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REVIEW

TRITERPENOID SAPONINS AND SAPOGENINS: 1973–1978*

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Key Word Index—Angiospermae; triterpenoids; saponins; sapogenins; natural distribution; structural variation.

Abstract—The triterpenoid saponins identified in plants during the period 1973 to 1978 inclusive are reviewed. Their natural occurrence, chemistry and biological activities are discussed. A compilation of all saponins, the structures of which have been fully elucidated, is included.

INTRODUCTION

Saponins are widely distributed in nature, being present in more than 90 plant families [1] and of these, the triterpenoid saponins constitute the major group. Since the last review [2] on triterpenoid saponins, significant developments have taken place and, therefore, the present review has been compiled to present a consolidated account of their distribution in nature and their chemistry and biological activities, as reported during the years 1973–1978.

In some cases the saponins from different parts of the same plant have been found to possess different properties, e.g. the roots of *Spinacia oleracea* contain spinasaponins A and B which show good antibiotic activity but the leaves are practically free from saponin; again, the saponin from the wood of *Guaiacum officinale* has scarcely any biological activity whereas the leaf saponin has marked haemolytic action. Differences in saponin constituents have also been observed in the case of ginseng as cultivated in different Korean climatic and soil areas as well as after being subjected to heat treatment and exposure to sunlight [3]. Similarly leaf saponins of *Panax japonicus* were found to be significantly different in plants collected from four localities in Japan [4].

DETECTION AND ISOLATION

The Liebermann–Burchard test has been employed in most instances to detect saponins. It has also been used to advantage in differentiating between the triterpenoid and steroidal saponins, since the former give pink or purple whereas the latter exhibit blue–green colours. Thionyl chloride, phosphomolybdic acid, silicotungstic acid or haemolysis of blood have generally been used for detection. A colorimetric method using vanillin and H_2SO_4 has been developed and applied to estimate the ginsenosides Rb_1, Rd and Rg_1 in crude preparations from *Panax ginseng* roots [5]. A method for the determination of saponin content based on circular zone of haemolysis on blood–agar plates has been described [6].

Recent additions to purification procedures are chromatography over polyamide [7] in the case of *Panax ginseng* saponins and DEAE-Sephadex [8] in the case of alfalfa saponins. A colourless saponin mixture has been obtained by passing a crude methanolic solution through a charcoal–celite column [9]. A new technique, droplet counter-current chromatography (DCCC), has been applied to separate complex saponins of *Bacopa monniera* [10], *Hovenia dulcis* [11], *Platycodon grandiflorum* [12] and *Panax japonicus* [13]. Recent work is reported on the separation of a variety of partially and completely substituted carbohydrates by high-performance liquid chromatography (HPLC) and, this will undoubtedly be a valuable tool in resolving complex mixtures of saponins as well [14].

CHEMICAL STRUCTURE

The hydrolysis of saponins, normally achieved with 2–4 N mineral acids, has also been reported with perchloric acid [15, 16] with good results. The acid hydrolysis of saponins often gives rise to artefacts in sapogenols owing to the rather drastic reaction conditions. In order to avoid these undesirable artefacts,

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alternative cleavage methods have been explored. The ultraviolet photolysis [17] of a methanolic solution of some types of oleanane-derived saponins resulted in the liberation of genuine sapogenins and the attachment of sapogenol to the carbohydrate moiety through a uronic acid was found to be an essential requirement for this cleavage. Another method has been concerned with the splitting of arabinoside or galactoside linkages [18] in 2′-keto derivatives of arabino- and galactosidosaponins, which are conveniently prepared by reaction with DMSO and acetic anhydride. The photolysis by ultraviolet irradiation of these derivatives furnished the aglycones in their respective oxidized forms but acid-labile groupings in the molecule remain intact during this treatment.

The permethylated derivatives of glucuronide saponins [19], which retain the free glucuronido carboxylic acid function, are selectively cleaved at the β-D-glucuronide linkage to the constituent carbohydrate and sapogenol moieties in excellent yields on $Pb(OAc)_4$ oxidation followed by treatment with alkali. The β-D-galacturonide linkage shows considerable resistance to this degradation but the method seems to be of wider applicability to the cleavage of other uronide linkages in saponins and polysaccharides.

Treatment with acetic anhydride and pyridine has also proved to be an effective cleavage method for glycosidic linkage in saponins selectively at the glucoronide moiety [20] and the degradation is different from ordinary acetolysis. A glucuronide saponin which possesses a free carboxylic function and two carbohydrate residues at C-2′ and C-4′ in its glucuronide moiety was decomposed to furnish the acetylated derivatives of the genuine sapogenols and carbohydrate residues.

Enzymatic hydrolysis [21–23] has been frequently used for the structure elucidation of saponins. Soil bacteria hydrolysis [24] has led to the characterization of protobassic acid as the genuine sapogenol of *Madhuca longifolia* saponins and it has been suggested it may be the common sapogenol of several Sapotaceous plants, in place of what was hitherto thought to be bassic acid. This method has also been employed to show that spergulagenin A is one of the true sapogenols of the saponin mixture from *Mollugo spergula*. In addition, naringinase enzymatic hydrolysis of this saponin mixture has yielded a new bisnorhopane-type genuine sapogenol, spergulatriol [25], and was readily converted to isoanhydrospergulatriol, which is isolated as a minor constituent from the acid hydrolysate of the total saponin mixture.

The appearance of new products by acetyl migration has been discovered among the monoacetylated saponins of *Platycodon grandiflorum*. Compounds with an acetyl at the 2-*O* or 3-*O* position in a rhamnose moiety were found to be interconvertible in dilute alcoholic solutions (*ca* 5 mg/ml) to give their *ca* 1:1 mixture and then produce the parent deacetylated saponin after long standing [26]. Chiksetsusaponin L10 has been shown to be the first 12-*O*-glycosylated dammarene saponin in nature [27]. Chiksetsusaponins LT5, LT8 and LN4 are the first examples of the dammarene-type glycosides having a 12-keto function in the aglycone moiety [28].

It was suggested earlier that saikosaponin b of *Bupleurum falcatum* was an artefact derived from saikosaponin d during the isolation procedure. On re-investigation, saikosaponins b_2 and b_4 have been isolated as components of saikosaponin b and it has been established by conversions through various acid treatments that both are artefacts derived from saikosaponin d. Similarly saikosaponin a has been resolved through peracetylation into saikosaponins a and b_3 in the ratio of 9:1. The methoxyl group at C-11 in the sapogenins of saikosaponins b_3 and b_4 has been shown to originate from MeOH used as a reaction solvent [29].

The mass spectra of permethylated derivatives of about twenty oleanane-type saponins containing one to five sugar units were studied in order to elucidate the sequence of sugar units in the saponins [30]. Mass spectral analysis of the decaacetate of ginsenoside Rg_1 and related compounds has played a major role in structure elucidation of these saponins [31].

Sugars

In addition to the common eight sugars (D-glucose, D-galactose, D-glucuronic acid, D-ribose, D-xylose, L-arabinose, L-fucose and L-rhamnose), 3-methyl glucose and quinovose have been reported. Saponins containing apiose have been characterized for the first time [32]. The sugar units are generally identified as methylated derivatives or as alditol acetates by GLC; their characterization as aldonitrile acetates [33] has also been reported.

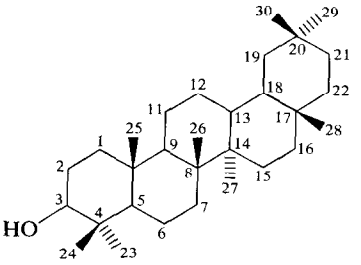
Sapogenins

It has been suggested that ^{13}C NMR is a useful technique for structural studies on plant glycosides, especially those which are isoprenoid-derived and have acid-labile groups. It has been successfully used to elucidate the structures of saikosaponins [34] and sapogenins [35]. The ^{13}C NMR assignments of cucurbitacin aglycones isolated from *Anagallis arvensis* are given and general features of chemical shifts have been described [36]. Six saponins and prosapogenins of *Platycodon* along with their peracetates have been studied and in cases of monoacetylated products, the position of acetylation in the carbohydrate chain has been elucidated [37–40]. For the purpose of application to *Panax* saponins, the stereochemistry of the β-glucosylation effect and assignments of carbon chemical shifts of dammarane-type triterpenes have been explored [41].

