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REVIEW

STEROID SAPONINS

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Key Word Index—Steroid saponins; sapogenins; isolation; structure elucidation; natural distribution.

Abstract—Steroid saponins isolated from various plants are reviewed. The newer techniques used in their isolation and strucure elucidation are discussed. A compilation of the saponins isolated up to 1980 along with their available physical data is included. The basic steroidal saponins isolated after 1972 are also compiled.

INTRODUCTION

The saponins are plant glycosides which have the property of forming a soapy lather when shaken with water. The cardiac glycosides also possess this property but these are classified separately because of their specific biological activity. The saponins are classified as steroid or triterpenoid saponins depending upon the nature of the aglycone. The aglycone of a steroid saponin is usually a spirostanol or its modification. A third group of saponins which are called basic steroid saponins contain nitrogen analogues of steroid sapogenins as aglycones. Some natural products may produce froth with water but only exhibit some of the properties of saponins.

Excellent general reviews on saponins [1–7] have been published. Particular mention may be made of the comprehensive reviews on the triterpenoid saponins by Rastogi *et al.* [8–10]. Steroid saponins have been reviewed briefly by Elks [11, 12] and Takeda [13]. The basic steroid saponins have been reviewed by Schreiber [14], Roddick [15], Herbert [16] and Harrison [17]. This review deals with recent developments with regard to isolation and structure elucidation of steroid saponins including the configuration of the carbohydrate moieties.

ISOLATION

The methods of isolation of steroid saponins are essentially the same as those of triterpenoid saponins. The classical methods of isolation of triterpenoid saponins have been reviewed [8–10]. The separation of a saponin mixture into individual components is a formidable task. The development of recent chromatographic techniques has provided valuable means for isolation of pure saponins and their derivatives. A convenient method of separation of steroidal glycosides has been described by Nohara *et al.* [18].

Sephadex LH-20 chromatography and droplet countercurrent chromatography (DCC)

Sephadex LH-20 has successfully been used for the separation of steroidal saponins. A typical isolation procedure involving Si gel CC and Sephadex LH-20 for the separation of furostanol oligosides of *Asparagus cochinchinensis* has been described by Konishi and Shoji [19]. The technique of DCC [20, 21] has been applied successfully for the separation of saponins. The technique is based on the difference of the partition coefficients of compounds in liquid–liquid phases such as countercurrent distribution. Those solvent systems which form two immiscible layers are selected for the separation of the compounds by this method. In the case of Sephadex LH-20 chromatography, plant extracts are partially purified by the usual Si gel CC methods before subjecting them to DCC. This technique is useful for the small scale and semi-micro qualitative and quantitative determination of saponins. Nevertheless, it requires a longer time, viz., a period of four days to a week even for effective semi-micro separation. The molluscidal saponins from *Cornus florida* have been separated by Hostettman *et al.* [22]. The methanol extract of the plant was first fractionated by Sephadex LH-20 CC followed by the separation of pure saponins by DCC. This method has also been applied for the separation of the dammarane-type saponins of *Panax ginseng* and *P. japonicum* by Tanaka *et al.* [23, 24]. The separation of the major saponins of *Bupleuri radix* has been achieved using the DCC technique by Otsuka *et al.* [25].

High performance liquid chromatography (HPLC)

The very efficient newer technique of HPLC is increasingly being used for the separation of various compounds including saponins. The technique has been described in a recent book by Simpson [26]. Rapid, selective, and highly sensitive separation of saponins can be effected by HPLC using a variety of stationary and mobile phases. Successful separation of the major saponin components in liquorice has been achieved using HPLC [27]. Tanaka *et al.* [28] have analysed the saponin constituents of *Bupleuri radix* on a column of octadecylsilylated (ODS) Si gel LS-410 with a mixture of methanol, water, acetic acid

and triethylamine as the mobile phase. Anthracene was used as an appropriate int. standard for quantitative analysis. The saponin mixture obtained from *Tribulus terrestris* (Mahato, S. B. *et al.*, unpublished results) was separated on a column of μ-Bondapak C_{18} using methanol as the mobile phase. The very complex mixtures of saponins which were not amenable to separation previously can now be effectively separated by a combination of silica gel CC, gel chromatography on Sephadex LH-20 and HPLC on a reversed phase column.

STRUCTURE ELUCIDATION

The conventional method of structure elucidation of steroidal saponins starts with acid hydrolysis which yields the aglycone and the sugar moieties which are separately investigated. Extensive chemical studies on the aglycones revealed that they are almost exclusively spirostane derivatives. But furostanol glycosides, which according to Marker and Lopez [29] are precursors of spirostane glycosides, have also been isolated and characterized. A simple qualitative test for furostanol glycoside has been developed by Kawasaki *et al.* [30]. The furostanol glycosides with some exceptions [18], show a characteristic red colour on a TLC plate when sprayed with *p*-dimethylaminobenzaldehyde and hydrochloric acid (Ehrlich reagent). Moreover, the furostane skeleton does not exhibit the characteristic IR absorptions of spirostane derivatives [6]. Confirmatory evidence for the furostane structure is obtained by examination of the products of Marker's degradation or Baeyer–Villiger oxidation followed by hydrolysis. The first isolation of a furostanol glucoside, jurubine (**1**), was announced by Schrieber and Ripperger [31] and later Tschesche *et al.* [32, 33] isolated and characterized a furostanol bisglycoside, sarsaparilloside (**2**), corresponding to the spirostanol glycoside, parillin. Moreover, some glycosides have been isolated whose aglycones are not spirostanol but a modification. In general, the sugar moieties of steroidal saponins are oligosaccharides which consist of 2–4 kinds of sugar units, e.g. D-glucose, D-galactose, D-xylose and L-rhamnose. D-Xylose and L-rhamnose generally occur at the terminal positions. Arabinose-containing steroidal saponins are also known. In a very few cases, quinovose occurs as the carbohydrate moiety. Trillenoside A, a novel 18-norspirostanol glycoside, contains xylose, rhamnose, arabinose and apiose as the sugar constituents [34–36]. Another unusual saponin consisting of kammogenin and five molecules of 2-deoxyribose has been reported by Backer *et al.* [37]. The furostanol bisglycosides so far isolated contain a glucose unit attached to the C-26 hydroxyl.

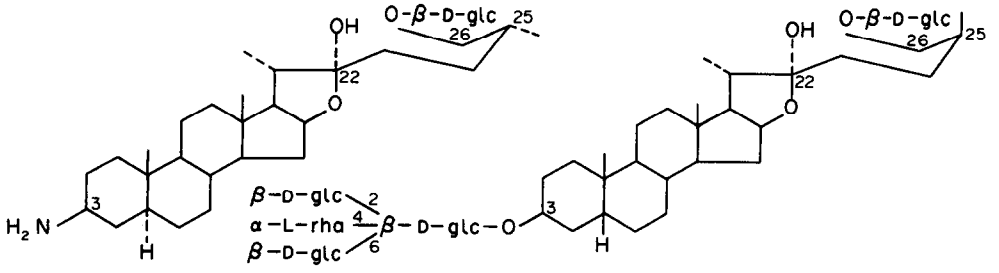
In the classical method, the structure of the sugar moieties of the saponins is determined by identification of the monosaccharides obtained on acid hydrolysis by PC and GLC, quantitative determination of monosaccharides by GLC, partial hydrolysis followed by isolation and characterization of prosapogenins and also, where possible, by characterization of oligosaccharides. The points of attachment of different sugar units are revealed by permethylation of the saponins followed by hydrolysis or methanolysis and identification of the methylated sugars by PC or GLC. The mode of sugar linkage in saponins is determined by enzymic hydrolysis with α- and β-glycosidases or by the application of Klyne's rule [38] on molecular rotation difference. However, both of these methods are not always applicable, particularly in the case of complex glycosides.

Mass spectrometry

Until very recently MW determination of saponins was a difficult task. But newer developments in mass spectrometry have almost solved this problem. Electron impact mass spectrometry (EIMS) has been shown to be a very useful method [39–42] for identification, determination of purity and structural elucidation of saponins, although volatile derivatives have to be produced. Moreover, saponins containing more than four sugars do not give molecular ions, even when derivatized.

