40.3	40.1	39.1	39.8	40.2	40.0	40.3	39.9	39.1	40.0
13.	41.2	41.2	41.2	41.3	41.2	41.2	40.6	40.5	40.6	40.7	40.2	40.5
14.	56.2	56.5	56.5	56.5	56.2	56.2	56.5	56.2	56.5	56.5	56.5	56.8
15.	32.3	31.4	32.4	31.4	32.3	31.4	31.8	31.7	31.7	31.7	31.8	32.2
16.	81.3	81.0	81.5	81.2	81.3	81.0	80.8	80.8	81.0	80.9	80.7	81.7
17.	63.9	63.8	63.9	63.8	63.9	63.8	62.3	61.9	62.3	62.3	62.1	62.8
18.	16.7	16.5	16.6	16.5	16.7	16.5	16.5	16.5	16.4	16.4	16.3	16.4
19.	23.6	19.6	24.2	19.6	23.6	19.6	12.3	12.4	24.2	23.9	19.7	19.6
20.	40.6	42.0	40.6	42.1	40.6	42.0	41.6	42.1	41.6	42.2	41.6	42.5
21.	16.4	16.5	16.4	16.5	16.4	16.5	14.5	14.3	14.5	14.3	14.5	14.9
22.	110.7	112.5	110.9	112.7	110.7	112.5	109.0	109.5	109.2	109.7	109.9	109.7
23.	30.2	30.3	30.2	30.3	30.2	30.3	31.4	27.0	31.4	27.1	31.4	27.6
24.	29.9	28.0	29.8	28.0	29.9	28.0	28.9	25.9	28.8	25.8	28.8	26.2
25.	29.9	35.2	29.9	35.4	29.9	35.2	30.3	25.8	30.3	26.0	30.3	26.4
26.	68.1	67.6	68.2	67..8	68.1	67.6	66.7	65.0	66.8	65.2	66.7	65.1
27.	14.4	17.4	17.4	17.4	17.4	17.4	17.1	16.0	17.1	16.1	17.1	16.0
OMe	—	48.9	—	48.9	—	48.9	—	—	—	—	—	—

*Values derived by comparisons of the data in various references.

^{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[130–131]. For pyranose with an axial H_1 (β-anomer, 160 Hz) the value is about 10 Hz lower than the corresponding value in equatorial H_1 (α-anomer, 170 Hz).

The point of attachment of sugar with the aglycone leads to the downfield shift of the α-carbon atom and upfield shift of adjacent carbon atom.[132–136] In most of the cases (C_3-sugar chain) it is 6.6 ± 1.0 ppm downfield shift with lower shielding of C_2 (1.1–3.0 ppm) than C_4 (1.8–4.6 pm). In oligofurostanosides, in most of the cases having D-glucose at C_{26}, a 6.8 ± 0.3 ppm downfield shift along with usual 1.8 ± 0.4 ppm upfield shft of C_{25} has been observed. Table-3 shows the ^{13}C-NMR chemical shifts and J_{CH} values (in parentheses) of methyl glycopyranosides which commonly occur in oligofurostanosides (D_2O as a solvent). The application and utility of this technique can be exemplified by the structure elucidation of chloromaloside-A and chloromaloside-B[137].



Chloromaloside-A Chloromaloside-B

TABLE-3

Methylglycoside	C_1	C_2	C_3	C_4	C_5	C_6
β-D-glucopyranoside	103.7 (160)	73.7 (145)	75.5 (143)	70.3 (141)	75.5 (143)	61.7 (144)
α-D-glucopyranoside	99.9 (170)	72.2 (148)	73.9 (147)	70.4 (145)	71.9 (146)	61.5 (145)
β-D-galactopyranoside	104.1 (160)	71.2 (146)	73.3 (141)	69.1 (146)	75.3 (141)	61.4 (144)
α-D-galactopyranoside	99.8 (170)	69.9 (146)	70.2 (145)	68.9 (146)	71.2 (143)	61.8 (143)
β-D-xylopyranoside	104.8 (159)	73.9 (144)	76.7 (144)	70.1 (147)	66.0 (150)	—
α-D-xylopyranoside	100.3 (170)	72.3 (146)	74.2 (145)	70.3 (146)	61.9 (148)	—
β-L-arabinopyranoside	100.7 (169)	69.8 (145)	69.8 (145)	69.1 (145)	63.4 (149)	—
α-L-arabinopyranoside	104.7 (160)	71.6 (148)	73.3 (143)	69.1 (146)	66.9 (150)	—
β-L-rhamnopyranoside	105.7	72.2	75.4	73.8	73.5	18.5
α-L-rhamnopyranoside	102.4	71.9	72.5	73.6	69.4	18.4

^{13}C-NMR CHEMICAL SHIFTS OF SUGAR MOIETIES IN Py

Sugars	Carbons	Chloromaloside-A	Chloromaloside-B
	1	102.4	102.5
	2	73.1	73.1
Galactose	3	75.5	75.6
	4	79.8	79.9
	5	76.0	76.1
	6	60.7	60.7
	1	104.8	105.6
	2	81.2	82.1
Glucose	3	87.0	87.2
	4	74.4	70.4
	5	77.4	77.5
	6	62.4	62.5
	1	104.8	105.0
	2	75.0	75.2
Glucose	3	78..5	78.6
	4	71.1	71.1
	5	77.7	77.8
	6	62.9	62.9
	1	104.6	104.7
	2	75.3	75.3
Xylose	3	78.5	78.6
	4	70.7	70.7
	5	67.3	67.3
	1	—	105.0
	2	—	75.0
26-O-Glucose	3	—	78.5
	4	—	71.8
	5	—	78.4
	6	—	62.9

^{13}C-NMR CHEMICAL SHIFTS OF AGLYCONE MOIETIES IN Py

Carbons	Chloromaloside-A	Chloromaloside-B
1.	36.6	36.7
2.	29.6	29.7
3.	77.3	77.3
4.	34.6	34.7
5.	44.5	44.5
6.	28.6	28.6
7.	31.4	31.4
8.	34.3	34.4
9.	55.6	55.7
10.	36.3	36.3

Carbons	Chloromaloside-A	Chloromaloside-B
11.	38.0	37.9
12.	212.9	212.8
13.	55.3	55.5
14.	55.9	55.9
15.	31.7	31.7
16.	79.8	79.8
17.	54.1	55.3
18.	16.3	16.0
19.	11.7	11.7
20.	43.1	41.1
21.	13.7	15.0
22.	109.8	112.8
23.	26.4	30.9
24.	26.1	28.2
25.	27.5	34.4
26.	65.2	74.6
27.	16.1	17.5
OMe	—	47.4

2D-NMR[106]: 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[138–141] reveals the 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.[142] 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[143] reveals the Nuclear Overhauser Effect [NOE] between intra- and inter-protons of sugar molecules, which makes the identification of monosaccharides and their sequencing even more easy.

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[144–151].

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 oligospirostanosides[33, 151] also impart invaluable information about the sequence of sugars in the glycone part through the characteristic ion peaks as:

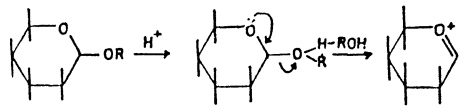
m/z	**Sugars**
219, 187	D-Glucose
189, 157	L-Rhamnose
175, 143	L-Arabinose or D-Xylose
331	D-Glucose peracetate
273	L-Rhamnose peracetate
259	D-Xylose peracetate

(*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)[152–154] and FI (Field Ionisation)[155] 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[156], 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 information about the sequence of the sugar moieties 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.

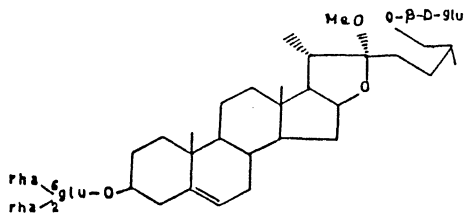
Inorganic impurities, mostly alkali halides, present in the plant glycosides, play an important role in the formation of ions. After a detailed study of FDMS of a series of oligofuro- and oligospirostanosides[157–162], the following generalisations have been drawn:

(i) Alkali metal ions cationisation leads to the formation of most intense $[M + Na]^+$ and less intense $[M + K]^+$ peaks.
(ii) Sometimes less intense $[M + 2Na]^{2+}$ ions are also recorded.
(iii) $[M]^+$ and $[M + H]^+$ ions, 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.[157, 159]

The application and utility of this technique can easily be exemplified by the structure elucidation of Sprengeroside-B[19] as follows:



(a) m/z 1069 $[(M + K)\text{-MeOH}]^+$, 1053 $[(M + Na)\text{-MeOH}]^+$ (base peak) and 538 $[(M\text{-MeOH}) + 2Na]^{2+}$ not only confirm the purity but also prove the presence of C_{22} methoxy group.
(b) The molecular ion peak at m/z 1062 is also observed.
(c) The peaks at m/z 939 $[(M + Na)\text{-}146]^+$ and 793 $[(M + Na)\text{-}(146 + 146)]^+$ confirm the presence of two terminal rhamnose units.
(d) The peaks at m/z 923 $[(M + Na)\text{-}162]^+$ and 777 $[(M + Na)\text{-}(162 + 146)]^+$ prove the presence of terminal glucose and a terminal rhamnose unit..
(e) The peaks displayed at m/z 613 $[(M + Na + H_2O)\text{-}454]^+$ confirm the complete sugar chain at C_3 of aglycone.
(f) The results clearly establish the structure as:

$$\begin{matrix}\text{rha}\\ \text{rha}\end{matrix}\!\!>\text{glu-}(C_3)\text{ diosgenin—glu }(C_{26}),\ C_{22}\text{-OMe}$$

(*c*) *D/CIMS*: As compared to few informations obtained from FDMS the new technique D/CIMS[163–164] 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.