Complete structural elucidation of lyofoligenic acid (**1**) [42], papyriogenin [43], spergulagenin A [44] and panaxoside A progenin I acetate [45] has been accomplished by X-ray crystallographic studies.

Earlier reviews have shown [3, 46] that sapogenins derived from β-amyrin outnumber, both in variety and frequency, any other class of triterpenes. A similar picture emerges from the present review: 24 new sapogenins belonging to oleanane group have been characterized (Table 1); two of these are the rather unusual cyclamiretin C (**2**) containing a hemi-acetal grouping and papyriogenin (**3**), containing a conjugated diene system. The structures of cyclamiretins A and D, given in earlier review [46], have been revised. The major saponin, cyclamin of *Cyclamen* spp., yielded on acid hydrolysis a mixture of cyclamiretin A (**4**) and, depending upon the conditions, the artefacts

Table 1. New sapogenins of the β-amyrin group



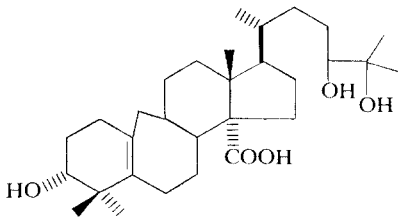
Trivial name	Structure
Acinosolic acid	2β-OH,28,30-COOH, Δ^{12}
Arjungenin	2α,19α,23-OH,28-COOH, Δ^{12}
Astrantigenin G	15→28 lactone, Δ^{12}
Barrigenic acid	2α,19β-OH,23,28-COOH, Δ^{12}
Barrigenol A_1-22 angelate	15α,16α,28-OH,22-angeloyloxy, Δ^{12}
Caccigenin	2α,21β,23-OH, Δ^{12}
Cadambagenic acid	27,28-COOH, Δ^{12}
Careagenol D	21α,22α,28-OH, $\Delta^{12,15}$
Cyclamiretin D	16α,28-OH,30-CHO, Δ^{12}
Eryngiumgenin E	16α,22α,28/OAc, angeloyloxy and/or tigloyloxy, Δ^{12}
28-Hydroxyglycyrrhetic acid	11-Oxo,28-OH,30-COOH, Δ^{12}
Entagenic acid	15α,16α-OH,28-COOH, Δ^{12}
Hydrocotylegenin C	15α,16α-OH,28-OAc,21β,22α-OH/OCOCMeEtOAc, Δ^{12}
Hydrocotylegenin F	15α,16α,28-OH,21β,22α-OH/OCOCMeEtOAc, Δ^{12}
Jaligonic acid	2β,23-OH,28,30-COOH, Δ^{12}
11-Methoxy-16α,23,28-trihydroxy-β-amyrin	11α-OMe,16α,23,28-OH, Δ^{12}
11-Methoxy-16β,23,28-trihydroxy-β-amyrin	11α-OMe,16β,23,28-OH, Δ^{12}
Norarjunolic acid	2α,23-OH,28-COOH, $\Delta^{12,20(29)}$, 30-*nor*
Ovalifoliogenin	1β,23-OH, Δ^{12}
Platicogenic acid A	2β,16α,23-OH,28-COOH, Δ^{12}
Presenegenin	2β,27-OH,23,28-COOH, Δ^{12}
Protobassic acid	2β,6β-OH,28-COOH, Δ^{12}

cyclamiretins B, C and D. A number of species of *Eryngium* have been studied and a saponin–sapogenin relationship has been established. A study of Polygalaceae has shown 2β,3β,27-hydroxy-olean-23,28-dioic acid (presenegenin) to be an essential constituent of plants of this family.

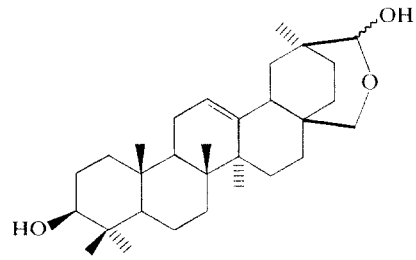
Amongst the ursane group, four new members have been identified and one of these, larreagenin A (**5**), is the first example of a 29-nor ursane. Two sapogenols having a new migrated hopane skeleton, spergulagenin A (**6**) and spergulatriol (**7**), have also been discovered.

Among the tetracyclic triterpenoids, three novel sapogenins, bacogenin A_1, A_2 and A_3 (**8–10**), having a rearranged side chain of the dammarane skeleton have been obtained along with ebelin lactone (A_4) as a result of acid hydrolysis of bacosides A and B of *Bacopa monniera*. Bacoside A was further resolved into A_1 and A_2 components and both yielded genins A_1 and A_4 on acid hydrolysis in 1:2 and 2:1 ratio, but both give jujubogenin (**11**) and pseudojujubogenin (**12**) on Smith degradation though the ratio of the products was again different. Thus, these crystalline components are still mixtures and give well-separated peaks on a DCC chromatogram. Pseudojujubogenin on acid treatment yields bacogenin A_1. Thus, bacogenin A_1 arises from the saponin constituent whose genuine sapogenin is pseudojujubogenin [10]. Two sapogenins, protolyofoligenic acid (**13**) and cimicifugenin (**14**), belonging to 9,19-cyclo(9β)lanostane (cycloartane) group have been characterized. Cimicifugenin is obtained by cellulase hydrolysis of cimicifugoside, whereas 50% MeCOOH hydrolysis produced an artefact, cimicifugenin A (**15**).

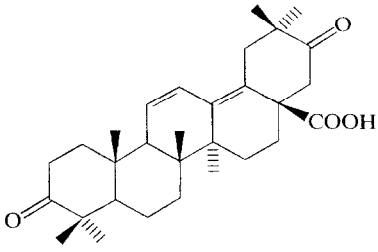
In recent years, the toxic saponins from starfish and sea cucumber, steroidal in the case of the former and triterpenoid (lanostane type) in the case of the latter, have been studied. A new sapogenin, 25-methylsticopogenin A_4, has been isolated from sea



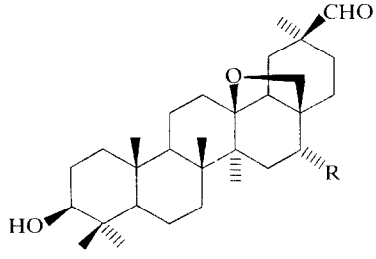
Lyofoligenic acid (**1**)



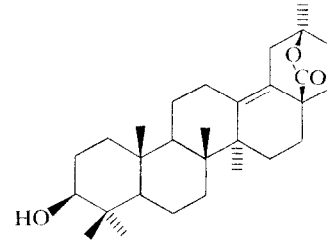
Cyclamiretin C (**2**)



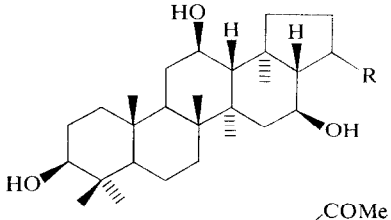
Papyriogenin (**3**)



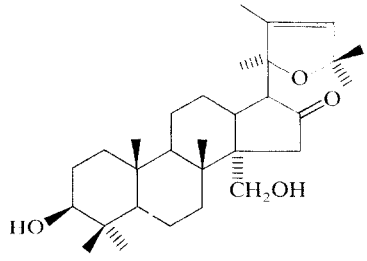
4 R = OH Cyclamiretin A
23 R = O Cyclamigenin B



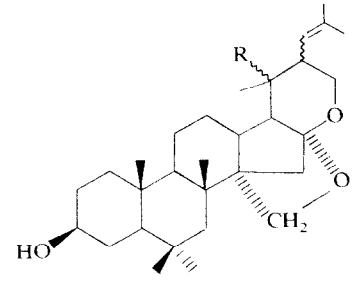
Larreagenin A (**5**)



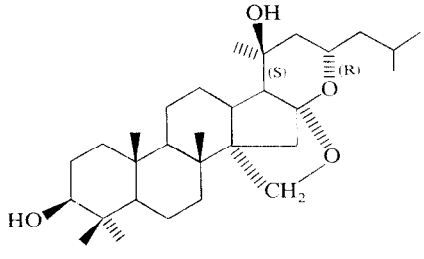
6 Spergulagenin A R = COMe
7 Spergulatriol R = $=CH_2$