Field ionization mass spectrometry (FIMS) has been applied to the structural analysis of permethylated oligosaccharides [43, 44], underivatized nucleosides [45], naturally occurring glycosides, e.g. somalin [46] and cardiac glycosides [47, 48].

However, mass spectrometry has had limited application in the field of underivatized oligosaccharides because it requires volatilization and ionization of the sample. Ionization and volatilization are coupled in one process in field desorption mass spectrometry (FDMS) [49, 50]. Very little of the energy goes into internal excitation and the degree of fragmentation is relatively small. FDMS of underivatized steroid and triterpenoid saponins have been reported [51–55]. The spectra show the intense ions formed by attachment of alkali cations to the neutral molecule. The FDMS of the saponins not only gives the MW but also clear



1 Jurubine

2 Sarsaparilloside

information with regard to the sequence of the sugar units in the molecule and their individual chemical structures by the fragment ions formed by the direct bond cleavages in the oligosaccharide moiety of the saponins. The formation of the fragment ions in FDMS has been discussed in relation to the well established mechanisms of glycosidic bond cleavage by the acidic hydrolysis.

The new technique of plasma desorption mass spectrometry (PDMS) [56, 57] has also been successfully employed for MW determination of underivatized steroidal saponins [22]. This technique utilizes energetic fission fragments from the decay of ^{252}Cf to volatilize and ionize a solid sample. The rapid sample heating (flash desorption) technique has been used for the structural analysis of α-hederin, a triterpenoid saponin [58].

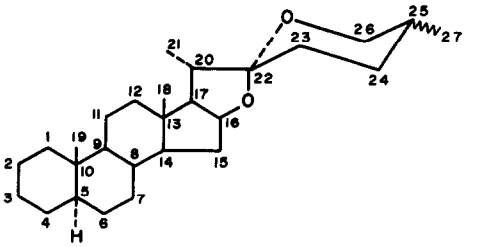
^1H *NMR spectroscopy*

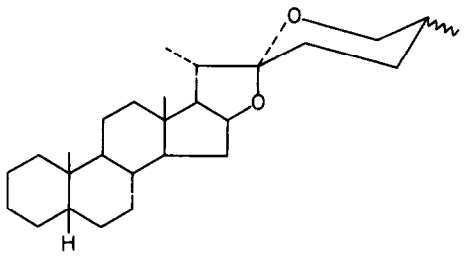
The ^1H NMR spectrum of a saponin peracetate or permethylate is sometimes helpful in determining the mode of sugar linkages. When the spectrum shows an anomeric proton signal as a doublet with $J \sim 7$ Hz which is assignable to that of a D-glucopyranose (or L-arabinopyranose) unit, the sugar may be regarded as having the β-configuration in $^4C_1$ (normal) conformation (α- and $^4C_1$ in L-arabinose) because the J value suggests a *trans*-diaxial relationship of the protons at C-1 and C-2 of the pyranose residues. However, when several anomeric proton signals appear and when J is small (1–3 Hz), suggesting the equatorial–equatorial or axial–equatorial orientation of the C-1 and C-2 protons, the stereochemistry cannot be ascertained on this basis alone. Moreover, it is observed that the anomeric proton signal of α-D-glucosides, α-D-mannosides, α-L-rhamnosides and β-L-arabinosides appears generally at lower field (δ 5.0–6.0) than those of the corresponding β- and α-anomers respectively (δ 4.5–5.0). This difference is also helpful in some cases in the differentiation of the anomeric structure.

^{13}C *NMR spectroscopy*

^{13}C NMR spectroscopy is a recently developed and very useful tool for the elucidation of the structures of saponins without chemical degradation provided the ^{13}C NMR spectral data of the aglycones and sugar moieties are available. The ^{13}C chemical shifts of various sugar moieties are available [59–64] and the carbon chemical shifts of a number of steroidal sapogenins have been reported [65]. For the assignments of the carbon signals of both the carbohydrate and aglycone moieties of saponins the glycosylation shift rules (carbon resonance displacements for both the sugar and aglycone moieties on glycoside formation) derived from ^{13}C NMR studies of a variety of prepared α- and β-anomeric pairs of D-glucopyranosides [64, 66–69], D-mannopyranosides, L-rhamnopyranosides [70] and L-arabinopyranosides [71] are very helpful. The glycosylation shifts of a number of natural steroid-, steroidal alkaloid- and triterpenoid-oligoglycosides have been reported [63, 72–75].

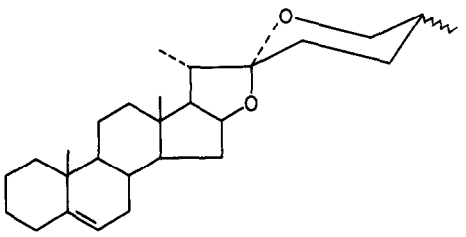
The anomeric configuration of different sugar moieties in a saponin can also be determined by ^{13}C NMR spectroscopy. Apart from the difference in chemical shifts of α- and β-anomeric carbons, the direct bonded C–H coupling constant of the C-1 signal ($J_{C\text{-}1,H\text{-}1}$) of hexapyranoses and pentopyranoses are characteristic of the anomeric configuration. $J_{C\text{-}1,H\text{-}1} \sim 155$ Hz when H-1 is axial whereas it is *ca* 165 Hz when H-1 is equatorial [76]. Thus it is evident that ^{13}C NMR spectroscopy is of immense help in the elucidation of the structure of saponins.



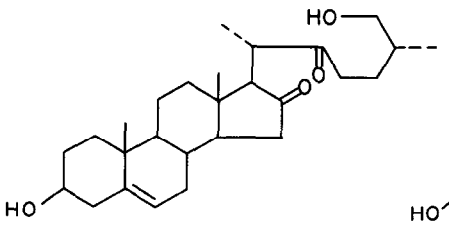


3 Tigogenin, 25*R*, 3β-OH
4 Gitogenin, 25*R*, 2α, 3β-OH
5 Karatavegenin, 25*R*, 2α-OBz, 3β, 5α, 6β-OH
6 Alliogenin, 25*R*, 2α, 3β, 5α, 6β-OH
7 Hecogenin, 25*R*, 3β-OH, 12-CO
8 Agigenin, 25*R*, 2α, 3β, 6β-OH
9 Digalogenin, 25*R*, 3β, 15β-OH
10 Rockogenin, 25*R*, 3β, 12β-OH
11 β-Chlorogenin, 25*R*, 3β, 6β-OH
12 Digitogenin, 25*R*, 2α, 3β, 15β-OH
13 Neotigogenin, 25*S*, 3β-OH
14 Neochlorogenin, 25*S*, 3β, 6α-OH
15 Paniculogenin, 25*S*, 3β, 6α, 23β-OH
16 Neoagigenin, 25*S*, 2α, 3β, 6β-OH
17 Neoalliogenin, 25*S*, 2α, 3β, 5α, 6β-OH
18 Solagenin, 25*S*, 3-CO, 6α-OH
19 Sisalagenin, 25*S*, 3β-OH, 12-CO

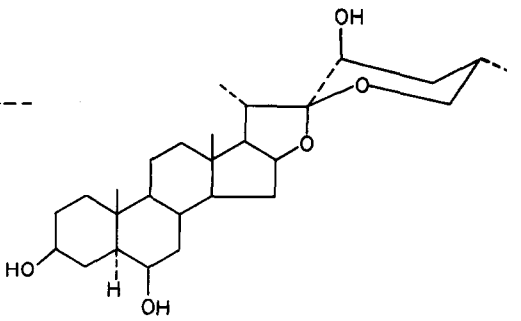
20 Yonogenin, 25 *R*, 2β, 3α-OH
21 Tokorogenin, 25 *R*, 1β, 2β, 3α-OH
22 Epimetagenin, 25 *R*, 2β, 3α, 11α-OH
23 Metagenin, 25 *R*, 2β, 3β, 11α-OH
24 Protometagenin, 25 *R*, 2β, 3β, 11α-OH, 4-ene
25 Nogiragenin, 25 *R*, 3β, 11α-OH
26 Isorhodeasapogenin, 25 *R*, 1β, 3β-OH
27 Sarsasapogenenin, 25 *S*, 3β-OH
28 Rhodeasapogenin, 25 *S*, 1β, 3β-OH
29 Convallagenin A, 25 *S*, 1β, 3β, 5β-OH
30 Convallagenin B, 25 *S*, 1β, 3β, 4β, 5β-OH
31 Neotokorogenin, 25 *S*, 1β, 2β, 3α-OH