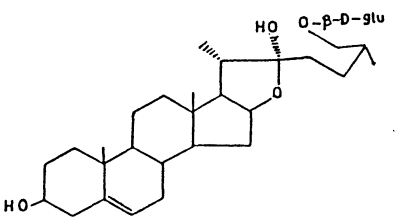
(*d*) *FABMS*: Barber *et al.*[165] invented the technique of FABMS in 1981 to overcome some of the problems of FDMS as it was difficult in practice and the ions providing molecular weight information were produced only transiently. In FABMS an ion surface is developed to accommodate the solid materials and the phenomenon of ion sputtering employing a beam of fast neutral atom, especially of Ar if 2–8 KeV as the primary particle 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 $[M + H]^+$ ions in + ve ion spectrum and from $[M - H]^-$ ion in –ve ion spectrum. Odd-electron molecular ions are not normally produced in abundance which give structural informations. Barber *et al.* believed that the $[M + H]^+$ and $[M - H]^-$ 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[166] molecular ions, which give 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.*[19] have for the first time successfully used this technique for structure elucidation of oligofurostanosides. FABMS has been found to have some specific advantages, *viz.*,

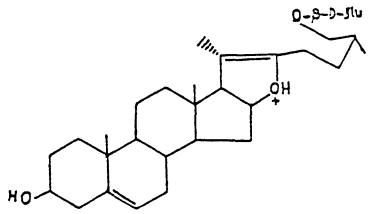
(i) Mass spectra of molecules with relatively high molecular weight can easily be obtained.
(ii) Volatilisation of sample is not required and so no thermal effects are observed.
(iii) No sample derivatisation is required.
(iv) The method works in either polarity and gives pseudomolecular ion sensitivity 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.[19]



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*[167]: 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 forthcomming for lower energy reactions, occurring in Unimolecular Mass Analysed Ion Kinetic Energy (MIKE) Spectrometry. This is because

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

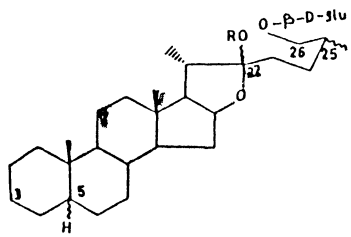
(ii) The occurrence of unimolecular reactions of metastable ion is very sensitive to change in the critical energies of these reactions.

By the study of MIKE spectra of various steroidal compounds, the following generalisations have been carried out:

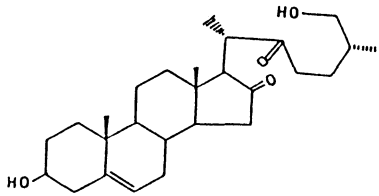
(a) For *cis* A/B ring junction (5β) the change in critical energy for reaction involing C_{19} methyl group loss is less as compared to *trans* A/B ring junction (5α).

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

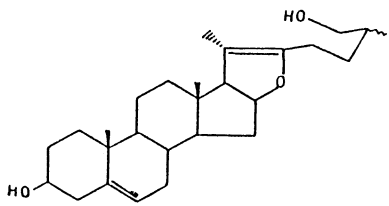
A list of the furostanol saponins reported till 1993, from various plants is tabulated below:



Structure of aglycone (Furostanol)	Corresponding spirostanol (F ring closed)
1. (25S)-5α-furostan-3β-amino-22α, 26-diol	Jurubidine
2. (25S)-5α-furostan-12-on-3β, 22α, 26-triol	Neohecogenin
3. (25R)-5α-furostan-3β, 22α, 26-triol	Tigogenin
4. (25R)-5α-furostan-2β, 3β, 22α, 26-tetraol	Gitogenin
5. (25R)-5α-furostan-12-on-3β, 22α, 26-triol	Hecogenin
6. (25R)-5α-furostan-2α, 3β, 6β, 22α, 26-pentaol	Agigenin
7. (25S)-5α-furostan-2α, 3β, 6β, 22α, 26-pentaol	Neoagigenin
8. (25R)-5α-furostan-3β, 6β, 22α, 26-tetraol	β-Chlorogenin
9. (25R)-5α-furostan-2α-OBz, 3β, 5α, 6β, 22α, 26-pentaol	Karatavegenin
10 (25S)-5α-furostan-3β, 22α, 26-triol	Neotigogenin
11. (25R)-5α-furostan-6-on-3β, 22α, 26-triol	Laxogenin
12. (25S)-5β-furostan-3β, 22α, 26-triol	Sarsasapogenin
13. (25R)-5β-furostan-1β, 2β, 3α, 22α, 26-pentaol	Tokorogenin
14. (25R)-5β-furostan-2β, 3α, 22α, 26-tetraol	Yonogenin
15. (25S)-5β-furostan-2β, 3α, 22α, 26-tetraol	Neoyonogenin
16. (25R)-5β-furostan-2β, 3β, 11α, 22α, 26-pentaol	Metagenin
17. (25S)-5β-furostan-1β, 3β, 4β, 5β, 22α, 26-hexaol	Convellagenin-B
18. (25S)-5β-furostan-1β, 2β, 3β, 4β, 5β, 22α, 26-heptaol	Neopentologenin
19. (25R) -furost-5-en-3β, 22β, 26-triol	Diosgenin
20. (25S) -furost-5-en-3β, 22α, 26-triol	Yamogenin
21. (25R) -furost-5-en-2α, 3β, 22α, 26-tetraol	Yuccagenin
22. (25R) -furost-5-en-3β-17β, 22α, 26-tetraol	Pennogenin
23. (25R) -furost-5-en-1β, 3β, 22α, 26-tetraol	Rescogenin
24. (25S) -furost-5-en-1β, 3β, 22α, 26-tetraol	Neorescogenin
25. (25R) -furost-5-en-3β, 17α, 22α, 26-tetraol	Gentrogenin
26. (25R) -furost-5 en-3β, 14α, 22α, 26-tetraol	Prazerigenin-A
27. (25S) -furost-5-en-3β, 14α, 22α, 26-tetraol	Neoprazerigenin-A
28. 5β-furost-25(27)-en-3β, 22α, 26-triol	Macranthogenin
29. 5β-furost-25 (27)-en-1β, 3β, 22α, 26-tetraol	Convallamarogenin
30. furost-5, 25(27)-dien-1β, 3β, 22α, 26-tetraol	Δ^5Convallamarogenin
31. (25R)-5α-furostan-26-O-acetyl-3β, 14α, 17α, 22α, 26-pentaol	—
32. (25R)-5α-furostan-26-O-acetyl-3β, 17α, 22α, 26-pentaol	—
33. (25S)-5β-furostan-4β-acetoxy-2β, 3α, 22α, 26-tetraol	Diotigenin-4-acetate