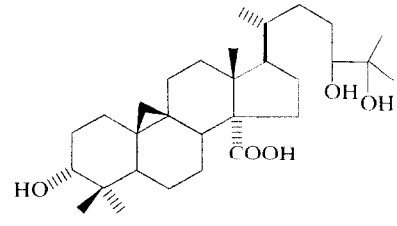
Bacogenin A_1 [20(*S*)] (**8**)
Bacogenin A_2 [20 *R*] (**9**)



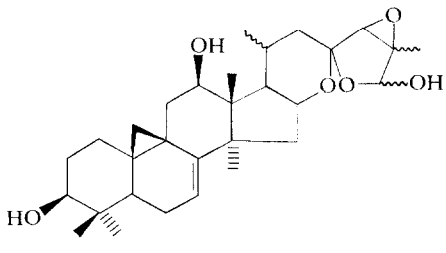
12 Pseudojujubogenin R = OH
10 Bacogenin A_3 R = $\Delta^{20(21)}$



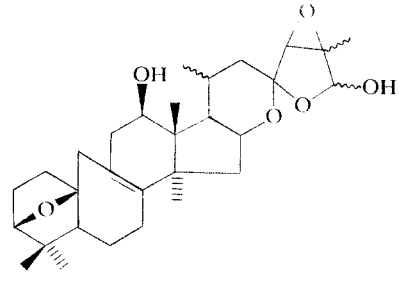
Jujubogenin (**11**)



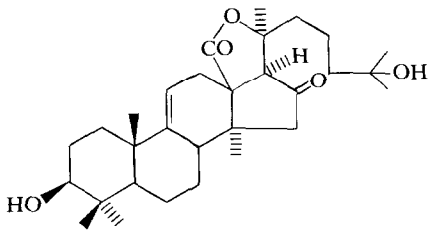
Protolyofoligenic acid (**13**)



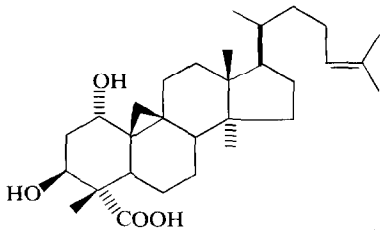
Cimicifugenin (**14**)



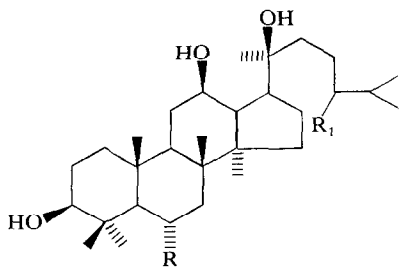
Cimicifugenin A (**15**)



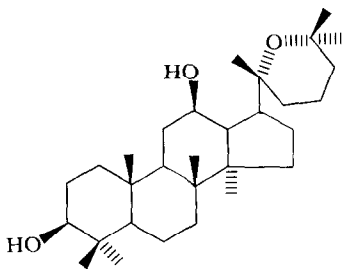
Stichopogenin A_4 (**16**)



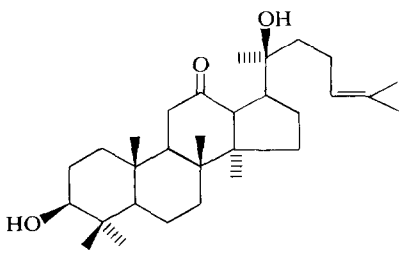
Mollic acid (**17**)



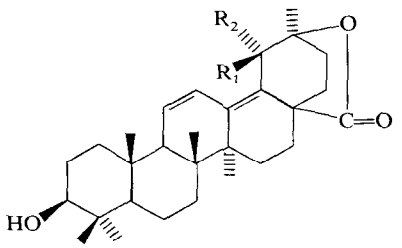
18 20(*S*) Protopanaxadiol R = H, $R_1 = \Delta^{24}$
19 20(*S*) Protopanaxatriol R = OH, $R_1 = \Delta^{24}$
21 24-Hydroxy 20(*S*) protopanaxatriol R = OH, R_1 = OH



Panaxadiol (**20**)



3β, 20(*S*)-OH, 12-oxo, dommar-24-ene (**22**)



Latifoloside aglycones

	R_1	R_2
24	OMe	Me
25	OH	Me
26	Me	OH

cucumber (*Stichopus japonicus*) and a revised structure of sticopogenin A_4 (**16**) has been reported.

LIST OF SAPONINS CHARACTERIZED FROM 1973 TO 1978

The available data have been divided into four sections based on the isolation and characterization of saponins and their sapogenins, including the configuration of the carbohydrate moieties. The sugar components, wherever identified, are included (Table 2 A–D), but reports where the presence of saponin in a plant has only been demonstrated by some tests have been excluded from the review.

BIOLOGICAL ACTIONS

The saponins are a pharmacodynamic group of natural products with a wide spectrum of biological activities. Ginseng radix is an important crude tonic drug whose saponin along with its nine purified chromatographic fractions (TLC-analysed), have been evaluated for haemolytic as well as protective activity against haemolysis [175]. The haemolytic activity was shown by certain fractions while the remaining fractions exhibited protective activity which was measured against haemolysis caused by saponaria saponin and several other reagents. Total saponin did not show haemolytic activity. One of the fractions had almost the same activity (25 μg/ml) as saponaria saponin which is known to be one of the strongest haemolytic agents. It is interesting that the hydrolysis of haemolytic fractions yielded 20(*S*)panaxatriol whereas the protective fractions gave 20(*S*)panaxadiol. Panaxadiol and panaxatriol, which are artefacts derived from genuine sapogenins, by themselves show neither of the activities. Both types of components were present in Chinese crude drug and, thus, both activities were masked in crude preparations owing to the presence of the artefacts.

The biochemical aspects of the saponins of Korean ginseng have been reviewed [176]. The administration of root extract and ginsenosides Rb_2, Rc, Rc_2, Rd, Re and Rg_1 stimulated the incorporation rate of labelled precursors into nuclear and cytoplasmic RNA in rat liver, and consequently resulted in increased incorporation of labelled leucine into rat serum protein. Ginsenoside Rb_1 was ineffective, Rd was most active and the incorporation rate was directly proportional to its

Table 2A. Saponins whose chemistry has been completely elucidated including the configuration of the carbohydrate chain

Plant	Saponin, mp	Structure	Reference
1. *Acanthophyllum gypsophiloides*	Acantophylloside B	Gypsogenin, β-D-Gal(1→4)β-D-Xyl(1→4)[β-D-Gal(1→4)]β-D-Glc A-C_3; β-D-Xyl(1→3)β-D-Xyl(1→3)β-D-Xyl(1→4)α-L-Rha(1→4)[α-L-Rha(1→2)]β-D-Fuc-C_{28}	47
	Acanthophylloside C	Gypsogenin, β-D-Gal(1→4)β-D-Xyl(1→4)[β-D-Glc(1→6)][β-D-Gal(1→2)]β-D-Glc A-C_3; β-D-Xyl(1→3)β-D-Xyl(1→3)β-D-Xyl(1→4)α-L-Rha(1→4)α-L-Ara(1→2)]β-D-Fuc-C_{28}	48
2. *A. paniculata*	Paniculatoside C	3β-OH,23,28-COOH,olean-12-ene, β-D-Glc(1→6)β-D-Glc(1→6)[β-D-Glc(1→4)]β-D-Glc-C_{28} *or* β-D-Glc(1→6)[β-D-Glc(1→6)β-D-Glc(1→4)]β-D-Glc-C_{28}	49
3. *Agrostemma githago*	Githagoside	Gypsogenin, β-D-Glc(1→3)α-L-Rha(1→2)[β-D-Xyl(1→4)]β-D-Fuc-C_3	50
4. *Akebia quinata* (from seed)	Saponin D >225° dec.	Hederagenin, α-L-Ara-C_3; β-D-Glc(1→6)β-D-Glc-C_{28}	51
	Saponin E 210–214° dec.	Hederagenin, β-D-Xyl(1→2)α-L-Ara-C_3; β-D-Glu(1→6)β-D-Glc-C_{28}	
	Saponin F 211–214° dec.	Hederagenin, β-D-Glc(1→2)α-L-Ara-C_3; β-D-Glc(1→6)β-D-Glc-C_{28}	
	Saponin G >218° dec.	Hederagenin, β-D-Glc(1→2)[α-L-Rha(1→4)]-α-L-Ara-C_3; α-L-Rha(1→4)β-D-Glc(1→6)β-D-Glc-C_{28}	
(from fresh pericarp)	Saponin PA 228–230° dec.	Hederagenin, α-L-Ara-C_3	52
	Saponin PB 222–225° dec.	Oleanolic acid α-L-Rha(1→2)-α-L-Ara-C_3	
	Saponin PC 236–240° dec.	Hederagenin, β-D-Xyl(1→3)-α-L-Ara-C_3	
	Saponin PD 256–259° dec.	Hederagenin, α-L-Rha(1→2)-α-L-Ara-C_3	
	Saponin PE 263–266° dec.	Oleanolic acid, β-D-Glc(1→2)-α-L-Ara-C_3	
	Saponin PF 248–250° dec.	Hederagenin β-D-Glc(1→2)-α-L-Ara-C_3	
	Saponin PG 218–220° dec.	Hederagenin, β-D-Xyl(1→3)-α-L-Rha(1→2)-α-L-Ara-C_3	
	Saponin PJ2* (as permethylate)	Hederagenin, α-L-Ara-C_3; α-L-Rha(1→4)-β-D-Glc(1→6)-β-D-Glc-C_{28}	
	Saponin PJ3 (as permethylate)	Oleanolic acid, α-L-Rha(1→2)-α-L-Ara-C_3; α-L-Rha(1→4)-β-D-Glc(1→6)-β-D-Glc-C_{28}	
	Saponin PK 212–215° dec.	Hederagenin, α-L-Rha(1→2)-α-L-Ara-C_3; α-L-Rha(1→4)-β-D-Glc(1→6)-β-D-Glc-C_{28}	
	Saponin PH 207–210° dec.	Norarjunolic acid, α-L-Rha(1→4)β-D-Glc(1→6)β-D-Glc-C_{28}	53
	Saponin PJ1 (as permethylate)	Arjunolic acid, β-D-Xyl(1→3)α-L-Rha(1→4)β-D-Glc(1→6)β-D-Glu-C_{28}	
5. *Anthocephalus cadamba*	Saponin A 240°	Cadambagenic acid, β-D-Glc(1→2)α-L-Rha(1→3)β-D-Glc-C_3	54
	Saponin B	Cadambagenic acid,	55