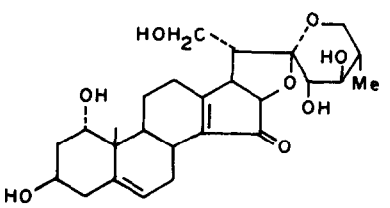
32 Diosgenin, 25*R*, 3β-OH
33 Ruscogenin, 25*R*, 1β, 3β-OH
34 Yuccagenin, 25*R*, 2α, 3β-OH
35 Kammogenin, 25*R*, 2α, 3β-OH, 12-CO
36 Pennogenin, 25*R*, 3β, 17α-OH
37 Prazerigenin A, 25*R*, 3β, 14α-OH
38 Epidiosgenin, 25*R*, 3α-OH
39 Epiruscogenin, 25*R*, 1β, 3α-OH
40 Yamogenin, 25*S*, 3β-OH



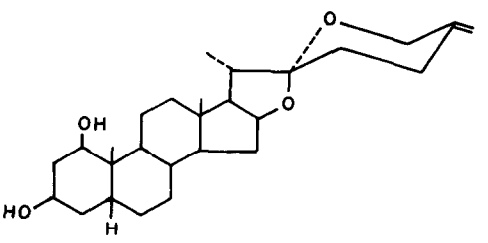
41 Cryptogenin
42 17(20)-Dehydrocryptogenin



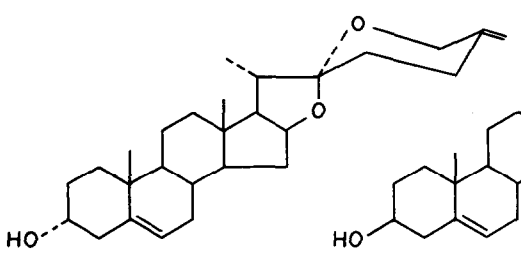
43 Hispigenin



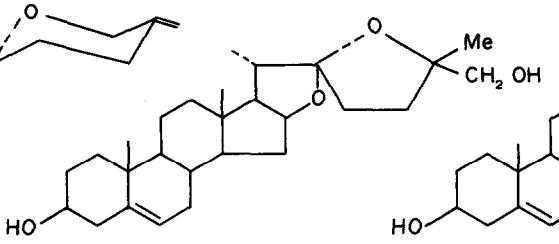
44 Trillenogenin



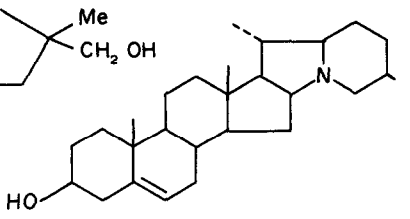
45 Convallamarogenin
46 Δ^5-Convallamarogenin



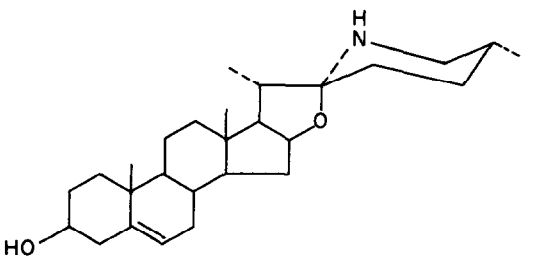
47 Episceptrumgenin



48 Nuatigenin



49 Solanidine



50 Solasodine

Table 1. Steroidal saponins whose genins and sugars have been fully characterized

Saponins (mp, $[\alpha]_D$)	Source	Structure	Reference
Agave saponin C′	*Agave americana*	Hecogenin (**7**), xyl-^{2}glc-^{4}glc-^{4}gla-(3β-OH)	77–79
Agave saponin D	*Agave americana*	Hecogenin (**7**), rha; $^3_2$glc-^{4}glc-^{4}gal-(3β-OH); xyl	77–79
Agave saponin E, 304–308°, −130° (MeOH)	*Agave americana*	Hecogenin (**7**), rha-^{4}rha; $^3_2$glc-^{4}glc-^{4}gal-(3β-OH); xyl	77, 78, 80
Agave saponin H	*Agave americana*	Hecogenin (**7**), rha-^{4}rha; $^3_2$glc-^{4}glc-^{4}gal-(3β-OH); xyl; glc-(26-OH)	77, 80
Agavoside A	*Agave americana*	Hecogenin (**7**), gal-(3β-OH)	77, 83
Agavoside B	*Agave americana*	Hecogenin (**7**), glc-^{4}gal-(3β-OH)	77, 83
Agavoside C 275°, −55° (DMF)	*Agave americana*	Hecogenin (**7**), glc-^{4}glc-^{4}gal-(3β-OH)	77, 84
Agavoside G	*Agave americana*	Hecogenin (**7**), rha; $^3_2$glc-^{4}glc-^{4}gal-(3β − OH); xyl; glc-(26-OH)	78, 81
Aginoside	*Allium gigantenin*	Agigenin (**8**), xyl; $^3_2$glc-^{4}gal-(3β-OH); glc	82
Allionin	*Allium karataviense*	Alliogenin (**6**), glc-(3β-OH)	85
Alliumoside B	*Allium narcissiflorum*	Diosgenin (**32**), glc-^{3}glc-^{3}glc-(3β-OH); glc-(26-OH)	86
Alliumoside C	*Allium narcissiflorum*	Diosgenin (**32**), rha-^{4}rha-^{4}rha-^{6}gal-^{6}glc-(3β-OH); glc-(26-OH)	86
Alliumoside D	*Allium narcissiflorum*	Diosgenin (**32**), rha-^{4}rha-^{6}glc; $^2_3$glc-(3β-OH); glc; glc-(26-OH)	86
Alliumoside E	*Allium narcissiflorum*	Diosgenin (**32**), glc-^{4}rha-^{4}rha-^{6}glc; — $^2_3$glc-(3β-OH); glc; glc-(26-OH)	86
ASP-IV, 165–167° −23° (MeOH)	*Asparagus cochinchinensis*	Sarsasapogenin (**27**), xyl-^{4}glc-(3β-OH); glc-(26-OH); (22-OMe)	19
ASP-V, 150–156° (dec), −45.5° (MeOH)	*Asparagus cochinchinensis*	Sarsasapogenin (**27**), rha-^{6}glc-(3β-OH); glc-(26-OH); (22-OMe)	19