34. 17(20) Dehydrokryptogenin



35. Pseudodiosgenin (25R)

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
1.	*Agave americana* (Lf)		
	168, 169	Agavoside-G	rha, xyl >(2,3) glu–^{4}glu–^{4}gal–O–^{3}[5]; R = H
	168–170	Agavoside-H 228–30;–113 (MeOH)	rha–^{4}rha, xyl >(2,3) glu–^{4}gal–O–^{3}[5]; R = H
2.	*Allium ampeloprasus*		
	171	Ampeloside-BF$_1$	glu–^{3}glu–^{4}gal–O–^{3}[6]; R = H
	171	Ampeloside-BF$_2$	glu–^{4}gal–O–^{3}[6]; R = H
3.	*Allium karataviense* (Lf)		
	172	Karatavioside-C	xyl, xyl >(2,3) glu–^{4}gal–O–^{3}[21]; R = H
	173	Karatavegenin-β-glucoside 294–98	glu–O–^{3}[9]; R = H
4.	*Allium narcissiflorum*		
	174	Alliumoside-B	glu–^{3}glu–^{3}glu–O–^{3}[19]; R = H
	174	Alliumoside-C	rha–^{4}rha–^{4}rha–^{6}gal–^{6}glu–O–^{3}[19]; R = H
	174	Alliumoside-D	rha–^{4}rha–^{6}glu, glu >(2,3) glu–O–^{3}[19]; R = H
	174	Alliumoside-E	glu–^{4}rha–^{4}rha–^{6}glu, glu >(2,3) glu–O–^{3}[19]; R = H
	175	Glycoside-B	glu–^{3}glu–^{6}glu–O–^{3}[19]; R = H
5.	*Allium ostowskianum* (Blb)		
	176		xyl, glu >(2,3) glu–^{4}gal–O–^{3}[6, 7]; R = Me
6.	*Allium sativum* (Blb)		
	177	Protoeruboside-B	glu, glu >(2,3) glu–^{4}gal–O–^{3}[8]; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
7.	*Allium schubertii* (Blb)		
	178	Aginoside and Turcoside-A –34.5 (Py)	xyl, glu $>^{3}_{2}$glu–^{4}gal–O–^{3}[6, 7]; R = H
8.	*Allium turcomanicum* (Blb)		
	179	Turcoside-C	xyl, glu $>^{3}_{2}$glu–^{4}gal–O–^{3}[7]; glu–^{2}glu R = H
9.	*Anemarrhena asphodeloides* (Rh)		
	180	Anemarsaponin-B 226	glu–^{2}gal–O–^{3}[35];
10.	*Arecastrum romanzoffianum* (Lf)		
	181	Methyl proto Pb 192–5; –91.8 (Py)	rha–^{4}rha, rha $>^{3}_{2}$glu–^{3}[19]; R = Me
11.	*Aparagus adscendens* (Ft)		
	18	Asparoside-A 180–84; –53 (MeOH)	rha, glu $>^{4}_{2}$glu–O–^{3}[12]; R = Me
	18	Asparoside-B 170–78; –58 (Py)	—do—; R = H
	17	Asparoside-C 167–72; 75 (MeOH)	rha, ara $\rightarrow^{6}_{4}$glu–O–^{3}[12]; R = Me, glu ^{2}
	17	Asparoside-D 161–66; –66 (Py)	—do—; R = H
	182	Adscendoside-A –89 (MeOH)	rha, rha $>^{6}_{4}$glu–O–^{3}[10]; R = Me
	182	Adscendoside-B –92 (H_2O)	—do—; R = H
12.	*Asparagus cochinchinensis* (Rt)		
	121	ASP-IV 165–7; –22.9 (MeOH)	xyl–^{4}glu–O–^{3}[12]; R = Me
	121	ASP-IV 146–49; –30.9 (Py)	—do—; R = H
	121	ASP-V 150–56; –45.5 (MeOH)	rha–^{6}glu–O^{3}[12]; R = Me
	121	ASP-V 270–75; –45.5 (Py)	—do—; R = H
	121	ASP-VI 165–68; –50 (MeOH)	rha, xyl $>^{6}_{4}$glu–O^{3}[12]; R = Me
	121	ASP-VI 169–72; –49.5 (Py)	—do—; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
	121	ASP-VII 179–81; –27 (MeOH)	rha$\diagdown^{6}$ xyl—$_{4}$glu–O^{3}[12]; R = Me glu$\diagup_{2}$
	121	ASP-VII 187–90; –31.6 (Py)	—do—; R = H
	52	ASP-VIII –76.4 (MeOH)	rha–^{4}glu–O^{3}[35];
	52	Methylprotodioscin	rha$\diagdown^{4}$ rha$\diagup_{2}$glu–O–^{3}[19]; R = Me
	52	Pseudoprotodioscin	rha–^{4}glu–O–^{3}[19]; R = H
13.	*Asparagus curillus* (Ft)		
	25	Curilloside-A 180–84; –53 (MeOH)	rha$\diagdown^{6}$ rha$\diagup_{4}$glu–O–^{3}[12]; R = Me
	25	Curilloside-B 170–74; –58 (Py)	—do—; R = H
	(Rt) 26	Curilloside-E –47 (MeOH)	ara$\diagdown^{4}$ glu$\diagup_{2}$glu–O–^{3}[12]; R = Me
	26	Curiloside-F –51 (H_2O)	—do—; R = H
	27	Curilloside-C –78	ara$\diagdown^{6}$ rha—$_{4}$glu–O–^{3}[12]; R = Me glu$\diagup_{2}$
	27	Curilloside-D –66	—do—; R = H
	183	Curilloside-G 173–75; –50	glu$\diagdown^{4}$ rha$\diagup_{2}$glu–O–^{3}[12]; R = Me
	183	Curilloside-H 181–83; –53	—do—; R = H
14.	*Asparagus filicinus* (Rt)		
	184	Aspafiloside-C	ara$\diagdown^{6}$ xyl$\diagup_{4}$glu–O–^{3}[12]; R = Me
	184	—	—do—; R = H
15.	*Asparagus officinalis* (Rt)		
	77	Officinalisnin-I 162–68; –23.8 (MeOH)	glu–^{2}glu–O–^{3}[12]; R = H
	77	Officinalisnin-II 175–82; –41.6 (MeOH)	xyl$\diagdown^{4}$ glu$\diagup_{2}$glu–O–^{3}[12]; R = H
	185	Asparagoside-B	[12]; R = H
	186	Asparagoside-E 254–60; –38 (H_2O)	glu–^{3}glu–O–^{3}[12]; R = H
	187	Asparagoside-G	glu$\diagdown^{4}$ glu$\diagup_{3}$glu–O–^{3}[12]; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
	186	Asparagoside-H	xyl–^{4}glu$\rangle_{3}^{4}$glu–O–^{3}[12]; R = H
	(Sh) 188	Furastanol Saponin-1 192–95; –92.5 ($CHCl_3$: MeOH)	rha$\rangle_{2}^{4}$glu–O–^{3}[20]; R = H
	188	Furastanol Saponin-2 188–92; –74.6 ($CHCl_3$: MeOH)	rha–^{4}glu–O–^{3}[20]; R = H
16.	*Asparagus plumosus*		
	189	Furostanol glycoside-I 171–3; –78 (MeOH)	rha$\rangle_{2}^{3}$glu–O–^{3}[20]; R = Me
	189	Furostanol glycoside-II 183–5; –81 (H_2O)	—do—; R = H
17.	*Asparagus racemosus* (Rt)		
	190	Asparacemoside-A 213–14	rha$\rangle_{2}^{6}$glu–O–^{3}[12]; R = H
	190	Asparacemoside-B 180–83	—do—; R = Me
18.	*Asparagus sprengeri* (Rt)		
	19	Sprengeroside-A 180–84; –100.3 (MeOH)	xyl$\rangle_{2}^{4}$glu–O–^{3}[20]; R = Me
	19	Sprengeroside-B 187–92; –99.5 (MeOH)	rha$\rangle_{2}^{6}$glu–O–^{3}[20]; R = Me
	19	Sprengeroside-C 186–90; –84.5 (Py)	xyl$\rangle_{2}^{4}$glu–O–^{3}[20]; R = H
	19	Sprengeroside-D 192–98; –83.4 (Py)	rha$\rangle_{2}^{6}$glu–O–^{3}[20]; R = H
	191	Sprengeroside-I 186–90; –95.5 (Py)	rha$\rangle_{2}^{4}$glu–O–^{3}[20]; R = Me
	191	Sprengeroside-J 195–98; –79.5 (Py)	—do—; R = H
19.	*Aspidistra elatior*		
	192	— 235–6; –34.8 (MeOH)	glu–O–^{5}[17]; R = Me
	192	— 195–8; –60.4	glu–O–^{5}[17]; R = H
	120	Methylprotoaspidistrin 202–7; –63.4 (Py)	xyl$\rangle_{2}^{3}$glu–^{4}gal–O–^{3}[19]; R = Me
	120	Protoaspidistrin –64 (Py)	—do—; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
20.	*Balanites aegyptica* (Ft)		
	193	Balanitoside-A	rha–^{2}glu–^{4}glu–^{3}[19]; R = Me
	193	Balanitoside-B	—do—; R = H
21.	*Balanites roxburghii* (Sbk)		
	194	Protodeltonin	$\begin{matrix}\text{glu}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}\text{glu–O–}^3$[19]; R = H
22.	*Beshorneria yuccoides* (Lf)		
	195	Beshornoside 219–21; –25 (Py)	$\begin{matrix}\text{rha–}^4\text{glu}\\ \text{rha–}^4\text{glu}\end{matrix}\!>\!{}^{3}_{2}\text{glu–O–}^3$[3]; R = H
23.	*Capsicum annum* (Sd)		
	196	Capsicoside 295; –35 ($CHCl_3$: MeOH)	$\begin{matrix}\text{glu}\\ \text{glu}\end{matrix}\!>\!{}^{3}_{2}\text{glu–}^4\text{gal–}^3\text{glu–O–}^3$[4]; R = H
24.	*Chamaerops humilies* (Wp)		
	197	Methylprotodioscin [Cst_1, Cu_3] 185–89; –102.9 (Py)	$\begin{matrix}\text{rha}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}\text{glu–O–}^3$[19]; R = Me
	197	Methylproto Pb. [Cl_2, Cst_2, Cu_4] 189–90; –86.4 (Py)	$\begin{matrix}\text{rha–}^4\text{rha}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}\text{glu–O–}^3$[19]; R = Me
	197	Methylprotorhapissaponin [Cu_5] 196–99; –92.4 (Py)	$\begin{matrix}\text{glu–}^4\text{rha–}^4\text{rha}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}\text{glu–O–}^3$[19]; R = Me
25.	*Chlorophytum malayense* (Rh)		
	137	Chloromaloside-B 295–98; –48.3 (Py)	$\begin{matrix}\text{xyl}\\ \text{glu}\end{matrix}\!>\!{}^{3}_{2}\text{glu–}^4\text{gal–O–}^3$[2]; R = Me
26.	*Convallaria majalis* (Rt)		
	198	Convallamaroside –66 (MeOH)	$\begin{matrix}\text{rha–}^2\text{qui–O}\\ \text{glu–}^4\text{rha–O}\end{matrix}\!>\!{}^{1}_{3}$[29]; R = H
27.	*Costus speciosus* (Sd)		
	199	Costusoside-I 220–24; –76.5 (Py)	$\text{glu–}^2\begin{matrix}\text{rha}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}\text{glu–O–}^3$[19]; R = Me
	199	Costusoside-J 248–50; –79.1 (Py)	—do—; R = H
	200	— 194–7; –70.4 (Py)	rha–^{2}glu–O–^{3}[19]; R = Me
	200	Methyl protodioscin 185–7; –102.9 (Py)	$\begin{matrix}\text{rha}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}\text{glu–O–}^3$[19]; R = Me
	200	Protodioscin 190–6; –57.8 (Py)	—do—; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
28.	*Digitalis lanata* (Lf)		
	32	Lanagitoside 260–83; –18.6 ($CHCl_3$: MeOH)	$\begin{matrix}\text{xyl}\\ \text{glu}-^3\text{gal}\end{matrix}>^3_2\text{glu}-^4\text{gal}-\text{O}-^3[4]$; R = Me
	32	—	—do—; R = H
	32	Lanatigoside 268–92; –28.4 ($CHCl_3$: MeOH)	$\begin{matrix}\text{xyl}\\ \text{glu}-^4\text{gal}\end{matrix}>^3_2\text{gal}-\text{O}-^3[3]$; R = H
	32	—	—do—; R = H
29.	*Digitalis purpurea* (Lf)		
	201	Purpureogitoside	$\begin{matrix}\text{xyl}\\ \text{glu}\end{matrix}>^3_2\text{glu}-^4\text{gal}-\text{O}-^3[4]$; R = H
30.	*Dioscorea collettii* (Rh)		
	202	Saponin-C 183–5; –81 (H_2O)	$\begin{matrix}\text{rha}\\ \text{rha}\end{matrix}>^3_2\text{glu}-\text{O}-^3[20]$; R = H
31.	*Dioscorea deltoidea* (Rh)		
	203	Deltoside-II	$\begin{matrix}\text{glu}\\ \text{rha}\end{matrix}>^3_2\text{glu}-\text{O}-^3[19]$; R = H
	203	Deltoside-III	—do—; R = Me
32.	*Dioscorea floribunda* (Rh)		
	35	Methylprotodioscin	$\begin{matrix}\text{rha}\\ \text{rha}\end{matrix}>^4_2\text{glu}-\text{O}-^3[19]$; R = Me
	35	— 182	[19]; R = Me
	204	Floribundasaponin-E 226–29; –66 (Py)	$\text{rha}-^3\text{rha}-^3\text{rha}-^3\text{rha}-^4\text{glu}-\text{O}-^3[19]$; R = Me
	204	Floribundasaponin-F (243–47); –74.6 (Py)	—do—; R = H
33.	*Dioscorea gracillima* (Rh)		
	33	Methylprotodioscin	$\begin{matrix}\text{rha}\\ \text{rha}\end{matrix}>^4_2\text{glu}-\text{O}-^3[19]$; R = Me
	33	Protodioscin 190–96; –57.8 (Py)	—do—; R = H
34.	*Dioscorea tenuipes* (Ap)		
	205	Diotigenin-4-acetate furastanol-26-O-glucoside 172–74; + 134.4	[33]; R = Me
35.	*Dioscorea tokoro* (Tc)		
	206	Prototokorin 177–78; –31.8 (MeOH)	$\text{glu}-\text{O}-^1[12]$; R = H
	207	—	[14]; R = H
	207	—	[15]; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
36.	*Dioscorea septemloba*		
	33	Methylprotogracillin 249–51; –76.9 (MeOH)	glu, rha >(2→3) glu–O–3[19]; R = Me
	33	Protogracillin 235–38; –57.8 (Py)	—do—; R = H
	33	Methlprotodioscin	rha, rha >(2→4) glu–O–3[19]; R = Me
	33	Protodioscin	—do—; R = H
37.	*Dioscorea zingiberensis*		
	208	Zingiberenin-C	rha, glu >(2→3) glu–O–3[19]; R = H
	208	Zingiberenin-D	glu, rha >(2→3) glu–O–3[20]; R = Me
38.	*Dracaena afromontana* (Twg)		
	209	Afromontoside > 300; –69.3 (Py)	rha–4glu–O–3[19]; R = H But 26–O–rha.
39.	*Funkia ovata* (Lf)		
	210	Funkioside-B 258–66; –135 (MeOH)	glu–O–3[19]; R = H
	210–211	Funkioside-I	rha–4rha, xyl >(3→4) glu–3glu–4gal–O–3[19]; R = H
40.	*Helleborus macranthus* (Rt + Rh)		
	212	Macranthoside-I 228–31	glu–6glu–O–3[28]; R = H
	212	Macranthoside-I 263–66	—do—; R = Me
41.	*Heloniopsis orientalis* (Wp)		
	213	Hb (Methylprotodioscin) 189–92; –98.2	rha, rha >(2→4) glu–O–3[19]; R = Me
	213	Hd(III) –92.1	rha–4rha, rha >(2→4) glu–O–3[22]; R = H
	213	Hd(III) –100.2	—do—; R = Me
	213	Hc(VI)	rha–4rha, rha >(2→4) glu–O–3[34];
42.	*Kallstroemia pubescens* (Wp)		
	214	Kallstroemin-A 235–38; –82 (Py)	rha–2rha–2rha–6glu–O–3[19]; R = H
	214	Kallstroemin-B 232–35; –79.5 (Py)	—do—; R = Me
43.	*Licuala spinosa* (Lf)		
	215	Methylprotodioscin 166–68; –73 (Py)	rha, rha >(2→3) glu–O–3[19]; R = Me