Table 2A. (*Continued*)

Plant	Saponin, mp	Structure	Reference
	302°	α-L-Rha(1→2)α-L-Rha(1→3) α-L-Fuc-C_3	
6. *Bupleurum falcatum*	Saikosaponin b_1 237–241°	Saikogenin A, β-D-Glc(1→3)β-D-Fuc-C_3	56
	Saikosaponin b_2 235–240°	Saikogenin D, β-D-Glc(1→3)β-D-Fuc-C_3	
	Saikosaponin b_3 260°	3β,16β,23,28-OH,11α-OMe,olean-12-ene, β-D-Glc(1→3)β-D-Fuc-C_3	
	Saikosaponin b_4 245–250°	3β,16α,23,28-OH,11α-OMe-olean-12-ene, β-D-Glu(1→3)β-D-Fuc-C_3	
7. *Calendula officinalis*	Calenduloside F	Oleanolic acid, β-D-Glur-C_3; β-D-Glc-C_{28}	57
8. *Caulophyllum robustum*	Cauloside D	Hederagenin, α-L-Ara-C_3; α-L-Rha(1→4)β-D-GLc(1→6) β-D-Glc-C_{28}	58
	Cauloside F	Hederagenin, β-D-Glc(1→2)α-L-Ara-C_3; α-L-Rha(1→4)β-D-Glc(1→6) β-D-Glc-C_{28}	
	Cauloside G	Hederagenin, β-D-Glc(1→2)α-L-Ara-C_3; α-L-Rha(1→4)β-D-Glc(1→6) β-D-Glc-C_{28}	59
9. *Cimicifuga simplex*	Cimicifugoside 237° (=Δ^7-acetein)	Cimicifugenin, cimicifugenin A(**15**) β-D-Xyl-C_3	60
10. *Clematis songarica*	Songaroside A 228–230°	Hederagenin, α-L-Rha(1→4)α-L-Rha(1→2) α-L-Ara-C_3; α-L-Rha(1→4)β-D-Glc(1→6)β-D-Glc-[(1→2) α-L-Ara(1→2)β-D-Glc]-C_{28}	61
11. *C. vitalba*	Vitalboside B†	Hederagenin, β-D-Glc-C_3	62
	Vitalboside D	Hederagenin, α-L-Rha(1→4)β-D-Glc(1→2) [β-D-Rib(1→2)]α-L-Ara-C_3	63
	Vitalboside G	Hederagenin, α-L-Rha(1→3)α-L-Rha(1→4) β-D-Glc(1→2)[β-D-Rib(1→2)]α-L-Ara C_3; α-L-Rha(1→4)β-D-Glc(1→6) β-D-Glc-C_{28}	33
	Vitalboside H	Hederagenin, α-L-Rha(1→3)α-L-Rha(1→4)β-D-Glc (1→2)[β-D-Rib(1→2)]β-D-Rib-C_3	64
12. *Combretum molle*	Mollic acid glucoside 248–250° dec.	Mollic acid (**17**), β-D-Glc-C_3	65
13. *Cordia obliqua*	— 186°	Lupeol, β-D-Glc(1→4)β-D-Glc-C_3	66
14. *Ecballium elaterium*	—	Cucurbitacin B, β-D-Glc-C_2	67
	—	Cucurbitacin D, β-D-Glc-C_2	
15. *Eryngium bromeliifolium*	—	Oleanolic acid, β-D-Glc-C_3; β-D-Xyl-C_{28}	68
16. *Fatsia japonica*	Saponin I 235	Hederagenin, β-D-Glc(1→4)β-D-Glc-C_3	69
17. *Gleditsia triacanthos*	Triacanthoside A_1	Echinocystic acid, β-D-Xyl(1→4)α-L-Ara(1→4)	70

Table 2A. (*Continued*)

Plant	Saponin, mp	Structure	Reference
		β-D-Glc-C_3	
	Triacanthoside F	Echinocystic acid, β-D-Xyl(1→3)β-D-Glc-C_3; β-D-Xyl(1→3)β-D-Glc(1→4) β-D-Xyl(1→4)α-L-Rha-C_{28} *or* β-D-Xyl(1→4)β-D-Xyl(1→3)β-D-Glc (1→4)α-L-Rha-C_{28}	71
	Triacanthoside G	Echinocystic acid, β-D-Xyl(1→4)α-L-Ara(1→4) β-D-Glc-C_3; Xyl(1→3)-L-Ara(1→4)α-L-Rha-C_{28}	69, 72
18. *Glycine max* (soya bean)	Soyasaponin I 238–240°	Soyasapogenol B, α-L-Rha(1→2)β-D-Gal(1→2) β-D-Glc-C_3	73
	Soyasaponin II 245–249°	Soyasapogenol B, α-L-Rha(1→2)α-L-Ara(1→2) β-D-Glc-C_3	
	Soyasaponin III 215°	Soyasapogenol B, β-D-Gal(1→2)β-D-Glc-C_3	
19. *Gypsophila patrinii*	Phyloside B	Gypsogenin, α-L-Ara(1→2)β-D-Xyl(1→2) β-D-Gal(1→3)[β-D-Xyl(1→2)][β-D-Gal(1→4)] β-D-Glur-C_3; α-L-Rha(1→4)β-D-Xyl(1→2)β-D-Fuc-C_{28}	74
20. *Hedera rhombea*	Saponin K12 222–226°	Same as saponin PJ2 from *Akebia quinata*	75
21. *Ladyginia bucharica*	Ladyginoside A	Oleanolic acid, β-D-Glc(1→4)β-D-Glur-C_3	76
	Ladyginoside B	Hederagenin, β-D-Glc(1→4)β-D-Glur-C_3	
	Ladyginoside C	Oleanolic acid, β-D-Glc(1→4)α-L-Ara(1→4) β-D-Glur-C_3	77
	Ladyginoside D	Hederagenin, β-D-Glc(1→4)β-D-Glur-C_3; β-D-Gal(1→4)β-D-Glc(1→6) β-D-Glc-C_{28}	78
	Ladyginoside E 200–202°	Oleanolic acid, β-D-Glc(1→4)β-D-Glur-C_3; β-D-Glc(1→6)β-D-Glc(1→6) [β-D-Gal(1→4)]β-D-Glc(1→6) β-D-Glc-C_{28}	79
	Ladyginoside F	Hederagenin, β-D-Glc(1→4)β-D-Glur-C_3; β-D-Glc(1→6)β-D-Glc(1→6) [β-D-Gal(1→4)]β-D-Glc(1→6) β-D-Glc-C_{28}	78
22. *Lyonia ovalifolia* var. *elliptica*	Ovalifolioside	Ovalifoliogenin α-L-Ara-C_3	80
23. *Madhuca longifolia*	Mi-saponin A 235–238° dec.	Protobassic acid, β-D-Glc-C_3; α-L-Rha(1→3)β-D-Xyl(1→4)α-L-Rha(1→2) α-L-Ara-C_{28}	31
	Mi-saponin B 250–253°	Protobassic acid, β-D-Glc-C_3; α-L-Rha(1→3)β-D-Xyl(1→4) α-L-Rha(1→2)[β-D-Apio *f*(1→3)] α-L-Ara-C_{28}	
	Mi-saponin C 254–256°	Protobassic acid, β-D-Glc-C_3; α-L-Rha(1→3)[β-D-Glc(1→4)]α-	81