Table 1—*continued*

Saponins (mp, $[\alpha]_D$)	Source	Structure	Reference
ASP-VI, 165–168° (dec), −50° (MeOH)	*Asparagus cochinchinensis*	Sarsasapogenin (**27**), rha, $^{6}_{4}$glc-(3β-OH); glc-(26-OH); (22-OMe), xyl	19
ASP-VII, 179–181° (dec), −27° (MeOH)	*Asparagus cochinchinensis*	Sarsasapogenin (**27**), rha, xyl–$^{4}_{2}$ $^{6}_{2}$ glc-(3β-OH); glc-(26-OH); (22-OMe), glc	19
Asparagoside A	*Asparagus officinalis*	Sarsasapogenin (**27**), glc-(3β-OH)	87
Asparagoside B	*Asparagus officinalis*	Sarsasapogenin (**27**), glc-(26-OH)	87
Asparagoside D	*Asparagus officinalis*	Sarsasapogenin (**27**), glc, $^{4}_{3}$glc-(3β-OH), glc	88
Asparagoside G	*Asparagus officinalis*	Sarsasapogenin (**27**), glc, $^{4}_{3}$glc-(3β-OH); glc-(26-OH), glc	88
Asperin, 222–231°, −100° (pyridine)	*Smilax aspera*	Yamogenin (**40**), rha–^{4}rha, $^{4}_{2}$glc-(3β-OH), rha	89
Asperoside	*Smilax aspera*	Yamogenin (**40**), rha–^{4}rha, $^{4}_{2}$glc-(3β-OH); glc-(26-OH), rha	89
Aspidistrin, 265–267°, −65°	*Aspidistra elatior*	Diosgenin (**32**), glc, $^{2}_{3}$glc–^{4}gal-(3β-OH), xyl	90
Avenacoside A	*Avena sativa*	Nuatigenin (**48**), rha, $^{4}_{2}$glc-(3β-OH); glc-(26-OH), glc	91
Avenacoside B	*Avena sativa*	Nuatigenin (**48**), rha–^{4}glc-(3β-OH); glc-(26-OH), ^{3}, glc–^{2}glc	92
Balanitiscin A, 274–278°, −39°	*Balanites roxburghii*	Diosgenin (**32**), rha, $^{4}_{3}$glc-(3β-OH), glc	93
Capsicoside, 295°, −35° ($CHCl_3$ + MeOH)	*Capsicum annum*	Gitogenin (**4**), glc, $^{3}_{2}$glc–^{4}gal–^{3}glc-(3β-OH); glc-(26-OH), glc	94
Capsicosin	*Capsicum annum*	Gitogenin (**4**), glc, $^{3}_{2}$glc–^{4}gal–^{3}glc-(3β-OH), glc	94
Convallamaronin, 215–218°, −30° (MeOH)	*Convallaria majalis*	Convallamarogenin (**45**), rha-(3β-OH); rha–^{2}qui-(1β-OH)	95

Table 1—*continued*

Saponins (mp, $[\alpha]_D$)	Source	Structure	Reference
Convallamaroside	*Convallaria majalis*	Convallamarogenin (**45**), glc-^{4}rha-(3β-OH); rha-^{2}qui-(1β-OH); glc-(26-OH)	95
Convallasaponin A, 238–240°, −40° ($CHCl_3$)	*Convallaria keisukei*	Convallagenin A (**29**), ara-(3β-OH)	96
Convallasaponin B, 273–274°, −56° ($CHCl_3$ + MeOH)	*Convallaris keisukei*	Convallagenin B (**30**), ara-(5β-OH)	96
Convallasaponin C, 218–221°, −89.7° ($CHCl_3$ + MeOH)	*Convallaria keisukei*	Isorhodeasapogenin (**26**), rha-^{3}rha-^{2}ara-(3β-OH)	97
Convallasaponin D, 264–265°, −66° (MeOH)	*Convallaria keisukei*	Rhodeasapogenin (**28**), glc-(1β-OH); rha-^{2}xyl-^{3}rha-(3β-OH)	98, 99
Convallasaponin E, 213–217°, −149°	*Convallaria keisukei*	Diosgenin (**32**), ara-^{2}ara-^{2}ara-(3β-OH)	100
Cryptogenin glycoside, 238–241° (dec), −129° (EtOH)	*Paris tetraphylla*	Cryptogenin (**41**), glc-(3β-OH)	18
Degalactotigonin, 284–286°, −64° (pyridine)	*Digitalis purpurea*	Tigogenin (**3**), xyl $\searrow^3_2$glc-^{4}gal-(3β-OH) glc	6, 101
Deglucoderhamnoruscin	*Ruscus aculteatus*	Δ^5-Convallamarogenin (**46**), ara-(1β-OH)	103
Deglucodigitonin	*Digitalis purpurea*	Digitogenin (**12**), xyl $\searrow^3_2$glc-^{4}gal-(3β-OH) gal	104
Deglucoruscin	*Ruscus aculeatus*	Δ^5-Convallamarogenin (**46**), rha-^{2}ara-(1β-OH)	103
Deglucoruscoside	*Ruscus aculeatus*	Δ^5-Convallamarogenin (**46**), rha-^{2}ara-(1β-OH); glc-(26-OH)	105
Dehydrocryptogenindiglycoside, 265–268° (dec), −80° (pyridine)	*Trillium kamtschaticum*	17(20)-Dehydrocryptogenin (**42**), rha-^{2}glc-(3β-OH); glc-(26-OH)	18
Dehydrocryptogenintetraglycoside	*Paris tetraphylla*	17(20)-dehydrocryptogenin (**42**), rha-^{4}rha $\searrow^4_2$glc-(3β-OH); glc-(26-OH) rha	18, 106
Deltonin	*Dioscorea deltoidea*	Diosgenin (**32**), glc $\searrow^4_2$glc-(3β-OH) rha	107
Deltoside	*Dioscorea deltoidea*	Diosgenin (**32**), glc $\searrow^4_2$glc-(3β-OH); glc-(26-OH) rha	108
Desgluco-desrhamnoparillin, 250–265°, −65.5° ($CHCl_3$ + MeOH)	*Smilax aristolochiaefolia*	Sarsasapogenin (**27**), glc-^{6}glc-(3β-OH)	109
Desgluco-lanatigonin, 246–251°, −47.6° ($CHCl_3$ + MeOH)	*Digitalis lanata*	Tigogenin (**3**), gal $\searrow^3_2$glc-^{4}gal-(3β-OH) xyl	110
Desglucoparillin, 250–265°, −67.5° (EtOH)	*Smilax aristolochiaefolia*	Sarsasapogenin (**27**), glc $\searrow^6_2$glc-(3β-OH) rha	109
Digalonin, 250–295°	*Digitalis purpurea*	Digalogenin (**9**), glc-^{3}gal xyl $\nearrow^3_2$glc-^{4}gal-(3β-OH)	6, 104

Table 1—*continued*

Saponins (mp, $[\alpha]_D$)	Source	Structure	Reference
Digitonin, 245–285°, −40° (pyridine)	*Digitalis purpurea*	Digitogenin (**12**), glc-^{3}gal xyl$^{2}\diagup\diagdown^{3}$glc-^{4}gal-(3β-OH)	104
	Digitalis lanata		
Dioscin, 275–277°, −115° (EtOH)	*Costus speciosus*, *Dioscorea septemloba*, *Paris polyphylla*, *Solanum introsum*, *Tribulus terrestris*, *Trigonella foenum-graecum*, *Trillium tschonoskii*	Diosgenin (**32**), rha $^{2}\diagup\diagdown^{4}$glc-(3β-OH) rha	111–119
Diosgenin-3-*O*-rhamnoside	*Smilax excelsa*	Diosgenin (**32**), rha-(3β-OH)	120
Diosgenin triglucoside, 290° (dec), −77° (pyridine)	*Dioscorea deltoidea*	Diosgenin (**32**), glc $^{2}\diagup\diagdown^{3}$glc-(3β-OH) glc	121
Epidiosgeninglucoside, 218–221°, −122°	*Gynura japonica*	Epidiosgenin (**38**), glc-(3α-OH)	122
Epimetageninglycoside, amorphous, −154° ($CHCl_3$)	*Metanarthecium luteo-viride*	Epimetagenin (**22**), (tri-OAc)ara-(11α-OH), 2β-OAc	123
Epiruscogeninglucoside	'Senshokushichiken' (Chinese name)	Epiruscogenin (**39**), glc-(3α-OH)	124
Episceptrumgeninglucoside, 236–238°, −109°	*Gynura japonica*	Episceptrumgenin (**47**), glc-(3α-OH)	122
Eruboside B	*Allium erubescens*	β-Chlorogenin (**11**), glc $^{2}\diagup\diagdown^{3}$glc-^{4}gal-(3β-OH) glc	125
Filiferine A, 292°, −50.5° (DMSO)	*Yucca filifera*	Sarsasapogenin (**27**), xyl-^{2}gal-(3β-OH)	126
Filiferine B, 319–321°, −35° (DMSO)	*Yucca filifera*	Sarsasapogenin (**27**), glc-^{2}gal-(3β-OH)	126
Floribundasaponin B, 251–253° (dec), −86.5° (pyridine)	*Dioscorea floribunda*	Pennogenin (**36**), rha-^{4}glc-(3β-OH)	127
Floribundasaponin C, 255–258°, −93.6° (pyridine)	*Dioscorea floribunda*	Diosgenin (**32**), rha-^{3}rha-^{4}glc-(3β-OH)	128
Floribundasaponin D, 232–234°, −85° (pyridine)	*Dioscorea floribunda*	Diosgenin (**32**), rha-^{3}rha-^{3}rha-^{4}glc-(3β-OH)	128
Floribundasaponin E, 226–229° (dec), −66° (pyridine)	*Dioscorea floribunda*	Diosgenin (**32**), rha-^{3}rha-^{3}rha-^{3}rha-^{4}glc-(3β-OH); glc-(26-OH); (22α-OMe)	128
Floribundasaponin F, 243–247° (dec), −74.6° (pyridine)	*Dioscorea floribunda*	Diosgenin (**32**), rha-^{3}rha-^{3}rha-^{3}rha-^{4}glc-(3β-OH); glc-(26-OH)	128
Funkioside B, 258–266°, −135° (MeOH)	*Funkia ovata*	Diosgenin (**32**), glc-(3β-OH); glc-(26-OH)	129
Funkioside C	*Funkia ovata*	Diosgenin (**32**), glc-^{4}gal-(3β-OH)	129–131
Funkioside D	*Funkia ovata*	Diosgenin (**32**), glc-^{2}glc-^{4}gal-(3β-OH)	129–131
Funkioside E	*Funkia ovata*	Diosgenin (**32**), rha-^{4}glc-^{2}glc-^{4}gal-(3β-OH)	129, 130, 132
Funkioside F	*Funkia ovata*	Diosgenin (**32**), glc $^{2}\diagup\diagdown^{3}$glc-^{4}gal-(3β-OH) xyl	129, 130