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
44.	*Lilium cordatum* (Pt)		
	216	Compound-I –47.1 (MeOH)	rha–^{2}glu–O–^{3}[19]; R = Me
	216	Compound-II –75.8 (MeOH)	rha–^{2}(6–O–acetyl)–glu–O–^{3}[19]; R = Me
45.	*Lilium hansonii* (Blb)		
	217	Compound-9 –48.8 (MeOH)	$\begin{matrix}\text{glu}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}$glu–O–^{3}[3]; R = H
	217	Compound-10	$\begin{matrix}\text{glu}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}$glu–O–^{3}[19]; R = H
46.	*Lilium paradarinum* (Bib)		
	218–219	Pardarinoside-A –56.4 (MeOH)	rha–^{2}glu–O–^{3}[31]; R = Me But 26-O-Ac.
	218–219	Pardarinoside-B –62 (MeOH)	rha–^{2}glu–O–^{3}[32]; R = Me
	219	Pardarinoside-C –50.5 (MeOH)	$\begin{matrix}\text{glu}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}$glu–O–^{3}[31]; R = Me
	219	Pardarinoside-D –59.7 (MeOH)	$\begin{matrix}\text{glu}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}$glu–O–^{3}[32]; R = Me
	219	Paradarinoside-F –32.8 (MeOH)	$\begin{matrix}\text{ara}\\ \text{rha}\end{matrix}\!>\!{}^{3}_{2}$glu–O–^{3}[31]; R = Me
	219	Pardarinoside-G –40.8 (MeOH)	$\begin{matrix}\text{ara}\\ \text{rha}\end{matrix}\!>\!{}^{3}_{2}$glu–O–^{3}[32]; R = Me
47.	*Lilium regale (Blb)*		
	220	—	$\begin{matrix}\text{glu}\\ \text{rha}\end{matrix}\!>\!{}^{3}_{2}$glu–O–^{3}[20]; R = Me
48.	*Liriope platyphilla*		
	221	Methylprotodioscin 185–7; –102.9 (Py)	$\begin{matrix}\text{rha}\\ \text{rha}\end{matrix}\!>\!{}^{4}_{2}$glu–O–^{3}[19]; R = Me
	221	Protodioscin 190–6; –57.8 (Py)	—do—; R = H
49.	*Liriope spicata*		
	222	Spicatoside-A	$\begin{matrix}\text{xyl}\\ \text{glu}\end{matrix}\!>\!{}^{3}_{2}$fuc–O–^{1}[23]; R = Me
	222	Spicatoside-B	—do—; R = H
50.	*Lycopersicum esculentum* (Sd)		
	223	Furastanol saponin 217–20; –24 (MeOH + $CHCl_3$)	glu–^{2}glu–^{4}gal–O–^{3}[10]; R = Me
	223	TFI 217–18; –24 (MeOH + $CHCl_3$)	–do—; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
51.	*Metanarthecium uteoviride*		
	224	— 166–68; –73 (Py)	ara–O–^{11}[16]; R = Me
52.	*Ophiopogon jaburan* (Rh)		
	225	Glycoside-J_5 165–68	rha–^{2}(4–O–S–fuc)–O–$^1_3$[23 + 24]; glu–O R = H
	225	Glycoside-J_6 201–3	rha–^{2}(4–O–S–ara)–O–$^1_3$[28]; glu–O R = H
53.	*Ophiopogon ohwii* (Rh)		
	225	Glycoside-O_6 183–85; –50.8 (Py)	rha–^{2}(4–O–S–fuc)–O–^{1}[23]
54.	*Ophiopgon planiscapus*		
	226	Glycoside-D 194–7; –70.4 (Py)	rha–^{2}glu–O–^{3}[19]; R = H
	226	Glycoside-F	glu–$^4_2$glu–O–^{3}[19]; R = Me rha
	226	—	—do—; R = H
	226	Glycoside-G 212–5; –55.2 (Py)	rha–^{2}(4–O–S–ara)–O–^{1}[23]; R = H
55.	*Paris formosana*		
	227	— 174–7; -87	rha–^{4}rha–$^4_2$glu–O–^{3}[19]; R = Me rha
56.*	*Paris polyphylla* (Tb)		
	228	Polyphyllin-G 177–81; –76.9 (Py)	ara–$^4_3$glu–O–^{3}[19]; R = Me rha
	228	Polyphyllin-H	—do—; R = H
57.	*Paris teraphylla*		
	30, 218	Dehydrokryptogenin tetraglycoside	rha–^{4}rha–$^4_2$glu–O–^{3}[34]; R = H rha
58.	*Phoenix canariensis* (Lf)		
	215	Methyl (25S) Proto Pb 255–8; –84.8 (MeOH)	rha–^{4}rha–$^4_2$glu–O–^{3}[20]; R = Me rha
59.*	*Phoenix dactylifera* (Lf)		
	215	Methylprotoprosapogenin-A of dioscin 173–77; –87.6 (Py)	rha–^{4}glu–O–^{3}[19]; R = Me
	215	Methylprotorectinatoside 150–2; –86.7 (Py)	rha–^{5}ara–$^4_2$glu–O–^{3}[19]; R = Me rha