Table 2A. (*Continued*)

Plant	Saponin, mp	Structure	Reference
		L-Rha(1→2)α-L-Ara-C_{28}	
24. *Mollugo hirta*	Mollugocin A 276–280° dec.	Mollugogenol A, α-L-Ara *f*(1→5)α-L-Ara *f* (1→4)β-D-Glc-C_3	82
25. *Naumburgia thyrsiflora*	Saponin A	Priverogenin A, β-D-Glc(1→2)[β-D-Glc(1→4)]α-L-Ara-C_3	83
	Saponin B	Priverogenin A, β-D-Glc(1→4)β-D-Glc(1→2)[β-D-Glc(1→4)] α-L-Ara-C_3	84
26. *Panax ginseng* (roots)	Ginsenoside Ro 239–241° (= Chikusetsu-saponin V)	Oleanolic acid, β-D-Glc(1→2)β-D-Glur-C_3; β-D-Glc-C_{28}	85
	Ginsenoside Rb_1 197°, amorph	20(*S*)Protopanaxadiol (**18**), β-D-Glc(1→2)β-D-Glc-C_3; β-D-Glc(1→6)β-D-Glc-C_{20}	
	Ginsenoside Rb_2 200–203° amorph	20(*S*)Protopanaxadiol, β-D-Glc(1→2)β-D-Glc-C_3; α-L-Ara(1→6)β-D-Glc-C_{20}	
	Ginsenoside Rc 199–201°, amorph	20(*S*)Protopanaxadiol, β-D-Glc(1→2)β-D-Glc-C_3; α-L-Ara *f*(1→6)β-D-Glc-C_{20}	
	Ginsenoside Rd 206–209°, amorph	20(*S*)Protopanaxadiol, β-D-Glc(1→2)β-D-Glc-C_3; β-D-Glc-C_{20}	
	Ginsenoside Rd 201–203°	20(*S*)Protopanaxatriol (**19**), α-L-Rha(1→2)β-D-Glc-C_6; β-D-Glc-C_{20}	86
	Ginsenoside Rf 197°	20(*S*)Protopanaxatriol, β-D-Glc(1→2)β-D-Glc-C_6	
	Ginsenoside Rg_2 187–189°	20(*S*)Protopanaxatriol, α-L-Rha(1→2)β-D-Glc-C_6	
	Ginsenoside Rg_1 194–196°	20(*S*)Protopanaxatriol, β-D-Glc-C_6; β-D-Glc-C_{20}	87
	Ginsenoside Rb_3 193–195°	20(*S*)Protopanaxatriol, β-D-Glc(1→2)β-D-Glc-C_3; β-D-Xyl(1→6)β-D-Glc-C_{20}	88
	20-Glucoginsenoside Rf 182–184°	20(*S*)Protopanaxatriol, β-D-Glc(1→2)β-D-Glc-C_6; β-D-Glc-C_{20}	
P. ginseng (leaves)‡	Ginsenoside F_1	20(*S*)Protopanaxatriol, β-D-Glc-C_{20}	6
	Ginsenoside F_2	20(*S*)Protopanaxatriol, β-D-Glc-C_3; β-D-Glc-C_{20}	
	Ginsenoside F_3	20(*S*)Protopanaxatriol, α-L-Ara(1→6)β-D-Glc-C_{20}	
27. *P. japonicus*	Chiksetsusaponin I 189–191°	Panaxatriol, α-L-Rha(1→2)β-D-Glc-C_6	89
	Chiksetsusaponin II 194°	Panaxadiol(**20**), β-D-Xyl(1→6)β-D-Glc-C_3	
	Chiksetsusaponin III 177°	Oleanolic acid, β-D-Glc(1→6)[α-L-Ara *f*(1→4)] β-D-Glur-C_3	
	Chiksetsusaponin IV 221°	Oleanolic acid, β-D-Glur-C_3; β-D-Glc-C_{28}	
	Chiksetsusaponin V	Same as ginsenoside Ro	
	Chiksetsusaponin L5 193–195°	20(*S*)Protopanaxatriol, β-D-Xyl(1→4)α-L-Ara(1→6)β-D-Glc-C_{20}	90
	Chiksetsusaponin L10	20(*S*)Protopanaxatriol,	

Table 2A. (*Continued*)

Plant	Saponin, mp	Structure	Reference
		β-D-Glc-C_{12}; β-D-Xyl(1→4)α-L-Ara(1→6)β-D-Glc-C_{20}	
	Chiksetsusaponin L9a	24-Hydroxy-20(*S*)protopanaxatriol(**21**), β-D-Glc-C_{12}	
	Chiksetsusaponin LT5 265–270°	3β,20(*S*)-OH,12-oxo-dammar-24-ene(**22**), β-D-Glc-C_3; β-D-Glc(1→6)β-D-Glc-C_{20}	91
	Chiksetsusaponin LT8 amorph.	As above, β-D-Glc-C_3; β-D-Glc-C_{20}	
	Chiksetsusaponin LN4 amorph.	As above, β-D-Xyl(1→6)β-D-Glc-C_3; α-L-Ara(1→6)β-D-Glc-C_{20}	
28. *P. pseudoginseng* subsp. *himalaicus* var. *angustifolius*	Saponin A 240° amorph.	Same as chiksetsusaponin V	92
	Saponin D (=Ginsenoside Rb_1) 189° amorph.	20(*S*)Protopanaxadiol, β-D-Glc(1→2)β-D-Glc-C_3; β-D-Glc(1→6)β-D-Glc-C_{20}	
29. *Pereskia grandiflora*	Saponin I 275–280° dec.	Oleanolic acid Me ester, β-D-Glc(1→2)[β-D-Glc(1→3)] β-D-Glur Me ester-C_3	93
30. *Phytolacca dodecandra*	Lemmatoxin	Oleanolic acid, β-D-Glc(1→4)[β-D-Gal(1→4)] β-D-Glc-C_3	94
	Oleanoglycotoxin A	Oleanolic acid, β-D-Glc(1→2)[β-D-Glc(1→4)] β-D-Glc-C_3	95
31. *P. americana*	Phytolaccoside B 215–218°	Jaligonic acid C-3 OMe ester, β-D-Xyl-C_3	96, 97
	Phytolaccoside G	Jaligonic acid, β-D-Xyl-C_3	
	Phytolaccasaponin B 218–220°	Phytolaccagenin, β-D-Glc(1→4)β-D-Xyl-C_3; β-D-Glc-C_{28}	98
	Phytolaccasaponin E 257°	Phytolaccagenin, β-D-Glc(1→4)β-D-Xyl-C_3	
	Phytolaccasaponin G 266–269°	Phytolaccagenin, β-D-Xyl-C_3	
32. *Platycodon grandiflorum*	Platycodin D 228–237°	Platycodigenin, β-D-Glc-C_3; D-Apio *f*(1→3)β-D-Xyl(1→4)α-L-Rha (1→2)α-L-Ara-C_{28}	32
	Platycodin A 227–233° dec.	2-O-Acetyl in Rha of platycodin D	37, 39
	Platycodin B 227–231° dec.	3-O-Acetyl in Rha of platycodin D	
	Platycodin D_2 227–235°	β-D-Glc(1→3)β-D-Glc-C_3; C-28 sugar chain as in plactycodin D	
	Saponin 5 225–231°	2-O-Acetyl in Rha of platycodin D_2	
	Saponin 6 224–232°	3-*O*-acetyl in Rha of platycodin D_2	
	Polygalacin D 221–226°	Polygalacic acid; C-3 and C-28 sugars as in platycodin-D	
	Saponin 8 223–227°	2-O-Acetyl in Rha of polygalacin D	
	Saponin 9 219–225°	3-O-Acetyl in Rha of polygalacin D	
	Polygalacin D_2 229–236°	Polygalacic acid, β-D-Glc(1→3)β-D-Glc-C_3;	