Table 1—*continued*

Saponins (mp, $[\alpha]_D$)	Source	Structure	Reference
Funkioside G	*Funkia ovata*	Diosgenin (**32**), rha–^{4}glc xyl/^{2,3}glc–^{4}gal-(3β-OH)	129, 130, 132
Funkioside I	*Funkia ovata*	Diosgenin (**32**), rha–^{4}rha xyl/^{4}glc–^{2}glc–^{4}gal-(3β-OH); glc-(26-OH)	129, 130
Furostanol bisglycoside, 189–193°	*Tribulus terrestris*, *Trigonella coerulea*	Diosgenin (**32**), rha ^{4}glc-(3β-OH); glc-(26-OH) rha	133–135
Furostanol glycoside, 242–246°	*Trigonella foenum-graecum*	Neotigogenin (**13**), rha ^{2}glc-(3β-OH); glc-(26-OH); (22-OMe) glc	136
Furostanol saponin, 217–220° (dec), −24° ($CHCl_3$ + MeOH)	*Lycopersicon esculentum*	Neotigogenin (**13**), glc–^{2}glc–^{4}gal-(3β-OH); glc-(26-OH); (22-OMe)	137
Furostanol saponin-1	*Asparagus officinalis*	Yamogenin(**40**), rha ^{2}glc-(3β-OH); glc-(26-OH) rha	138
Furostanol saponin-2	*Asparagus officinalis*	Yamogenin(**40**), rha–^{4}glc-(3β-OH); glc-(26-OH)	138
F-Gitonin, 251–255° (dec), −66° (pyridine)	*Digitalis purpurea*	Gitogenin (**4**), xyl ^{3}glc–^{4}gal-(3β-OH) glc	102
Gitonin, 276.5–282.5°	*Digitalis lanata*	Gitogenin (**4**), gal ^{2}glc–^{4}gal-(3β-OH) xyl	110
Glucoconvalla-saponin A, 213–41° (MeOH)	*Convallaria keisukei*	Convallagenin A (**29**), glc–^{2}ara-(3β-OH)	96
Glucoconvalla-saponin B, 221–222°, −35° (MeOH)	*Convallaria keisukei*	Convallagenin B (**30**), glc-(3β-OH), ara-(5β-OH)	96, 98
Glycoside A (identical to Kallstroemin E)	*Dioscorea prazeri*	Diosgenin (**32**), rha–^{6}glc-(3β-OH)	139
Glycoside B	*Dioscorea prazeri*	Prazerigenin A (**37**), rha–^{6}glc-(3β-OH)	121
Glycoside B	*Trigonella foenum-graecum*	Yamogenin (**40**), rha ^{4}glc-(3β-OH); glc-(26-OH);(22α-OMe) rha	140
Glycoside B	*Allium narcissiflorum*	Diosgenin (**32**), glc–^{3}glc–^{6}glc-(3β-OH), glc-(26-OH)	141
Glycoside C, 272–274°, −87°	*Discorea prazeri*	Diosgenin (**32**), rha–^{6}glc–^{6}glc-(3β-OH)	139
Glycoside D, 278–280°, −85°	*Dioscorea prazeri*	Prazerigenin A (**37**), rha–^{6}glc–^{6}glc-(3β-OH)	139
Glycoside I, 300–303°	*Methanarthecium luteo-viride*	Epimetagenin (**22**), ara-(11α-OH)	142
Glycoside II, 297–300°, −84° (pyridine)	*Methanarthecium luteo-viride*	Metagenin (**23**), ara-(11α-OH)	142

Table 1—*continued*

Saponins (mp, $[\alpha]_D$)	Source	Structure	Reference
Glycoside III	*Methanarthecium luteo-viride*	Nogiragenin (**25**), gal-(11α-OH)	143
Gracillin, 290–293°, −88° (pyridine)	*Costus speciosus,*	Diosgenin (**32**), rha, $^{2}_{3}$glc-(3β-OH), glc	111–113
	Dioscorea septemloba, *Dioscorea caucasica,* *Tribulus terrestris*		118, 134, 144
Hispigenin glycoside	*Solanum hispidum*	Hispigenin (**43**), rha-^{3}rha-(3β-OH)	145
Hispinin A, 220–224°, −44° (pyridine)	*Solanum hispidum*	Solagenin (**18**), rha-(6α-OH)	146
Hispinin B, 258–260°, −68° (pyridine)	*Solanum hispidum*	Solagenin (**18**), rha-^{3}rha-(6α-OH)	146
Hispinin C, 285–288°, −59° (pyridine)	*Solanum hispidum*	Neochlorogenin (**14**), rha-^{3}rha-(6α-OH)	146
Kallstroemin A, 235–238°, −82° (pyridine)	*Kallstroemia pubescens*	Diosgenin (**32**), rha-^{2}rha-^{2}rha-^{6}glc-(3β-OH); glc-(26-OH)	147
Kallstroemin B, 232–235°, −79.5° (pyridine)	*Kallstroemia pubescens*	Diosgenin (**32**), rha-^{2}rha-^{2}rha-^{6}glc-(3β-OH); glc-(26-OH); (22α-OMe)	147
Kallstroemin D, 275–276°, −94.5° (pyridine)	*Kallstroemia pubescens*	Diosgenin (**32**), rha-^{2}rha-^{2}rha-^{6}glc-(3β-OH)	147
Kallstroemin E, 218–219°, −101° (pyridine)	*Kallstroemia pubescens*	Diosgenin (**32**), rha-^{6}glc-(3β-OH)	147
Karatavegenin B, glucoside, 294–298°	*Allium karataviense*	Karatavegenin (**5**), glc-(3β-OH); glc-(26-OH)	148
Karatavioside A	*Allium* spp.	Yuccagenin (**34**), xyl, $^{3}_{2}$glc-^{4}gal-(3β-OH), glc	149
Karatavioside C	*Allium* spp.	Yuccagenin (**34**), xyl, $^{3}_{2}$glc-^{4}gal-(3β-OH); glc-(26-OH), glc	150
Kikuba saponin, 249–251°, −77° (MeOH)	*Dioscorea septemloba,* *Tribulus terrestris*	Diosgenin (**32**), glc-^{2}glc, $^{3}_{2}$glc-(3β-OH), rha	113, 134
Lanadigalonin	*Digitalis lanata*	Digalogenin (**9**), glc-^{3}gal, $^{2}_{3}$glc-^{3}gal-(3β-OH), xyl	151
Lanagitoside	*Digitalis lanata*	Gitogenin (**4**), glc-^{3}gal, $^{2}_{3}$glc-^{4}gal-(3β-OH); glc-(26-OH), xyl	110
Lanatigonin I, 275–285° (dec), +42° (pyridine)	*Digitalis lanata*	Tigogenin (**3**), glc-^{3}gal, $^{2}_{3}$glc-^{3}gal-(3β-OH), xyl	151
Lanatigoside	*Digitalis lanata*	Tigonenin (**3**), glc-^{3}gal, $^{2}_{3}$glc-^{4}gal-(3β-OH); glc-(26-OH), xyl	110
Metanartheticum prosapogenin	*Metanarthecium luteo-viride*	2β-acetyl metagenin (**23**), 2,3,4-tri-*O*-acetyl ara-(11α-OH)	152