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
	215	Methylproto Pb 176–9; –83.1 (Py)	rha–^{4}rha$\rangle_{2}^{4}$glu–O–^{3}[19]; R = Me (rha)
60.*	*Phoenix humilis* (Lf)		
	215	Methyl (25S) proto Pb 255–58; –84.8 (MeOH)	rha–^{4}rha$\rangle_{2}^{4}$glu–O–^{3}[20]; R = Me (rha)
	215	Methyl (25S) proto loureiroside 185–87; –78.3 (Py)	rha–^{5}ara$\rangle_{2}^{4}$glu–O–^{3}[20]; R = Me (rha)
61.*	*Phoenix loureirii* (Lf)		
	181	Methylproto Pb 192–95; –91.8 (Py)	rha–^{4}rha$\rangle_{2}^{4}$glu–O–^{3}[19]; R = Me (rha)
	181	Methylprotorupicolaside 195–99; –82.6 (Py)	glu–^{2}rha–^{4}rha$\rangle_{2}^{4}$glu–O–^{3}[19]; R = Me (rha)
	181	Methylprotoloureiroside 183–86; –84.1 (Py)	rha–^{5}ara$\rangle_{2}^{4}$glu–O–^{3}[19]; R = Me (rha)
62.*	*Phoenix reclinata* (Lf)		
	181	Methylproto Pb 192–95; –91.8 (Py)	rha–^{4}rha$\rangle_{2}^{4}$glu–O–^{3}[19]; R = Me (rha)
	181	Methylprotorupicolaside 195–99; –82.6 (Py)	glu–^{2}rha–^{4}rha$\rangle_{2}^{4}$glu–O–^{3}[19]; R = Me (rha)
	181	Methylprotoreclinata 165–68; –44.2 (Py)	rha–^{5}ara$\rangle_{2}^{4}$glu–O–^{3}[19]; (rha)
63.	*Phoenix rupicola* (Lf)		
	181	Methylprototaccaoside 180–83; –77.2 (Py)	rha$\rangle_{2}^{3}$glu–O–^{3}[19]; R = Me (rha)
	181	Methylproto Pb 192–95; –91.8 (Py)	rha–^{4}rha$\rangle_{2}^{4}$glu–O–^{3}[19]; R = Me (rha)
	181	Methylprotorupicolaside 195–99; –82.6 (Py)	glu–^{2}rha–^{4}rha$\rangle_{2}^{4}$glu–O–^{3}[19]; R = Me (rha)
64.	*Polygonatum kingianum* (Rh)		
	229	Kingianoside-C –27.4 (Py)	glu–^{4}gal–O–^{3}[25]; R = Me
	229	Kingianoside-C –34.4 (Py)	gal–^{4}fuc–O–^{3}[25]; R = H
	229	(25R) epimer of PO-8 –59.4 (Py)	glu–^{4}gal–O–^{3}[19]; R = Me
65.	*Polygonatum latifolium* (Lf)		
	230	Potopolygonatoside-E	glu–^{3}glu–^{4}gal–^{3}glu–O–^{3}[19]; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
66.	*Polygonatum odoratum*		
	231	PO-C 208–10; –49 (Py)	glu$\rightarrow^{3}_{2}$glu–^{4}gal–O–^{3}[27]; R = Me
	231	PO-d 208–13; –48.1 (Py)	glu$\rightarrow^{3}_{2}$glu–^{4}gal–O–^{3}[26 + 27]; R = Me
67.	*Polygonatum prattii* (Rt)		
	232	Pratioside-B –52.5 (H_2O)	glu–^{2}glu–^{4}gal–O–^{3}[25]; R = H
68.	*Polygonatum officinale* (Rh)		
	233	Polyfuroside-β 252–58; –68 (Py)	glu$\rightarrow^{4}_{2}$glu–^{4}gal–O–^{3}[19]; R = H
69.	*Polygonatum verticillatum*		
	234	Methyl protodioscin	rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me
	234	Protodioscin	—do—; R = H
70.	*Radix sarsaparilla*		
	22, 31	Sarsaparilloside –44 (H_2O)	rha^{6} xyl—^{4}glu–O–^{3}[12]; R = H R = H glu^{2}
71.	*Rhapis exelsa* (Wp)		
	235	Methylprotodioscin [Est_2, El_1, Eu_2] 185.90; –102.9 (Py)	rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me
	235	Methylprotodeltonin [Est_{4-a}] 196–99; –59.8 (Py)	glu$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me
	235	Methylproto Pb [El_2, Est_{4-b}, Eu_3] 189–90; –86.4 (Py)	rha–^{4}rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me
	235	Methylprotorhapissaponin [El_3] 196–99; –92.4 (Py)	glu–^{4}rha–^{4}rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me
72.	*Rhapis humilis* (Wp)		
	235	Methylprotoprosapogenin-A of dioscin [Hst_4, Hl_1, Hu_2] 178–80; –81.2 (Py)	rha–^{4}glu–O–^{3}[19]; R = Me
	235	Methylprotodioscin [Hl_2, Hst_5, Hu_2] 185–89; 102.9 (Py)	rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
	235	Methylprotodeltonin [Hst_6] 196–99; –59.8 (Py)	glu$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me rha
	235	Methylproto Pb [Hl_3, Hu_4] 189–90; –86.4 (Py)	rha–^{4}rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me rha
73.	*Ruscus aculeatus* (Rh)		
	236	Deglucoruscoside	rha–^{2}ara–O–^{1}[30]; R = H
	236	Ruscoside	glu–^{3}rha–^{2}ara–O–^{1}[30]; R = H
74.	*Smilax aristolochiaefolia* (Rt)		
	22, 31	Sarsaparilloside –44 (H_2O)	glu^{6} rha–^{4}glu–O–^{3}[12]; R = H rha^{2}
75.	*Smilax aspera (Lf)*		
	237	Asperoside	rha–^{4}rha$\rightarrow^{4}_{2}$glu–O–^{3}[20]; R = H rha
76.	*Smilax chinae*		
	33	Smilax saponin-B 183–86; –90 (MeOH)	rha–^{4}rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me rha
	(Rh and Rt) 238	Pseudoprotodioscin –72 (MeOH)	rha$\rightarrow^{4}_{2}$glu–O–^{3}[35]; rha
	238	Methyl protodioscin –86 (MeOH)	rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me rha
77.	*Smilax sieboldi* (Rh)		
	239	Compound-4 –44.8 (EtOH)	ara–^{6}glu–O–^{3}[11]; R = H
	239	Compound-5 –46.3 (EtOH)	ara$\rightarrow^{6}_{4}$glu–O–^{3}[11]; R = H glu
78.	*Solanum lyratum* (Ber)		
	249	Methylprotoaspidistrin 202–7; –63.4 (Py)	rha$\rightarrow^{3}_{2}$glu–O–^{3}[19]; R = Me glu
	240	Aspidistrin 210–14; –64 (Py)	—do—; R = H
	241	Furastanol glucuroside –61.4 (H_2O)	glu$\rightarrow^{3}_{2}$glu–O–^{3}[19]; R = H rha
79.	*Solanum melangena* (Sd)		
	242	Melongoside-N 187–89; –15 (MeOH)	glu–^{2}glu–O–^{3}[3]; R = H
	242	Melongoside-O 183.–84; –19 (MeOH)	glu–^{2}glu–O–^{3}[19]; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
	242	Melongoside-P 179–80; –75 (H_2O)	rha$\rightarrow^{3}_{2}$glu–O–^{3}[3]; R = H glu
80.	*Solanum nigrum* (Wp)		
	243	Uttroside-A 220–25; –49 (MeOH)	xyl$\rightarrow^{3}_{2}$glu–^{4}gal–O–^{3}[3]; R = Me glu
	243	Uttroside-B 210–15; –46 (Py)	—do—; R = H
81.	*Solanum paniculatum* (Rt)		
	20–21	Jurubine 212–14; –31 (Py)	[1]; R = H
82.	*Trachycarpus fortune*		
	244	Methylprotodioscin	rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me rha
	244	Protodioscin	—do—; R = H
	244	— 174–7; –87	rha–^{4}rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = H rha
83.	*Trachycarpus wagnerianus* (Wp)		
	197	Methylprotodioscin [Tst_1] 185–89; –102.9 (Py)	rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me rha
	197	Methylproto Pb [Tl_3, Tu_3] 189–90; –86..4 (Py)	rha–^{4}rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me rha
	197	Pseudoprotodioscin [Tst_2] 174–76; –80.4 (Py)	rha$\rightarrow^{4}_{2}$glu–O–^{3}[35] rha
	197	Pseudoproto Pb [Tl_4, Tu_4] 181–83; –84.4 (Py)	rha–^{4}rha$\rightarrow^{4}_{2}$glu–O–^{3}[35] rha
84.	*Tribulus terrestris*		
	245–247	Methylprotodioscin 189–90	rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me rha
	245–247	Protodioscin	—do—; R = H
	245–247	Methylprotogracillin	glu$\rightarrow^{3}_{2}$glu–O–^{3}[19]; R = Me rha
85.	*Trigonella coerulea* (Sd)		
	245–247	Methylprotodioscin 189–93	rha$\rightarrow^{4}_{2}$glu–O–^{3}[19]; R = Me rha
	245–247	Protodioscin	—do—; R = H
86.	*Trigonella foenumgraecum* (Sd)		
	247–249	Trigonelloside-B	rha$\rightarrow^{4}_{2}$glu–O–^{3}[20]; R = Me rha
	247–249	Trigonelloside-C	—do—; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
	250	Furostanol glycoside 242–46	glu$_{rha}^{3}$>^{2}glu–O–^{3}[10]; R = Me
	48	Trigofoenoside-A-1 219–21; –90.1 (Py)	rha–^{2}glu–O–^{3}[20]; R = Me
	48	Trigofoenoside-A 210–13	—do—; R = H
	251	Trigofoenoside-B 198–200; –62.1 (Py)	rha–^{4}glu–O–^{3}[10]; R = Me
	251	Trigofoenoside-C 210–12; –64.1 (Py)	rha$_{rha}^{4}$>^{2}glu–O–^{3}[4]; R = Me
	48	Trigofoenoside-D-1 246–48; –73.2 (Py)	glu$_{rha}^{3}$>^{2}glu–O–^{3}[20]; R = Me
	48	Trigofoenoside-D	—do—; R = H
	252	Trigofoenoside-F-1 256–58; –78.9 (Py)	rha–^{2}glu–^{6}glu–O–^{3}[19]; R = Me
	252	Trigofoenoside-F 233–36	—do—; R = H
	252	Trigofoenoside-G-1 270–74; 79.2 (Py)	xyl$_{rha}^{4}$>^{2}glu–^{6}glu–O–^{3}[19]; R = Me
	252	Trigofoenoside-G 275–8	—do—; R = H
	253	—	xyl$_{rha}^{4}$>^{2}glu–O–^{3}[3]; R = Me
87.	*Trillium kamtschaticum* (Ugp)		
	30	Furastanol bisglycoside 265–71; –83.1 (Py)	rha–^{2}glu–O–^{3}[19]; R = Me
	30	Protopennogenin, 3-O-rhamnosyl glucoside 275–80; –84.6 (Py)	rha–^{2}glu–O–^{3}[22]; R = H
	30	Dehydrokryptogenin-diglycoside 265–68; –80.1 (Py)	rha–^{2}glu–O–^{3}[34]; R = H
	254	Tj 205–12; –66.5	rha$_{rha}^{4}$>^{2}glu–O–^{3}[22]; R = Me
	254	Tk 194–200; –90 (Py)	rha–^{4}rha$_{rha}^{4}$>^{2}glu–O–^{3}[22]; R = Me
88.	*Trillium tschonoskii* (Rt)		
	255	Methylprotodioscin	rha$_{rha}^{4}$>^{2}glu–O–^{3}[19]; R = Me
89.	*Yucca filamentosa* (Rt)		
	34	Protoyuccoside-C 182–84; –30 (MeOH)	gal–^{2}glu–^{4}glu–O–^{3}[12]; R = H
	256	Protoyuccoside-E 150–52; –29 (MeOH)	gal$_{gal}^{6}$>^{2}glu–^{4}glu–O–^{3}[12]; R = H

S. No.	Source (Part) with reference	Saponin (m.p. °C: $[\alpha]_D^0$)	Structure
90.	*Yucca gloriosa* (Fl)		
	257	YG-4 +21 (Py)	$\begin{matrix}\text{xyl}\\ \text{xyl}-{}^{3}\text{glu}\end{matrix}\!\!>{}^{3}_{2}\text{glu}-{}^{4}\text{gal}-\text{O}-{}^{3}[4];$ R = H

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 = Fucose; Rt = Root; Rh = Rhizome; Lf = Leaf; Sd = Seed; Ugp = Underground part; Wp = Whole part; Blb = Bulb; Ap = Aerial part; Ft = Fruit; Sh = Shoot; Sbk = Stem bark; Tc = Tissue culture; Twg = Twigs; Tb = Tuber; Ber = Berry; Tl = 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 β.