Table 2A. (*Continued*)

Plant	Saponin, mp	Structure	Reference
		C-28 sugar chain as in platycodin D	
	Saponin 11 229–235°	2-*O*-Acetyl in Rha of polygalacin D_2	
	Saponin 12 226–233°	3-*O*-Acetyl in Rha of polygalacin D_2	
	Deapioplatycodin D	Platycodigenin, β-D-Glc-C_3; β-D-Xyl(1→4)α-L-Rha(1→2)α-L-Ara-C_{28}	40
	Platycodin D_3 218–225°	β-D-Glc(1→6)-β-D-Glc-C_3; C-28 sugar chain as in platycodin D	
	Deapoiplatycodin D_3 223–232°	D-Apiose unit of C-28 carbohydrate chain absent	
	Methyl platyconate A 224–231°	Platycogenic acid A, β-D-Glc-C_3 C-28 sugar chain as in platycodin D	
33. *Polygala senega* var. *latifolia*	Senigin II 247°	Presenegenin, β-D-Glc-C_3; β-D-Gal(1→4)β-D-Xyl(1→4)α-L-Rha(1→2) [4-dimethoxy(3′,4′)cinnamoyl]β-D-Fuc-C_{28}	99
	Senegin III 247° dec.	Presenegenin, β-D-Glc-C_3; β-D-Gal(1→4)β-D-Xyl(1→4)α-L-Rha(1→2)α-L-Rha (1→3)[(4-methoxy(4′)cinnamoyl]β-D-Fuc-C_{28}	100
	Senegin IV 249° dec.	Presenegenin, β-D-Gal(1→4)β-D-Xyl(1→4)[α-L-Rha(1→3)] α-L-Rha(1→2)[α-L-Rha(1→3)] [4-methoxy(4′)cinnamoyl]β-D-Fuc-C_{28}	
34. *Poterium polygamum* *P. lasiocarpum*	Poterioside 270–279°	Caccigenin, β-D-Glc-C_{28}	22
35. *Primula elatior*	—	Protoprimulagenin A, β-D-Glc(1→6)β-D-Gal(1→4) [α-L-Rha(1→2)]β-D-Glur-C_3	101
36. *Pulsatilla cernua*	Saponin II	Same as K12 from *Hedera rhombea*	102
	Saponin III 219–222°	Hederagenin, α-L-Rha(1→2)[β-D-Glc(1→4)]α-L-Ara-C_3; α-L-Rha(1→4)β-D-Glc(1→6)α-L-Ara-C_{28}	
	Saponin IV 239–242°	Hederagenin, α-L-Rha(1→2)[β-D-Glc(1→4)]α-L-Ara-C_3	
37. *Putranjiva*§ *roxburghii*	Putranoside A 185–190°	Oleanolic acid, α-L-Rha(1→3)β-D-Glur-C_3	103
	Putranoside B 230–235°	Oleanolic acid, α-L-Rha(1→3)[β-D-Xyl(1→4)]β-D-Glur-C_3	
	Putranoside C 190–194°	Oleanolic acid, α-L-Rha(1→3)β-D-Glur-C_3; β-D-Glc-C_{28}	
	Putranoside D 218–222°	Oleanolic acid, α-L-Rha(1→3)[β-D-Xyl(1→4)]β-D-Glur-C_3; β-D-Glc-C_{28}	
	Putranjiva saponin A 172–175°	Oleanolic acid, α-L-Rha(1→2)β-D-Glc(1→3)β-D-Glur-C_3	104
	Putranjiva saponin B 185–187°	Oleanolic acid, α-L-Rha(1→2)β-D-Glc(1→3)[β-D-Xyl(1→4)] β-D-Glc-C_3	
	Putranjiva saponin C 203–205°	Oleanolic acid, α-L-Rha(1→2)β-D-Glc(1→3)β-D-Glur-C_3; β-D-Glc-C_{28}	
	Putranjiva saponin D 196–199°	Oleanolic acid, α-L-Rha(1→2)β-D-Glc(1→3)[β-D-Xyl(1→4)] β-D-Glc-C_3;	

Table 2A. (*Continued*)

Plant	Saponin, mp	Structure	Reference
		β-D-Glc-C_{28}	
38. *Scabiosa soongorica*	Songoroside C	Oleanolic acid, α-L-Rha(1→3)β-D-Xyl-C_3	105
	Songoroside G	Oleanolic acid, β-D-Xyl(1→3)β-D-Xyl(1→3)α-L-Rha(1→3) β-D-Xyl-C_3	
	Songoroside I	Oleanolic acid, β-D-Xyl(1→3)β-D-Xyl(1→3)β-D-Xyl(1→3) β-D-Fuc(1→3)β-D-Xyl-C_3	
	Songoroside M	Oleanolic acid, β-D-Xyl(1→3)β-D-Xyl(1→3)β-D-Fuc(1→3) β-D-Rib-C_3; β-D-Glc(1→6)β-D-Glc-C_{28}	106
	Songoroside O	Oleanolic acid, β-D-Xyl(1→3)β-D-Xyl(1→3)β-D-Rib(1→3) α-L-Rha(1→3)β-D-Xyl-C_3; β-D-Glu(1→6)β-D-Glu-C_{28}	
39. *Schima mertensiana*	Desacyl bonin-saponin A 235–237°	Barrigenol A_1, α-L-Rha(1→2)β-D-Gal(1→4) [β-D-Glc(1→2)]β-D-Glur-C_3	9
40. *Styrax japonica*	Desacyl jegosaponin 248–251°	Barringtogenol C, α-L-Rha(1→2)β-D-Gal(1→4) [β-D-Glc(1→3)]β-D-Glur-C_3	107
41. *Terminalia arjuna*	Arjunglucoside I 231°	Arjungenin, β-D-Glc-C_{28}	108
	Arjunglucoside II 252°	Arjunolic acid, β-D-Glc-C_{28}	
42. *Tetrapanax papyriferum*	Papyrioside L-IIa 183–188°	Papyriogenin A, α-L-Rha(1→4)β-D-Glc(1→6) β-D-Glc-C_{28}	109
43. *Vaccaria segetalis*	Vaccegoside B	Gypsogenin, β-D-Gal(1→2)[β-D-Gal(1→3)] α-L-Ara(1→6)β-D-Glur-C_3; β-D-Xyl(1→4)α-L-Rha(1→3)β-D-Fuc-C_{28}	110, 111
	Vaccegoside C	Gypsogenin, [D-Gal(1→2)][D-Gal(1→3)][D-Xyl(1→4)] [L-Ara(1→6)]β-D-Glur-C_3: Rha(Fuc)Glc-C_{28} *or* Glc(Fuc)Rha-C_{28}	112
44. *Viscaria viscosa*	Viscoside	Gypsogenin, β-D-Xyl(1→2)β-D-Gal(1→3)[β-D-Xyl(1→2)] [β-D-Gal(1→4)]β-D-Glur-C_3; β-D-Glc(1→2)α-L-Rha(1→2)β-D-Fuc-C_{28}	113

* Identical with saponin K12 from *Hedera rhombea*.

† Vitalboside A was found to be oleanolic acid-3β-D-glucopyranoside.

‡ Ginsenosides Rd, Re and Rgl were also present.

§ Saponins isolated as methyl esters whose mps are given in parentheses.

dose [177]. Thus, it was ascertained that one of its tonic effects might be an increase in serum protein synthesis. The distribution of tritium-labelled ginseng extract in rat organs after intraperitoneal injection showed that radioactivity was localized mainly in the adrenal gland, liver and kidney. It also stimulated the renal nuclear and cytoplasmic RNA synthesis and it has been, therefore, suggested that RNA and protein synthesis in rat kidney are stimulated by those saponins which ultimately improve the functions of the kidney [178].