Table 1—*continued*

Saponins (mp, $[\alpha]_D$)	Source	Structure	Reference
Molluscicidal saponin-1, 240–245° (dec), −68.5°	*Cornus florida*	Sarsasapogenin (**27**), gal-(3β-OH)	22
Mulluscicidal saponin-2, 286–288°	*Cornus florida*	Sarsasapogenin (**27**), xyl-^{2}gal-(3β-OH)	22
Molluscicidal saponin-3, 320–322°	*Cornus florida*	Sarsasapogenin (**27**), glc-^{2}gal-(3β-OH)	22
Neochlorogenin glycoside	*Solanum hispidum*	Neochlorogenin (**14**), rha-^{3}rha-(3β-OH)	145
Neohecogenin glucoside 280–282° (dec), −41° (pyridine)	*Tribulus terrestris*	Sisalagenin (**19**), glc-(3β-OH)	153
Neotokoronin, 270–274° (dec), −11° (pyridine)	*Dioscorea tenuipes*	Neotokorogenin (**31**), ara-(1β-OH)	154
Ophiopogonin A, 183°, −98° (pyridine)	*Ophiopogon japonicus*	Ruscogenin (**33**), (3-*O*-acetyl) rha-^{2}fuco-(1β-OH)	155
Ophiopogonin B, 269–271°, −105° (pyridine)	*Ophiopogon japonicus*	Ruscogenin (**33**), rha-^{2}fuco-(1β-OH)	155, 156
Ophiopogonin D, 263–265°, −108° (pyridine)	*Ophiopogon japonicus*	Ruscogenin (**33**), rha $^{2}_{3}$fuco-(1β-OH) xyl	155, 157
Ophiopogonin B′, 245–248° (dec), −86° (pyridine)	*Ophiopogon japonicus*	Diosgenin (**32**), (4-*O*-acetyl) rha $^{2}_{3}$glc-(3β-OH) xyl	158
Ophiopogonin C′, 238–240° (dec), −99° (pyridine)	*Ophiopogon japonicus*	Diosgenin (**32**), rha-^{2}glc-(3β-OH)	158
Ophiopogonin D′, 255–257°, −41° (pyridine)	*Ophiopogon japonicus*	Diosgenin (**32**), xyl $^{3}_{2}$glc-(3β-OH) rha	158
Paniculonin A, 262–264°, −61° (pyridine)	*Solanum paniculatum*	Paniculogenin (**15**), xyl-^{3}qui-(6α-OH)	159
Paniculonin B, 237–238°, −79° (pyridine)	*Solanum paniculatum*	Paniculogenin (**15**), rha-^{3}qui-(6α-OH)	160
Paniculogenin glycoside, 262–264°, −61° (pyridine)	*Solanum paniculatum*	Paniculogenin (**15**), xyl-^{3}rha-(6α-OH)	160
Paniculogenin glycoside	*Solanum hispidum*	Paniculogenin (**15**), rha-^{3}rha-(3β-OH)	145
Parillin, 220–223°, −64° (EtOH)	*Smilax aristolochiaefolia*	glc rha—$^{2}_{4}$glc-(3β-OH) glc ^{6}	109
Paryphyllin, 294–298°, −104° (pyridine)	*Paris polyphylla*	Diosgenin (**32**), rha-^{4}ara-^{3}glc-(3β-OH)	161
Paryphyllin A, 212–214°, −85° (pyridine)	*Paris polyphylla*	Diosgenin (**32**), glc-^{3}rha $^{4}_{3}$glc-(3β-OH) rha	162
Paryphyllin B, 168–170°, −97.5° (pyridine)	*Paris polyphylla*	Diosgenin (**32**), glc-^{3}rha $^{4}_{3}$glc-(3β-OH) ara (fur)	162
Paryphyllin C, 262–266°, −97° (pyridine)	*Paris polyphylla*	Diosgenin (**32**), rha-^{4}glc-(3β-OH)	163
Pennogenin chacotrioside, 297–299° (dec), −127° (pyridine)	*Trillium kamtschaticum*	Pennogenin (**36**), rha $^{2}_{4}$glc-(3β-OH) rha	18

Table 1—*continued*

Saponins (mp, $[\alpha]_D$)	Source	Structure	Reference
Pennogenin diglycoside, 273–276° (dec), −118° (pyridine)	*Trillium kamtschaticum*	Pennogenin (**36**), rha-^{2}glc(3β-OH)	18
Pennogenin tetraglycoside, 224–228° (dec), −136° (pyridine)	*Heloniposis orientalis*	Pennogenin (**36**), rha-^{4}rha; $^{4}_{2}$glc-(3β-OH); rha	18, 106, 117
Polygonatoside E′	*Polygonatum latifolium*	Diosgenin (**32**), glc-^{3}glc-^{4}gal-^{3}glc-(3β-OH)	164
Prazerigenin glucoside, 260°, −79° (pyridine)	*Dioscorea prazeri*	Prazerigenin A (**37**), glc-(3β-OH)	121
Protodioscin, 190–196° (dec), −57.8 (pyridine)	*Dioscorea gracillima*	Diosgenin (**32**), rha; $^{2}_{4}$glc-(3β-OH); glc-(26-OH); rha	165
Protogracillin, 235–238° (dec), −57.8° (pyridine)	*Dioscorea septemloba*	Diosgenin (**32**), glc; $^{3}_{2}$glc-(3β-OH); glc-(26-OH); rha	165
Protometeogenin glycoside, 265–270°	*Metanarthecium luteo-viride*	Protometagenin (**24**), ara-(11α-OH)	166
Protopolygonatoside E′	*Polygonatum latifolium*	Diosgenin (**32**), glc-^{3}glc-^{4}gal-^{3}glc-(3β-OH); glc-(26-OH)	164
Prototokorin, 177–178°, −3.8° (MeOH)	*Dioscorea tokoro*	Tokorogenin (**21**), glc-(1β-OH); glc-(26-OH)	167
Protoyuccoside C, 182–184°, −30° (MeOH)	*Yucca filamentosa*	Sarsasapogenin (**27**), gal-^{2}glc-^{4}glc-(3β-OH); glc-(26-OH)	168
Protoyuccoside E	*Yucca filamentosa*	Sarsasapogenin (**27**), gal; $^{6}_{2}$glc-^{4}glc-(3β-OH); glc-(26-OH); gal	169
Rockoside A	*Agave americana*	Rockogenin (**10**), gal-(3β-OH)	170
Rockoside B	*Agave americana*	Rockogenin (**10**), glc-^{4}gal-(3β-OH)	170
Rockoside C′	*Agave americana*	Rockogenin (**10**), xyl-^{2}glc-^{4}glc-^{4}gal-(3β-OH)	170
Ruscin	*Ruscus aculeatus*	Δ^{5}-Convallamarogenin (**46**), glc-^{3}rha-^{2}ara-(1β-OH)	103
Ruscoside	*Ruscus aculeatus*	Δ^{5}-Convallamarogenin (**46**), glc-^{3}rha-^{2}ara-(1β-OH); glc (26-OH)	105
Saponin P-a, 276–278° −133°	*Paris polyphylla*	Diosgenin (**32**), rha; $^{2}_{4}$glc-(3β-OH); (fur)ara	116, 161
Saponin P-d, 203–206°, 153°	*Paris polyphylla*	Diosgenin (**32**), rha-^{4}rha; rha $^{4}_{2}$glc-(3β-OH)	116
Sarsaparilloside, amorphous, −44° (H_2O)	*Smilax aristolochiaefolia*	Sarsasapogenin (**27**), glc; rha $^{4}{}^{6}_{2}$glc-(3β-OH); glc-(26-OH); glc	32, 33
Taccaoside	*Taccacheancer*	Diosgenin (**32**), rha; $^{3}_{2}$glc-(3β-OH); rha	171