REFERENCES

1. K. Schreiber, *Alkal.*, **10**, 1 (1968).
2. J. Elks, *Rodd's Chem. Carbon Compd.*, Elsevier, Amsterdam, 2nd Edn., Vol. IIE, p.1 (1971).
3. K. Takeda, *Prog. Phytochem.*, Interscience, New York, Vol. 3, p. 287 (1972).
4. R. Tschesche and G. Wulff, *Fortsch. Chem. Nat. Stoffe*, **30**, 461 (1973).
5. J. Elks, *Rodd's Chem. Carbon Compd.*, Elsevier, Amsterdam, Supplementary of 2nd edn., Vol. IID, p. 205 (1974).
6. J.G. Roddick, *Phytochem.*, **13**, 9 (1974).
7. R.B. Herbert, *Alkal.* Specialist Periodical Reports, The Chem. Soc., London, Vol. 5, p. 256 (1975).
8. D.M. Harrison, *Alkal.* Specialist Periodical Reports, The Chem. Soc., London, Vol. 6, p. 285 (1976).
9. T. Kawasaki, *Method. Chem.*, **11**, 87 (1978).
10. L-C. Wang, *Ying Yung Chieh Mein Hua Hueh*, **13**, 30 (1981).
11. S.B. Mahato, A.N. Ganguly and N.P. Sahu, *Phytochem.*, **21**, 959 (1981).
12. S.B. Singh and R.S. Thakur, *J. Sci. Indi. Res.*, **42**, 319 (1983).
13. G. Voigt and K. Hiller, *Scientia Pharmaceutica*, **55**, 201 (1987).
14. W.A. Jacobs and J.C.E. Simpson., *J. Biol. Chem.*, **105**, 501 (1934).
15. _____, *J. Am. Chem. Soc.*, **56**, 1424 (1953).
16. H. Rochelmeyer, *Arch. Pharm.*, **274**, 543 (1936).
17. S.C. Sharma, R. Chand, B.S. Bhatti and O.P. Sati, *Planta Med.*, **46**, 48 (1982).
18. _____, *Phytochem.*, **21**, 2075 (1982).
19. S.C. Sharma and R. Kumar, IUPAC Conference, Cologne (Germany) (1983).
20. K. Schreiber and H. Ripperger, *Tet. Lett.*, 5997 (1966).
21. H. Ripperger, H. Budzikewicz and K. Schreiber, *Chem. Ber.*, **100**, 1725 (1967).
22. R. Tschesche, G. Lüdke and G. Wulff, *Tet. Lett.*, 2785 (1967).
23. E.S. Rothman, M.E. Wall and C.R. Eddy. *J. Am. Chem. Soc.*, **74**, 4043 (1952).
24. R.E. Marker and J. Lopez., *J. Am. Chem. Soc.*, **69**, 2389 (1947).
25. S.C. Sharma, O.P. Sati and R. Chand, *Planta Med.*, **47**, 117 (1983).

26. _____, *Phytochem.*, **21**, 1711 (1982).
27. O.P. Sati and S.C. Sharma, *Pharmazie*, **40**, 417 (1985).
28. S. Kiyosawa and M. Hutoh, *Chem. Pharm. Bull.*, **16**, 1162 (1968).
29. T. Konishi, S. Kiyosawa and J. Shoji, *Chem. Pharm. Bull.*, **33**, 591 (1985).
30. T. Nohara, K. Miyahara and T. Kawasaki, *Chem. Pharm. Bull.*, **23**, 872 (1975).
31. R. Tschesche, G. Lüdke and G. Wulf, *Chem. Ber.*, **102**, 1253 (1969).
32. R. Tschesche, L. Seidel, S.C. Sharma and G. Wulff, *Chem. Ber.*, **105**, 3397 (1972).
33. T. Kawasaki, T. Komori, K. Miyahara, T. Nohara, I. Hosokawa, M. Ichiro and K. Mihoshi, *Chem. Pharm. Bull.*, **22**, 2164 (1974).
34. I.P. Dragalin and P.K. Kintya, *Phytochem.*, **14**, 1817 (1975).
35. G.A. Hoyer, W. Sucrow and D. Winkler, *Phytochem.*, **14**, 539 (1975).
36. R. Tschesche, H. Rehkämper and G. Wulff, *Liebigs Ann. Chem.*, **726**, 125 (1969).
37. R. Tschesche, A. Weber and G. Wulff, *Liebigs Ann. Chem.*, **721**, 209 (1969).
38. T. Kawasaki and K. Miyahara, *Chem. Pharm. Bull.*,**11**, 1546 (1963).
39. J. Wagner and H. Hoffmann, *Z. Physiol. Chem.*, **348**, 1697 (1967).
40. A.J. Khorlin, L.V. Bakinoveskii, V.E. Vaskovskii, G.A. Venjaminova and J.S. Ovodov, *Izv. Akad. Nauk, SSSR. Ser. Khim. Nauk.*, 2008 (1963).
41. J. Shoji, S. Kawanishi and Y. Tsukitani, *Chem. Pharm. Bull.*, **19**, 1740 (1971).
42. N.J. Uvarova, R.P. Goreshkova, L.U. Strigina, C.B. Elyakov and N.K. Kochetkov, *Khim. Prir. Soedin.*, **1**, 82 (1965).
43. R. Tschesche and G. Wulff, *Chem. Ber.*, **94**, 2019 (1961).
44. _____, *Tetrahed.*, **19**, 621 (1963).
45. M. Kimura, M. Tohma, I. Joshizawa and H. Akiyama, *Chem. Pharm. Bull.*, **16**, 25 (1968).
46. N.J. Uvarova, R.P. Goreshkova and G.B. Elyakov, *Izv. Akad. Nauk. SSSR., Ser. Khim. Nauk.*, 1850 (1963).
47. T. Tanimura, J.J. Pisano, Y. Ito and R.L. Bowman, *Sci.*, **169**, 54 (1971).
48. R.K. Gupta, D.C. Jain and R.S. Thakur, *Phytochem.*, **24**, 2399 (1985).
49. H.W. Liu and K. Nakanishi, *J. Am. Chem. Soc.*, **103**, 7065 (1981).
50. _____, *Tetrahed.*, **38**, 513 (1982).
51. Y. Okada, S. Shibata, T. Ikekawa, A.M.J. Javelland and O. Kamo, *Phytochem.*, **26**, 2789 (1987).
52. Z.Z., Lianz, R. Aquino, F. De-Simone, A. Dini, O. Schettino and C. Pizza, *Planta Med.*, **54**, 344 (1988).
53. G.C. Uniyal, P.K. Agrawal, O.P. Sati and R.S. Thakur, *Phytochem.*, **30** 1336 (1991).
54. K. Maćek, Paper Chromatography, Academic Press, New York, p. 289 (1963).
55. R.W. Scoddast, A.J. Barrett and D.H. Northcote, *J. Bio. Chem.*, **102**, 194 (1967).
56. E. Gulbaran, *J. Am. Leather. Chem. Ass.*, **59**, 619 (1964).
57. S.M. Patridge, *Nature*, **158**, 270 (1946).
58. _____, *Biochem. J.*, **42**, 238 (1948).
59. B. Ledrer and M. Ledrer, Chromatography, Elsevier Publ. Co, Amsterdam, p. 237 (1957).
60. H. Kiliani, *Ber.*, **63**, 2866 (1930).
61. B. Wilkomirsky, V.A. Bobeiko and P.K. Kintya, *Phytochem.*, **14**, 2657 (1975).
62. T. Purdie and I.C. Irvine, *J. Chem. Soc.*, **83**, 1021 (1903).
63. R. Kuhn, H. Egge, R. Brossmer, A. Gauche, H. Trischmann, P. Klesse, W. Lochinger, E. Rohm and D. Tschampel, *Angew. Chem.*, **72**, 805 (1960).
64. S. Hakomori, *J. Biochem.*, **55**, 205 (1964).
65. N.K. Kochetkov, N.S. Wulfson, O.S. Chizhov and B.M. Zolotarev, *Tetrahed.*, **19**, 2209 (1963).

66. N.K. Kochetkov and O.S. Chizhov, *Tetrahed.*, **21**, 2029 (1965).
67. K. Heyns, K.R. Sperling and H.F. Grutzmacher, *Carbohyd. Res.* **9**, 79 (1969).
68. D. Gagnair and L. Odier, *Carbohyd. Res.*, **11**, 33 (1969).
69. S.C. Williams and J.K.N. Jones,*Can. J. Chem.*, **45**, 275 (1967).
70. H.C. Srivastava and G. Adams, *Can. J. Chem.*, **40**, 1415 (1962).
71. M.L. Wolform, D.L. Patin and R.M. De-Lederkremer, *J. Chromatog.*, **17**, 488 (1965).
72. R. Tschesche and G. Balle, *Tetrahed.*, **19**, 2323 (1963).
73. O.D. Hensens and K.G Lewis, *Tet. Lett..*, 4639 (1965).
74. R. Kuhn and I. Löw, *Liebigs Ann. Chem.*, **669**, 183 (1963).
75. R. Tschesche, F. Inchaurrondo and G. Wulff, *Liebigs Ann. Chem.*, **680** ,107 (1964).
76. T. Tschesche, T. Kottler and G. Wulff, *Liebigs Ann.. Chem.*, **699**, 212 (1966).
77. K. Kawano, K. Sakari, H. Sato and S. Sakamura, *Agr. Biol. Chem.*, **39**, 1999 (1975).
78. W. Klyne, *Biochem. J.*, **47**, 41 (1950).
79. C. Djerassi, E.W. Foltz and A.E. Lippman, *J. Am. Chem. Soc.*, **77**, 4354 (1955).
80. E.W. Foltz, A.E. Lippman and C. Djerassi, *J. Am.. Chem. Soc.*, **77**, 4359 (1955).
81. A.E. Lippman, E.W. Foltz and C. Djerassi, *J. Am. Chem. Soc.*, **77**, 4364 (1955).
82. C. Djerassi and R. Ehrlich, *J. Am. Chem. Soc.*, **78**, 440 (1956).
83. L. Velluz and M. Legrand, *Angew. Chem.*, **73**, 603 (1961).
84. C. Djerassi, *Tetrahed.*, **13**, 13 (1961).
85. C. Djerassi and W. Klyne, *J. Chem. Soc.*, **4**, 4929 (1962).
86. _____, *J. Chem. Soc.*, **2**, 2390 (1963).
87. K. Takeda and H. Minato, *Steroids*, **1**, 345 (1963).
88. A. Moscowitz, K.M. Wellman and C. Djerassi, *Proc. Nat. Acad. Sci.*, **50**, 799 (1963).
89. K.M. Wellman, R. Records, E. Bunnenberg and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 492 (1964).
90. P. Crabbé, Opt. Rot. Disp. Cir. Dich. Org. Chem., Holden-Day, San-Francisco (1965).
91. P.S. Ellington and G.D. Meakins, *J. Chem. Soc.*, 697 (1960).
92. L. Dorfman, *Chem. Reviews*, **53**, 47 (1953).
93. R.A. Micheli and T.H. Applewhite, *J. Org. Chem.*, **27**, 345 (1962).
94. R.C. Cookson, *J. Chem. Soc.*, 282 (1954).
95. P. Bladon, H.B. Henbest and G.W. Wood, *J. Chem. Soc.*, 2737 (1952).
96. E.S. Rothman, M.E. Wall and C.R. Eddy, *J. Am. Chem. Soc.*, **75**, 158 (1952).
97. M.E. Wall, C.R. Eddy, M.L. Mc-Clennan and M.E. Klump, *Anal. Chem.* ,**24**, 1337 (1952).
98. C.R. Eddy, M.E. Wall and M.K. Scott, *Anal. Chem.*, **25**, 266 (1953).
99. R.N. Jones, E. Katzenellenbogen and K. Dobriner, *J. Am. Chem. Soc.*, **75**, 158 (1953).
100. R.N. Jones and F. Herling, *J. Org. Chem.*, **19**, 1252 (1954).
101. M.E. Wall and H.A. Walene, *J. Am. Chem. Soc.*, **77**, 5661 (1955).
102. A.M. Smith and C.R. Eddy, *Anal. Chem.*, **31**, 1539 (1959).
103. K. Takeda, H. Minato, A. Shimaoka and Y. Matsui, *J. Chem. Soc.*, 4815 (1963).
104. G. Snatzke and H.W. Fehlhaber, *Liebigs Ann. Chem.*, **663**, 123 (1963).
105. H. Ripperger, K. Schreiber and H. Budzikiewicz, *Chem. Ber.*, **100**, 1741 (1967).
106. P.K. Agrawal, *Phytochem.*, **31**, 3307 (1992).
107. W.E. Rosen, J.B. Ziegler, A.C. Shabica and J.N. Shoolery, *J. Am. Chem. Soc.*, **81**, 1687 (1959).
108. J.P. Kutney, *Steroids*, **2**, 225 (1963).
109. K. Tori and K. Aono, *Ann. Report Shionogi Res. Lab.*, **14**, 136 (1964).