The stimulation of cholesterol synthesis in ginsenoside-treated rats has been observed and, among the five saponins tested, ginsenoside Rb_1 maximally enhanced the incorporation of acetate-[^{14}C] into serum and liver cholesterol. This was further supported by enhanced activity of HMG-CoA reductase in liver, a key enzyme in cholesterol biosynthesis, when the rats were given 5 mg/kg ginsenoside Rb_1 [179]. Rats fed on high-fat diet showed a higher level of cholesterol in liver, a lower incorporation of acetate-[^{14}C] into liver cholesterol and a repressed activity of HMG-CoA reductase. These effects were found to be reversed by ginsenoside Rb_1 when administered early during the feeding experiments [180].

It has been shown that ginsenosides of the Rg group

Table 2B. Saponins stated to be pure; sapogenins that have been characterized

Plant	Saponin, mp	Genins and sugars	Reference
1. *Acacia concinna*	Acacinin A 170°	Acacic acid + Glc + Ara + Xyl + Fuc + Rha	114
2. *Acanthophyllum gypsophiloides*	Acanthophylloside B	Gypsogenin + Glc + Xyl + Rha + Fuc + Glur	48
	Acanthophylloside C	Gypsogenin + Rha + Fuc + Glur + Glc + Xyl	
3. *Albizia lebbek*	Lebbekanin A 205°	Echinocystic acid + Glc + Gal + Ara + Xyl + Fuc + Rha	115
	Lebbekanin E 176–178°	Acacic acid + Glc + Ara + Xyl + Rha	116
Albizia procera	Proceranin A 180–182°	Proceric acid + Glc + Gal + Ara + Xyl + Fuc + Rha	117
4. *Aralia mandshurica*	Oleanosides A, B,C,D,E,F,G,H,I	Oleanolic acid	118
5. *Bacopa monniera*	Bacosides A,B	Bacogenins $A_1 + A_2 + A_3 + A_4$ (ebelin lactone) + Glc + Ara	119, 120
	Bacoside A_1 274–275°	Jujubogenin + pseudojujubogenin + Glc + Ara	10
	Bacoside A_2 258°	Jujubogenin + pseudojujubogenin + Glc + Ara	
6. *Blighia welwitchii*	—	Hederagenin + Glc + Xyl + Ara + Rha	121
7. *Camellia oleifera*	Oleipherone 203–208°	Dihydropriverogenin A + barringtogenol C + theasapogenol A + Glur + Glc + Gal + Xyl + angelic, tiglinic acids	122
8. *C. sasanqua*	Sasanquasaponin 226–230°	As above + α-Me butyric acid	
9. *Cephalaria kotchyi*	Cephalaroside E 192–196°	Hederagenin + Glc + Ara + Rha	123
10. Cucumber (seeds, leaves)	Cucurbitaside E 158–160°	2β,16α-OH,3,11,22-oxo,25-acetoxy-lanost-5,23-ene + Glc + Ara	23
11. *Cyclamen europaeum*	Cyclamin 282°	Cyclamiretins A,B,C,D	124
12. *C. hederifolium*	—	Cyclamigenins A,B(**23**),C,D	
13. *C. graecum*	amorph.		
14. *Entada scandens*	—	Entagenic acid + Glc + Ara + Xyl	125
15. *Fatsia japonica*	Fatsin β_3	Oleanolic acid	126
	Fatsin β_4	Echinocystic acid	
	Fatsiasides A–G	Oleanolic acid + hederagenin + Glc + Ara + Rha	127, 128
16. *Gypsophila bicolor*	Glycoside A	Gypsogenin	129
	Glycoside B	Gypsogenin lactone	
17. *Hedera colchica*	—	Oleic acid + Glc + Ara + Rha	130
18. *Hovenia dulcis*	Hovenoside G	Jujubogenin + Glc + Ara + Xyl	11
19. *Hydrocotyle vulgaris*	—	Hydrocotylegenins C + F	131
20. *Ilex latifolia*	Latifoloside A 235° dec.	Aglycones **24–26**	132
	Latifoloside B 210–211° dec.	Aglycones **24–26**	
21. *Larrea divaricata*	—	Larreagenin A	35
22. *Luffa aegyptica*	Aegyptinin A 244°	Oleanolic acid + Glur + Glc + Ara + Xyl + Rha	133
	Aegyptinin B 225°	Oleanolic acid + Glur + Gal + Glc + Ara + Xyl + Rha	
23. *Lychnis viscaria*	— 258–262°	Gypsogenin + Glc + Gal + Xyl + Fuc + Glur	134
24. *Lyonia ovalifolia* var. *elliptica*	Lyofolic acid	Protolyofoligenic acid + lyofoligenic acid + Glc	42, 135

Table 2B. (*Continued*)

Plant	Saponin, mp	Genins and sugars	Reference
25. *Olax gambecola*	—	Oleanolic acid + Glc + Xyl + Rha	136
26. *Phytolacca octandra*	—	Spergulagenic acid and its 3 OMe-ester (serjanic acid) + Rha + Man + Glc + Fru + Glur	137
27. *Pithecolobium saman*	Samanin A 192–194°	Acacic acid + Glc + Ara + Xyl + Rha	138
	Samanin B 194–196°	Acacic acid + Glc + Ara + Xyl + Rha	139, 140
	Samadin D 183–185°	Acacic acid + Glc + Ara + Xyl + Rha	141
28. *Polygala arenaria*	—	Presenegenin + Me salicylate	142
29. *Primula officinalis*	Primulic acid	Primulagenin A + priverogenin A monoacetate	143
30. *P. elatior*	Elatioric acid	Primulagenin A + Glc + Gal + Rha + Glur	
31. *Randia dumetorum*	Dumetornin A	Oleanolic acid + Glur + Glc + Rha + Ara + Xyl + unknown sugar	144
	Dumetoronin B	As A, differing in number of sugar units	
	Dumetoronin C	Oleanolic acid + Glc + Ara + Xyl + Rha + unknown sugar	
	Dumetoronin D 259–261°	As C, differing in number of sugar units	
	Dumetoronin E 301–303°	Oleanolic acid + Glc + Rha + unknown sugar	
	Dumetoronin F 306°	Oleanolic acid + Glc + unknown sugar	
32. *Schefflera capitata*	Scheffleroside 230°	Echinocystic acid + Fuc + Gal + Glur	145
33. *Vaccaria segetalis*	Vaccegosides A	Gypsogenin + Glur + Gal + Ara + Xyl + Fuc + Rha	146
	Vaccegoside D	Gypsogenin + Glur + Gal + Xyl + Fuc + Rha + Glc	
34. *Zizyphus jujuba*	Jujuboside B	Jujubogenin + Glc + Rha + Xyl + Ara	11

stimulate the central nervous system and the Rb group shows sedative effect. The ginseng saponin at a dose of 50 or 100 mg/kg i.p., decreases sleep and increases lying and grooming in rats and shows low toxicity in mice with LD_{50} of 765 mg/kg (i.p.). It was also observed that the saponin in low doses (2.5–5 mg/kg) increases spontaneous activity in rat and mice but at high doses (100 mg/kg) shows a decrease in motor activity. Thus, it apparently stimulates the central nervous system but at higher doses inhibits it [181]. All seven ginsenosides decrease acetylcholine-induced contractions of isolated guinea pig ileum and heart rate of rats, and exhibit biphasic activity on blood pressure. Two of them have weak vasodilator action in dogs but all of them show anti-fatigue activity [182]. Ginseng saponins at a dose of 1 mg/ml also increase the mobilization of free fatty acids from the intact epididymal fat pad of the rat, as well as from a homogenate of the epididymal fat pad containing a hormone-sensitive lipase system [183].