Table 1—*continued*

Saponins (mp, $[\alpha]_D$)	Source	Structure	Reference
'TFI', 217–220°, −24° (MeOH + $CHCl_3$)	*Lycoperscicum esculentum*	Neotigogenin (**13**), glc-^{2}glc-^{4}gal-(3β-OH); glc-(26-OH)	172
Tigonin	*Digitalis lanata*	Tigogenin (**3**), glc-^{3}gal; $^{2}_{3}$glc-^{4}gal-(3β-OH); xyl	6, 104
	Digitalis purpurea		
Timosaponin A-I, 240–245° (dec), −68° (dioxan)	*Anemarrhenae asphodeloides*	Sarsasapogenin (**27**), gal-(3β-OH)	173
Timosaponin A-III, 320–322°	*Anemarrhenae asphodeloides*	Sarsasapogenin (**27**), glc-^{2}gal-(3β-OH)	173
Tokorogenin glucoside, 275–284°, −43° ($CHCl_3$)	*Dioscorea tokoro*	Tokorogenin (**21**), glc-(1β-OH)	174
Tokoronin, 275–277°, −13° (pyridine)	*Dioscorea tokoro*	Tokorogenin (**21**), ara-(1β-OH)	175
Tribulosin, >300°, −61° (pyridine)	*Tribulus terrestris*	Neotigogenin (**13**), xyl; $^{2}_{3}$glc-^{4}gal-(3β-OH); xyl, ^{2}rha	153
Trigonelloside C	*Trigonella foenum-graecum*	Yamogenin **40**), rha; $^{4}_{2}$glc-(3β-OH); glc-(26-OH); rha	176
Trillenoside A, 209–220° (dec), −142°	*Trillium kamtschaticum, Trillium small, Trillium eschonoskii*	Trillenogenin (**44**), apio(fur)-^{3}rha; $^{2}_{3}$ara-(1β-OH); xyl	34–36
Trillin, 260°, −89° (dioxan)	*Dioscorea sativa, Polygonatum latifolium*	Diosgenin (**32**), glc-(3β-OH)	177, 178
Trillioside A	*Trillium kamtschatscense*	Diosgenin (**32**), glc-^{4}rha-^{2}glc-(3β-OH)	179
Trillioside B	*Trillium kamtschatscense*	Diosgenin (**32**), glc; $^{4}_{2}$glc-(3β-OH); glc	180
Turoside A	*Allium turcomanicum*	Neoagigenin (**16**), xyl; $^{3}_{2}$glc-^{4}gal-(3β-OH); glc	181
Turoside A-6-*O*-benzoate	*Allium turcomanicum*	Neoagigenin (**16**), xyl; $^{3}_{2}$glc-^{4}gal-(3β-OH); 6-*O*-benzoate; glc	182
Turoside C	*Allium turcomanicum*	Neoagigenin (**16**), glc-^{2}glc; $^{2}_{3}$glc-^{4}gal-(3β-OH); glc-(26-OH); xyl	183
Yononin, 238–240°, −14°	*Dioscorea tokoro*	Yonogenin (**20**), ara-(2β-OH)	184, 185
Yuccagenin glycoside	*Yucca schottii*	Yuccagenin (**34**), gal-(3β-OH)	37
Yuccoside B	*Yucca filamentosa*	Tigogenin (**3**), gal-^{4}glc-(3β-OH)	186
Yuccoside C, 282–284°, −41°	*Yucca filamentosa*	Sarsasapogenin (**27**), gal-^{2}glc-^{4}glc-(3β-OH)	168, 187–189
Yuccoside E	*Yucca filamentosa*	Sarsasapogenin (**27**), gal; $^{6}_{2}$glc-^{4}glc-(3β-OH); gal	188, 190

Abbreviations used: glc, β - D - glucopyranosyl; rha, α - L - rhamnopyranosyl; ara, α - L - arabinopyranosyl; gal, β - D - galactopyranosyl; xyl, β - D - xylopyranosyl; ara - fur, α - L - arabinofuranosyl; qui, β - D - quinovopyranosyl; api - fur, β - D - apiofuranosyl.

Table 2. Steroidal saponins whose genins and sugars have been identified

Saponins (mp, $[\alpha]_D$)	Source	Genins and sugars	Reference
Amolonin	*Chlorogalum pomeridianum*	Tigogenin (3), glc (3) + gal (1) + rha (2)	11
Asparagoside C, 287–290°, −130° (MeOH)	*Asparagus officinalis*	Sarsasapogenin (27), glc	191
Balanitscin B	*Balanites roxburghii*	Diosgenin (32), glc + rha	192
Balanitscin C	*Balanites roxburghii*	Diosgenin (32), glc + rha (1:3)	192
Balanitscin D	*Balanites roxburghii*	Diosgenin (32), glc + rha	192
Balanitscin E	*Balanites roxburghii*	Diosgenin (32), glc + ara + xyl + rha	192
Caucasosaponin, 218–220° (dec) −62.5° (pyridine)	*Dioscorea caucasica*	Diosgenin (32), rha (1) + glc (3)	144
Dioscinin, 202–203°, −70° (MeOH)	*Dioscorea polystachya*	Diosgenin (32), glc (2) + rha (2)	193
Diosgenin glycoside	*Tribulus terrestris*	Diosgenin (32), glc + glc	134
Diosgenin glycoside	*Polygonatum multiflorum*	Diosgenin (32), glc + gal + xyl	194
Diosgenin rhamnoglucosyl	*Tribulus terrestris*	Diosgenin (32), glc + rha	195
Fenugrin B	*Trigonella foenum graecum*	Diosgenin (32), glc + ara + rha	196
Graecunin B, 154–156°, −47° (MeOH)	*Trigonella foenum-graecum*	Diosgenin (32), glc + xyl + rha	197
Graecunin C	*Trigonella foenum-graecum*	Diosgenin (32), glc + rha	198
Ophiopogonin C, 238–240°, −93° (pyridine)	*Ophiopogon japonicus*	Ruscogenin (33), fuc + xyl + rha	158
Polygonatoside C	*Polygonatum latifolium*	Diosgenin (32), glc + gal	178
Polygonatoside E	*Polygonatum latifolium*	Diosgenin (32), glc + gal + xyl	178
Polygonatoside G	*Polygonatum latifolium*	Diosgenin (32), glc + gal + xyl + ara	178
Ruscoside A	*Ruscus hyrcanus*	Ruscogenin (33), gal + glc + rha (2)	199
Ruscoside B	*Ruscus hyrcanus*	Ruscogenin (33), gal + glc + ara + rha (2)	199
Saponin C, 187°	*Tribulus terrestris*	Ruscogenin (33), rha + glc + ara	200
Saponin D_n, 272°	*Tribulus terrestris*	Diosgenin (32), rha + glc	200
Saponin of kammogenin	*Yucca schotti*	Kammogenin (35), 5 units of deoxyribose	37
Sarsasapogenin glycoside, 285°, −35° (EtOH)	*Narthecium essifragum*	Sarsasapogenin (27), ara + glc + gal + xyl	201
Sarsasaponin, 245°	*Smilax aristolochiaefolia, Yucca schottii*	Sarsasapogenin (27), glc (2) + rha (1)	11
Tigogenin glycoside, 260° (dec)	*Cestrum diurnum*	Tigogenin (3), xyl + glc + gal	202
Tigogenin glycoside	*Yucca glorisa*	Tigogenin (3), glc + gal + xyl + rha	203
Terrestroside F, 238–240°	*Tribulus terrestris*	Tigogenin (3), glc + rha	204
Trillarin, 211°, −116° (EtOH)	*Trillium erectum*	Diosgenin (32), glc (2)	11
T. T. Saponin	*Tribulus terrestris*	Diosgenin (32), glc + ara + rha	205