110. R.F. Zurcher, *Helv. Chim. Acta*, **46**, 2054 (1963).
111. T. Nohara, T. Komori and T. Kawasaki, *Chem. Pharm. Bull.*, **28**, 1437 (1980).
112. H. Okabe and T. Kawasaki, *Chem. Pharm. Bull.*, **20**, 514 (1972).
113. T. Nohara, H. Yabuta, M. Suenobu, R. Hida, K. Miyahara and T. Kawasaki, *Chem. Pharm, Bull.*, **21**, 1240 (1973).
114. S.B. Mahato, N.P. Sahu and A.N. Ganguly, *Ind. J. Chem.*, **19B**, 817 (1980).
115. J.B. Stothers, ^{13}C-NMR Spectroscopy, Academic Press, New York (1972).
116. P.K. Agrawal, D.C. Jain, R.K. Gupta and R.S. Thakur, *Phytochem.*, **24**, 2479 (1985).
117. R.R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).
118. K. Tori, S. Seo, Y. Terui, J. Nishikawa and F. Yasuda, *Tet. Lett..*, **22**, 2405 (1981).
119. K. Nakano, Y. Kashiwada, T. Nohara, T. Tomimatsu, H. Tsukatani and T. Kawasaki, *Yakugaku Zasshi*, **102**, 1031 (1982).
120. Y. Hiari, T. Konishi, S. Sanada, Y. Ida and J. Shoji, *Chem. Pharm. Bull.*, **30**, 3476 (1982).
121. T. Konishi and J. Shoji, *Chem. Pharm. Bull.*, **27**, 3086 (1979).
122. J.W. Blunt and J.B. Stothers, *Org. Magn. Reson.*, **9**, 430 (1977).
123. K. Bock and C. Pedersen, *J. Chem. Soc. Perkin Trans.*, **2**, 293 (1975).
124. _____, *Acta Chem. Scand.*, **B29**, 258 (1977).
125. J. Azuma and T. Koshijima, *Wood-Res. Tech. Notes*, **17**, 132 (1983).
126. P.A.I. Gorin and M. Majurek, *Can. J. Chem.* **53**, 1212 (1975).
127. K. Tori, S. Seo, Y. Yoshimura, H. Arita and Y. Tomita, *Tet. Lett.*, **2**, 179 (1977).
128. R.G.S. Ritchie, N. Cyr, B. Korsh, H.J. Koch and A.S. Perkin, *Can. J. Chem.*, **53**, 1424 (1975).
129. H.I. Kitagawa, K. Matsushita, K. Shirakawa, K. Tori, T. Tozyo, M. Yoshikawa and Y. Yoshimura, *Tet. Lett.*, **22**, 1529 (1981).
130. K. Bock and C. Pedersen, *Tet. Lett.*, **13**, 1037 (1973).
131. _____, *Acta Chem. Scand.*, **31B**, 354 (1977).
132. K. Yamasaki, H. Kohda, T. Kobayashi, R. Kasai and O. Tanaka, *Tet. Lett.*, **13**, 1005 (1976).
133. R. Kasai, M. Suzuo, J.T. Asakawa and O. Tanaka, *Tetrahed.*, **1**, 175 (1977).
134. K. Tori, Y. Yoshimura, S. Seo, K. Sakurawai, Y. Tomita and H. Ishii, *Tet. Lett..*, **46**, 4163 (1976).
135. R. Encarnacion, L. Kenne, G. Samuelsson and F. Sandberg, *Phytochem.*, **20**, 1939 (1981).
136. K. Tori, Y. Yoshimura, S. Seo, K. Sakurawai, Y. Tomita and H. Ishii, *Tet. Lett.*, **46**, 4167 (1976).
137. X.-C. Li, D.-Z. Wang and C-R. Yang, *Phytochem.*, **29**, 3893 (1990).
138. A. Bax, *Two-Dimensional-NMR in Lig.*, Delft Univ. Press, Delft (1984).
139. G. Batta and A. Liptak, *J. Am. Chem. Soc.*, **106**, 248 (1984).
140. R. Lanzetta, G. Laonigro, M. Parrilli and E. Breitmarier, *Can. J. Chem.*, **62**, 2874 (1984).
141. A. Bax, W. Egan and P. Kovac, *J. Carbohyd. Chem.*, **3**, 593 (1984).
142. G. Mossiot, C. Lavaud, D. Guillaume, L.L. Men-Oliver, and G.V. Binst, *J. Chem. Soc. Chem. Commun.*, **19**, 1485 (1986).
143. S.P. Sati, D.C. Chaukiyal, and O.P. Sati, *J. Nat. Prod.*, **52**, 376 (1989).
144. S. Bergstrom, R. Ryhage and E. Stenhagen, *Svensk. Kem. Tids.*, **73**, 566 (1961).
145. H. Budzikiewicz, J.M. Wilson and C. Djerassi, *Monatsh Chem.*, **1033** (1962).
146. H.J.M. Fitches, Adv. Mass. Spectrom., R.M. Elliot, Pergamon, Vol. 2 (1963)
147. H. Budzikiewicz, C. Djerassi and D.H. Williams, Structure Elucid. Nat. Prod. Mass. Spectrom., Holden-Day, Inc., San-Francisco, Vol. 2, p. 110 (1964).
148. W.H. Faul and C. Djerassi, *Org. Mass Spectrom.*, 1187 (1970).

149. C. Djerassi, Lecture at the 6th Int. Symp. on the Chem. of Nat. Prod., IUPAC, Butterworths, London, p. 205 (1970).
150. L. Ogunkoya, *Phytochem.*, **20**, 121 (1981).
151. T. Komori, Y. Ida, Y. Mutou, K. Miyahara, T. Nohara and T. Kawasaki, *Biomed. Mass Spectrom.*, **2**, 65 (1975).
152. C.W.A. Milne, M.J. Lacey, Mod. Ion. Tech. Mass. Spectrom., Critical Reviews in Analytical Chem., CRC, Cleveland, Ohio, p. 45 (1974).
153. F.H. Field, MTP Int. Review of Sci., Butterworths, London, p. 133 (1972).
154. W.J. Richter and H. Schwartz, *Angew, Chem.*, **90**, 449; *Angew. Chem. Int. Ed. Eng.*, **17**, 424 (1978).
155. G.R. Waller, Bioch. App. Mass Spectrom. Wiley-Inter science, New York (1972).
156. H.D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 500 (1969).
157. H.R. Schulten, *Int. J. Mass Spectrom. Ion. Phys.*, **32**, 97 (1979).
158. H.R. Schulten, T. Komori and T. Kawasaki, *Tetrahed.*, **33**, 2595 (1977).
159. H.R. Schulten, T. Komori, T. Nohara, R. Higuchi and T. Kawasaki, *Tetrahed.*, **34**, 1003 (1978).
160. T. Komori, M. Kawamura, K. Miyahara, T. Kawasaki, O. Tanaka, S. Yahara and H.R. Schulten, *Z. Naturforsch.*, **34C**, 1094 (1979).
161. H. Geiger and G. Schwinger, *Phytochem.*, **19**, 897 (1980).
162. H. Wagner, A. Habermeir, A. Liptak and H.R. Schulten, *Planta Med.*, **37**, 381 (1979).
163. P.J. Arpino and G. Devant, *Analysis.*, **7**, 348 (1979).
164. C. Beaugrand and G. Devant, Commun. Presented at 8th Int. Conf. on Mass Spectrom., Oslo (1979).
165. M. Barber, R.S. Bordoli, R.D. Sedgwick and A.N. Tyler, *J. Chem. Soc. Chem. Commun.*, 325 (1981).
166. Y. Chen, N. Chen, H. Li, F. Zhao and N. Chem., *Gaodeng Xuexiao Huaxue Xuebao*, **7**, 883 (1986).
167. F.A. Larka, I. Howe, J.H. Beynon and Zaretsku, *Tetrahed.*, **37**, 2626 (1981).
168. G.V. Lazurevskii, V.A. Bobeiko and P.K. Kintya, *Dokl. Acad. Nauk. SSSR*, **224**, 1442 (1975).
169. P.K. Kintya, V.A. Bobeiko and A.P. Gulya, *Khim. Prir. Soedin.*, 486 (1976).
170. P.K. Kintya, B. Wilkomirsky and V.A. Bobeiko, *Phytochem.*, **14**, 2657 (1975).
171. T. Morita, T. Ushiroguchi, N. Hayashi, H. Matsuura, Y. Itakura and T. Fuwa, *Chem. Pharm. Bull.*, **36**, 3480 (1988).
172. Y.S. Yollermer, M.B. Gorovits, T.T. Gorovits and N.K. Abubakirov, *Khim. Prir. Soedin.*, 355 (1980).
173. F.S. Khristulas, M.B. Gorovits and N.K. Abubakirov, *Khim. Prir. Soedin.*, **4**, 530 (1974).
174. G.V. Lazurevskii, V.V. Krokhmalyuk and P.K. Kintya, *Dokl. Akad. Nauk. SSSR.*, **221**, 744 (1975).
175. V.V. Krokhmalyuk and P.K. Kintya, *Khim. Prir. Soedin.*, **1**, 55 (1976).
176. Y. Mimaki, K. Kawashima, T. Kanmito and Y. Sashida, *Phytochem.*, **34**, 799 (1993).
177. H. Matsuura, T. Ushiroguchi, Y. Itakura, N. Hayashi and T. Fuwa, *Chem. Pharm. Bull.*, **36**, 3659 (1988).
178. K. Kawashima, Y. Mimaki and Y. Sashida, *Phytochem.*, **32**, 1267 (1993).
179. G.V. Pirtskhalava, M.B. Gorovits, T.T. Gorovits and N.K. Abubakirov, *Khim. Prir. Soedin.*, 514 (1979).
180. J.-K. Dong and G.-Y. Hang, *Planta Med.*, **57**, 460 (1991).
181. K. Idaka, Y. Hirai and J. Shoji, *Chem. Pharm. Bull.*, **39**, 1455 (1991).
182. S.C. Sharma and H.C. Sharma, *Phytochem.*, **23**, 645 (1984).