The saikosaponins of *Bupleurum falcatum*, a crude drug in oriental medicine for treatment of hepatobiliary and anti-inflammatory diseases, have shown several metabolic actions in rat, in addition to anti-inflammatory action. Hepatic protein synthesis from leucine-[^{14}C] was enhanced, glycogen content in the liver was increased, oxidation of glucose-[^{14}C] in the liver was not changed, while hepatic lipogenesis and cholesterogenesis from glucose-[^{14}C] were accelerated. Elevation of plasma cholesterol, triglycerides and phospholipids by cholesterol feeding was reduced. Although hepatic lipogenesis and cholesterogenesis from acetate-[1-^{14}C] were increased, the elimination of cholesterol-[4-^{14}C] from plasma was accelerated. Fecal excretion of cholesterol-[4-^{14}C] and its metabolites was increased. It is conceivable, therefore, that plasma cholesterol of the rats fed on a high-cholesterol diet was reduced by increased biliary and fecal excretion of cholesterol notwithstanding the enhanced hepatic cholesterogenesis, i.e. by accelerated cholesterol turnover. The mechanism of the plasma cholesterol-lowering effect of saikosaponins may be similar to those of structurally similar glycyrrhizin and anabolic steroids. The saikosaponins a and d, but not c, have a plasma cholesterol-lowering action. Similarly, saikosaponins a and d, but not c, have anti-inflammatory action. So either the —CH_2OH at C-4 of saikosaponins or the sugar portion, or both are the essential structural moieties for the metabolic as well as anti-inflammatory action, while the OH at C-16 is unlikely to be essential for these activities [184].

A single intraperitoneal injection or oral administration of 100 mg/kg for 7 days of the saponins of *Caltha palustris* decreased serum–cholesterol level and total protein, but increased blood sugar. The repeated oral treatment also decreased serum albumins but serum

Table 2C. Saponins isolated as impure powders; sapogenins that have been characterized

Plant	Saponin	Genins + sugars + acids	Reference
1. *Acacia concinna*	—	Ester of acacic acid + acacic acid lactone + machaerinic acid and its lactone	147
2. *Acanthophyllum paniculata*	amorph.	Gypsogenin + Ara + Xyl + Glc + Gal + Fuc + Rha + Glur	148
3. *Astrantia major*	—	Astrantigenin G	148a
4. *Barringtonia actangula*	—	Barrigenic acid	149
5. *Careya arborea*	amorph.	Careagenol D + barringtogenols C,D + 16-desoxy-barringtogenol C	150
6. *Carpolobia glabrescens*	—	Presenegenin	151
7. *C. lutea*	—	As above	152
8. *Dipsacus laciniatus*	—	Hederagenin + Glc + Ara + Rha	153
9. *Eryngium* sp.	—	Eryngiumgenin E	154
10. *Glycyrrhiza glabra*	—	28-Hydroxyglycyrrhetic acid	155
11. *Harpullia pendula*	—	A_1-barrigenol-22 angelate	156
12. *Medicago sativa*	—	Hederagenin + Glu + Ara	7
13. *Milletia laurentii*	—	Oleanolic acid + echinocystic acid + Ara + Glc + Rha + Xyl	157
14. *Mollugo spergula*	amorph.	Spergulagenin A + Me spergulagenate + spergulatriol + oleanolic acid	44, 158 159
15. *Phytolacca acinosa*	amorph.	Spergulagenic acid + jaligonic acid + acinosolic acid	160
16. *Polygala chamaebuxus*	—	Presenegenin	161
17. *P. erioptera*	—	As above	162
18. *P. exelliana*	—	As above	163
19. *P. microstigma*	—	As above	164
20. *P. nambalensis*	—	As above	165
21. *P. pygmaea*	—	As above	166
22. *Scabiosa micrantha*	—	Oleanolic acid + Glc	153
23. *S. oliveri*	—	Oleanolic acid + hederagenin + Glc + Rha	
24. *S. ochroleuca*	—	Oleanolic acid + Glc + Xyl + Rha	
25. *Solidago virgaurea*	amorph.	Oleanolic acid + polygalacic acid + Glc + Xyl + Rha	167
26. *Thea sinensis*	—	Barringtogenol C + R_1-barrigenol + Ara + Xyl + Gal + Glur + cinnamic, angelic, tiglic acids	168

globulins were not effected by either treatment. The saponins had LD_{50} of 460 mg/kg i.p. in rats and were not toxic when given p.o. at >1 gm/kg [185].

The roots of *Phytolacca americana*, reputed in Korean medicine to alleviate rheumatism, are rich in saponins having potent anti-inflammatory activity [186]. One of these, phytolaccoside B, has been shown to exhibit anti-rheumatic and anti-inflammatory actions [96]. The Mi saponin mixture of *Madhuca longifolia* showed anti-ulcerogenic and anti-inflammatory activities; the potency of the latter was more than 1/5 of phenylbutazone [81].

It has been observed that saponins possess marked antibiotic activity [1], such as cyclamin from *Cyclamen europaeum* and spinasaponins A and B from *Spinacia oleracea*. There are, however, many which are present in the plant as inactive precursors but are converted *in situ* to active antibiotics by enzymes released when the plant tissue is damaged. For example the main saponin, hederasaponin C, of *Hedera helix* (ivy) with nine sugar units is inactive but removal of sugars bound to the COOH by enzymes present in leaves produces α-hederin which shows a high order of activity. It has been postulated that as these active molecules may be fairly unstable and/or may be harmful to plant tissues because of their high activity, they are not produced until the plant tissues are damaged by fungal infection. These precursors and enzymes are formed in different cells and cannot react with each other until they are released by cell injury. Gypsoside from *Gypsophilla* species and the saponin from species of *Clematis* with nine and ten sugar residues, respectively, have no antibiotic activity but the observations in ivy suggest that the removal of the sugars joined to the COOH group might confer activity on the molecules.

The sea cucumber, *Stichopus japonicus*, has yielded holotoxins A, B and C showing a high order of activity against pathogenic fungi such as *Trichophyton mentagrophytes*, *Microsporum gypseum*, *Candida albicans* and *Candida utilis* [187]. The growth inhibitory activities

Table 2D. Saponins of animal origin from holothurians (sea cucumbers)

Name	Saponin	Genins and sugars	Reference
1. *Cucumaria frandatrix*	Cucumarcoside D_1	Genin + Glc + Xyl	169
	Cucumarcoside D_2	Genin + Glc + Xyl	
2. *Bohadshia tenuissima*	Holothurin S_1	17-Deoxyholothurinogenin	
3. *Holothuria leucospilota*	Holothurin B 213–223°	12β-Hydroxy-7,8-dihydroholothurinogenin, β-D-quinovose (1→2)-β-D-Xyl [sulphate at C-4']-C_3	170
4. *Stichopus chloronotus*		23-Acetoxy-17-deoxydihydroholothurinogenin	171
5. *S. japonicus*	Holotoxin A	Stichopogenin A_4, β-D-Xyl(1→4)α-D-quinovose(1→4) β-D-3 OMe Glc(1→3)β-D-Glc(1→2) β-D-Xyl-C_3	172, 173
	Holotoxin B	Holotoxin A + Glc	174
	Holotoxin C	Stichopogenin A_4 + Xyl + quinovose + 3-OMe Glc + Glc	

Note: All the reported sugars are present in pyranose form, unless otherwise mentioned.
Abbreviations used: Glc = glucose, Gal = galactose, Ara = arabinose, Fuc = fucose, Xyl = xylose, Rha = rhamnose, Rib = ribose, Man = mannose, Fru = fructose, Glur = glucuronic acid, *f* = furanosyl.

of holotoxins were significant (0.78–12.5 μg/ml) compared with those of vegetable saponins (>100 μg/ml), such as deacyl jegosaponin, horse-chestnut saponin, jegosaponin, soyasaponin, sakura saponin, Mi-saponin and ziyu glycoside I. The structure of the carbohydrate moieties, including the anomeric configuration, seems to be an important requisite for the activity. The saponins of *Cyclamen* spp. exhibited anti-fungal activity and they have been implicated in plant defence mechanism against fungal infection [124].

Saponins of *Aralia mandshurica* decreased the sedative effects of chloral hydrate-sleep in mice at a dose of 1.25–5 mg/kg s.c. These saponins, when given to rats loaded with glucose, produced hypoglycemic effect and also decreased blood β-lipoprotein levels. The LD_{50} of the saponins in mice was found to be 150 mg/kg and their daily administration of 15 mg to rats for 60 days did not produce any toxic effects [188].

The bark of *Schima mertensiana* used for catching fish, gave a saponin mixture, boninsaponin, possessing remarkable pescicidal activity [9]. Oleanoglycotoxin a from *Phytolacca dodecandra* has been found to be molluscicidal (ED_{90}, 3 ppm, 24 hr against *Biomphalaria glabrata*) [95].

The saponins of *Schifflera captita* showed significant activity against rat and human spermatozoa [145]. Samanin-D of *Pithecolobium saman* also showed similar activity against rat and human spermatozoa at a concentration of 0.25 mg and 0.5 mg/kg respectively [140].

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