Table 3. Basic steroid saponins (characterized and uncharacterized) isolated after 1972

Saponin (mp, $[\alpha]_D$)	Source	Genins and sugars	Reference
Dehydrocommersonine	*Solanum chacoense*	Solanidine (**49**), glc$\searrow^{3}$glc–^{4}gal-(3β-OH) glc$\nearrow$	206
Khasianine, 226–228°, −95° (MeOH)	*Solanum khasianum*	Solasodine (**50**), rha–^{4}glc-(3β-OH)	63
Solapersine, 282–284°, −46° (MeOH)	*Solanum persicum*	Solasodine (**50**), gal + glc + xyl	207
Solaplumbin, 180–181°, −90°	*Nicotiana plumbaginifolie*	Solasodine (**50**), glc–^{1}rha^{4}-(3β-OH)	208
Solaplumbinin, 184–185°, −39.5°	*Nicotiana plumbaginifolie*	Solasodine (**50**), rha^{4}-(3β-OH)	208
Solasodine glycoside	Unidentified solanum species (Spanish name: noranjilla de Jibaro)	Solasodine (**50**), glc + gal + rha	209
Solasodine glycoalkaloid	*Solanum schimperianum*	Solasodine (**50**), glc + rha	210
Solatifoline, 292–293°, −119°	*Solanum platanifolium*	Solasodine (**50**), glc + rha + gal	211

The steroidal saponins isolated and characterized up to 1980 are listed in Table 1 along with the mps and specific rotations and Table 2 shows the steroidal saponins which have not been fully characterized. As comprehensive reviews [14–17] of basic steroidal saponins are available, the characterized and uncharacterized basic steroidal saponins isolated after 1972 are compiled in Table 3.

BIOLOGICAL ACTIVITY

An extensive study of the physical, chemical and physiological properties of saponins has been conducted owing to their wide occurrence in nature. There are several excellent reviews on the properties of saponins [6–11, 14] and on tomatine [15]. Saponins, in general, are very powerful emulsifiers, toxic, haemolytic and able to form complexes with cholesterol. Here information on the biological activities of various saponins, particularly the steroidal saponins, reported during the period 1972 to 1979 is given.

Action on metabolism

Saponins (1%) in the diet of rats decreased the plasma cholesterol level and increased bile acid production [212]. The depression of growth *in vitro* caused by complex formation of saponin with fat-soluble vitamins has been studied [213]. A change in the thyroid gland in experimental haemolytic anaemia has been observed [214] when subcutaneous injection of saponin at doses of 1, 4 and 8 mg/kg once every third day is given to rabbits. The development of proteins, carbohydrate and lipid dystrophy in the liver of rabbits is prevented by the oral administration of *Tribulus terrestris* saponin at 10–15 mg/kg/day for 90 days with the simultaneous administration of cholesterol (200 mg/kg/day) [215]. Certain steroidal saponins isolated from egg-plant, which contain mainly tigogenin and neotigogenin as aglycones, partially normalize lipase activity in the mitochondria and increase cholinesterase activity in the cytoplasm [216]. The Na^+ or K^+ activated ATPase in rabbit red blood cell membranes is inhibited by low concentrations of saponin but activated by high concentrations while ouabain, a cardiac glycoside, inhibits the activating effect [217]. The effect of digitonin on glucose uptake by isolated fat cells in the presence or absence of insulin was studied by Akhtar and Perry [218] who observed that low concentrations of saponin inhibited the stimulation of glucose uptake by insulin without causing severe cell damage suggesting digitonin–cholesterol complex formation in the fat cell plasma membrane.

Action on the cardio-vascular system

The cardiotonic actions of g-strophanthin (0.15–3.25 mg/kg), α-solanine (2.5–5 mg/kg) and T.T. saponin were studied on a comparative basis. g-Strophanthin and T.T. saponin decreased the frequency of cardiac contraction whereas α-solanine had no effect [219]. Cardiotonic activity of some glycoalkaloids, when compared with K-strophanthoside by the use of isolated frog heart, is found to be directly related to the nature of the aglycone and the number of sugar units [220]. Saponin isolated from the seeds of *Achyranthes aspera* is found to increase the force of contraction of isolated frog heart, guinea-pig heart and rabbit heart [221]. Two new steroidal saponins ruscoside A (ruscogenin + 1 glc + 1 gal + 2 rha) and ruscoside B (ruscogenin + 1 gal + 1 glc + 2 rha + 1 ara) isolated from *Ruscus hyrcanus* [199] exhibit various biological activities. They decrease the cholesterol content of the blood, lipid deposition in the aorta and liver arterial tension. They also slow down the cardiac rhythm and respiration of humans and rabbits suffering from arteriosclerosis. Ruscoponin and ruscogiponin from *R. penticus* and *R. hypophyllum* exhibit fibrinolytic activity *in vitro* at 0.1 and 0.25% concentration, respectively. Ruscoponin

has a thrombolytic effect in dogs when given intravenously but no effect when given intramuscularly [222].

Antimicrobial activity

Saponins are generally good antifungal and antibacterial agents. The antifungal activity is found to be more effective with saponins than the sapogenins and the acetylated saponins, the activity being highly influenced by the number of component monosaccharides and their sequence. Digitonin has a considerable fungistatic activity [223]. Strong fungistatic action was observed with saponins when added to the culture medium at 31.2–62.5 μg/ml [224]. Digitonin and tomatin caused considerable leakage of free amino acids from the mycelium of *Botrytis cinerea* and *Rhizoctonia solani* [225]. Deltonin and deltoside isolated from *Dioscorea deltoidea* have a fungitoxic effect on the growth of *Fusarium solani* conidia and *Phytophthora infestans* [226]. Saponins from common ivy [227] are more active against Gram positive bacteria than gram negative ones with a minimum inhibitory concentration of 0.312–1.25 mg/ml. The growth of *Bacillus mycoides* was inhibited by the saponins extracted from *Allium atroyiolaceum*, *Saponaria viscosa*, *Caltha palustris* and *Verbascum aureum* [228].

Action on the reproductive system

Saponins from *Costus speciosus* have shown varied and interesting biological activities. They have a stimulating effect [229] and anti-inflammatory activity on uterus and they produced proliferative changes in both vagina and uterus showing a similar effect to that produced by stilbesterol [230, 231]. Prevention of pregnancy in rats when fed saponin at 5–500 μg/100 g body wt for 15 days has been reported [232]. An abortifacient effect has been shown by saponins from *C. speciosus* when given to pregnant goats, rats and cows [232]. A similar antifertility effect has also been reported in the case of the triterpenoid saponin isolated from *Gleditschia horrida* [233].

Miscellaneous

The haemolytic action of digitonin on human, pig and bovine erythrocytes is found to be higher than tomatine while human erythrocytes are very resistant to parillin [234]. Saponins from rhizomes of wolfberry inhibit the medicinally induced sleep in mice [235]. Two new steroidal saponins ruscoside A and ruscoside B isolated from *Ruscus hyrcanus* have antisclerotic and hypotensive activity [199]. The anti-inflammatory activity on rat paw edema is displayed by saponins from *Ruscus aculeatus* [236]. There are reported adjuvant effects of saponins on vaccine against Foot and Mouth Disease [237, 238]. Two sarsasapogenin glycosides isolated from *Cornus florida* [22] were found to exhibit strong molluscicidal activity. *Biomphalaria glabaratus* were killed within 24 hr by a 6 ppm solution of one glycoside and by a 12 ppm solution of the other. A saponin isolated from *Tribulus terrestris* has been found to be useful as an antisclerotic agent [239].

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