183. _____, *Phytochem.*, **33**, 683 (1993).
184. Y. Ding, C.R. Yang, *Yaoxue Xuebao*, **25**, 509 (1990).
185. G.M. Goryanu, V.V. Krokhmalyuk and P.K. Kintya, *Khim. Prir. Soedin.*, 400 (1976).
186. G.V. Lazurevskii, G.M. Goryanu and P.K. Kintya, *Dokl. Akad. Nauk. SSSR*, **231**, 1479 (1976).
187. G.M. Goryanu and P.K. Kintya, *Khim. Prir.* Soedin., 762 (1976).
188. K. Kawano, H. Sato and S. Sakamura, *Agr. Biol. Schem.*, **41**, 1 (1977).
189. O.P. Sati and G. Pant, *J. Nat. Prod.*, **48**, 390 (1985).
190. B.S. Bhatti, Ph.D. Thesis, H.P. University, Shimla (1990).
191. R. Kumar, Ph.D. Thesis, H.P. University, Shimla (1983).
192. T. Konishi, S. Kiyosawa and J. Shoji, *Chem. Pharm. Bull.*, **32**, 1451 (1984).
193. M. Hoseny, T. Khalifa, I. Calis, A.D. Wright and O. Saticher, *Phytochem.*, **31**, 3565 (1992).
194. D.C. Jain, Phytochem., **26**, 2223 (1987).
195. P.K. Kintya, V.A. Bobeyko, I.P. Dragalin and S.A. Shvets, *Phytochem.*, **21**, 1447 (1982).
196. R. Tschesche and H. Gutwinski, *Chem. Ber.*, **108**, 265 (1975).
197. Y. Hirai, S. Sanada, Y. Ida and J. Shoji, *Chem. Pharm. Bull.*, **34**, 82 (1986).
198. R. Tschesche, K.H. Hermann, R. Langlais, B.T. Tjoa and G. Wulff, *Chem. Ber.*, **106**, 3010 (1973).
199. S.B. Singh and R.S. Thakur, *Phytochem.*, **21**, 911 (1982).
200. _____, *J. Nat. Prod.*, **45**, 667 (1982).
201. R. Tschesche, A.M. Javellana and G. Wulff, *Chem. Ber.*, **107**, 2828 (1974).
202. T. Shirong and P. Zijie, *Zhiwu Xuebao*, **26**, 419 (1984).
203. A.F. Sviridov, V.A. Pareshnichenko, V.I. Kadentsev and O.S. Chizhov, *Izv. Akad. Nauk. SSSR Ser. Khim.*, **1**, 20 (1975).
204. S.B. Mahato, N.P. Sahu and B.C. Pal, *Ind. J. Chem.*, **16**, 350 (1978).
205. S. Kiyosawa and T. Kawasaki, *Yakugaku Zasshi*, **95**, 102 (1975).
206. Y. Tomita and A. Uomori, *Phytochem.*, **13**, 729 (1974).
207. A. Uomori, S. Seo, K. Tori and Y. Tomita, *Phytochem.*, **22**, 203 (1983).
208. T. Shirong, W. Yufen and P. Zijie, *Zhiwu Xuebao*, **25**, 556 (1983).
209. K.S. Reddy, M.S Shekhani, D.E. Berry, D.G. Lynn and S.M. Hecht, *J. Chem. Soc. Perkin Trans*-I, **5**, 987 (1984).
210. P.K. Kintya, N.E. Mashchenko, N.I. Kononova and G.B. Lazurevskii, *Khim. Prir. Soedin.*, 267 (1976).
211. G.V. Lazurevskii, P.K. Kintya and N.E. Mashchenko, *Dokl. Nauk.. SSSR*, **230**, 476 (1976).
212. R. Tschesche, R. Wagner and H.C. Jha, *Phytochem.*, **23**, 695 (1984).
213. T. Nohara, Y. Ogata, M. Aritome, K. Miyahara and T. Kawasaki, *Chem. Pharm. Bull.*, **23**, 925 (1975).
214. S.B. Mahato, N.P. Sahu, B.C. Pal and R.N. Chakravarti, *Ind. J. Chem.*, **15**, 445 (1977).
215. A. Asami, Y. Hirai and J. Shoji, *Chem. Pharm. Bull.*, **39**, 2053 (1991).
216. K. Nakano, K. Nishizawa, K. Murakami, Y. Takaishi and T. Tomimatsu, *Phytochem.*, **27**, 1897 (1988).
217. K. Ori, Y. Mimaki, K. Mito, Y. Sashida, T. Nikaido, T. Ohmoto and A. Masuko, *Phytochem.*, **31**, 2767 (1992).
218. H. Shimomura and Y. Sashida, Y. Mimaki, *Chem. Pharm. Bull.*, **36**, 3226 (1988).
219. _____, *Phytochem.*, **28**, 3163 (1989).
220. Y. Watanabe, S. Sanada, Y. Ida and J. Shoji, *Chem. Pharm. Bull.*, **31**, 1980 (1983).
221. L.Doyong. S. Kuntto, D. Jaechul, K. Samsik, *Arch. Pharm. Res.*, **12**, 295 (1989).

222. H. Satu and S. Sakamura, *Agr. Biol. Chem.*, **37**, 225 (1973).
223. I. Kitagawa and T. Nakanishi, *Chem. Pharm. Bull.*, **29**, 1299 (1981).
224. Y. Watanabe, S. Sanada, Y. Ida and J. Shoji, *Chem. Pharm. Bull.*, **32**, 3994 (1984).
225. _____, *Chem. Pharm. Bull.*, **31**, 3486 (1983).
226. J.Y. Lay and H.C. Chiong, *Tia-wan Yao Hsuch Tra Chin.*, **32**, 14 (1980).
227. S.B. Singh, R.S. Thakur and H.R. Schulten, *Phytochem.*, **21**, 2079 (1982).
228. X.-C. Li, C.-R. Yang, M. Ichikawa, H. Matsuura, R. Kasai and K. Yamasaki, *Phytochem.*, **31**, 3559 (1992).
229. P.K. Kintya, A.I. Stamova, L.V. Bakinovskii and V.V. Krokhmalyuk, *Khim. Prir. Soedin.*, 350 (1978).
230. M. Sugiyama, K. Nakano, T. Tomimatsu and T. Nohara, *Chem. Pharm. Bull.*, **32**, 1365 (1984).
231. X.-C. Li, C.-R. Yang, H. Matsuura, R. Kasai and K. Yamasaki, *Phytochem.*, **33**, 465 (1993).
232. Z. Janeczko, P.E. Jansson and J. Sendra, *Planta Med.*, **53**, 52 (1987).
233. Z. Janeczko and A. Sibiya, *Herba Pol.*, **28**, 115 (1982).
234. Y. Hirai, S. Sanada, Y. Ida and J. Shoji, *Chem. Pharm. Bull.*, **32**, 4003 (1984).
235. E. Bombardelli, A. Bonati, B. Gabetta and G. Mustich, *Fitoterapia*, **43**, 3 (1972).
236. R. Tschesche, A. Harz. and J. Petricic, *Chem. Ber.*, **107**, 53 (1974).
237. Y. Sashida, S. Kubo, Y. Mimaki, T. Nakaido and T. Ohmoto, *Phytochem.*, **31**, 2939 (1992).
238. S. Kubo, Y. Mimaki, Y. Sashida, T. Nikaido and T. Ohmoto, *Phytochem.*, **31**, 2445 (1992).
239. J. Zhon, C. Chen, R. Liu and C.R. Yang, *Zhiwu Xuebao*, **25**, 568 (1983).
240. S. Yoshara, N. Murakami, M. Yamasaki, T. Hamada, J.-E. Kinyo and T. Nohara, *Phytochem.*, **24**, 2748 (1985).
241. K.K. Pavel and A.S. Stepan, *Phytochem.*, **24**, 1567 (1985).
242. S.C. Sharma, R. Chand, O.P Sati and A.K. Sharma, *Phytochem.*, **22**, 1241 (1983).
243. Y. Hirai, S. Sanada, Y. Ida and J. Shoji, *Chem. Pharm. Bull.*, **32**, 195 (1984).
244. E.D. Perepelitra and P.K. Kintya, *Khim. Prir.* Soedin., **11**, 260 (1975).
245. M. Tomowa and R. Gjulemotowa, *Planta Med.*, **34**, 188 (1978).
246. N.G. Bogacheva, M.M. Gorokhova and L.M. Kogan, *Khim. Prir. Soedin.*, 421 (1977).
247. N.G. Bogacheva, V.P. Kiselev and L.M. Kogan. *Khim. Prir. Soedin.*, 268 (1976).
248. N.G. Bogacheva, V.I. Sheichenko and L.M. Kogan, *Khim. Prir. Zh.*, **11**, 65 (1977).
249. R. Hardman, J. Kosugi and R.R. Perfitt, *Phytochem.*, **19**, 698 (1980).
250. R.K. Gupta, D.C. Jain and R.S. Thakur, *Phytochem.*, **25**, 2205 (1986).
251. _____, *Phytochem.*, **23**, 2605 (1984).
252. _____, *Ind. J. Chem.*, **24B**, 1215 (1985).
253. K. Nakano, K. Murakami, T. Nohara, T. Tomimatsu and T. Kawasaki, *Chem. Pharm. Bull.*, **29**, 1445 (1981).
254. T. Nohara, K. Miyahara and T. Kawasaki, *Chem. Pharm.. Bull.*, **23**, 1158 (1975).
255. P.K. Kintya and I.P. Dragalin, *Khim. Prir. Soedin.*, **11**, 806 (1975).
256. K. Nakano, E. Matsuda, K. Tsurumi, T. Yamasaki, K. Murakami, Y. Takaishi and T. Tomimatsu, *Phytochem.*, **27**, 3235 (1988).
257. Y. Mimaki, Y. Sashida, O. Nakamura, T. Nakaido and T. Ohmoto, *Phytochem.*, **33**, 675 (1993).

(*Invited article received*: 8 November 1997) AJC-1467