Phytochemistry 1974, Vol 13 pp 2623 to 2645 Pergamon Press Printed in England

REVIEW

TRITERPENOID SAPONINS AND THEIR GENINS*

S. K. AGARWAL and R. P. RASTOGI
Central Drug Research Institute, Lucknow, India

(Received 1 May 1974)

Key Word Index—Triterpenoid saponins, genins, distribution, review

A REVIEW on triterpenoid saponins and sapogenins was published seven years ago.[1] Since then, due to improved techniques in the isolation and structural elucidation of saponins and their biological evaluation, considerable data has been accumulated on these compounds and this is covered, in the present review.

Some general reviews[2] on the distribution of saponins in plant kingdom and their properties have appeared during the period 1966–1972 and many new saponins have been found which possess important antimicrobial and antimycotic properties.[3] Further many saponins have been isolated, which possess the same sapogenin but exhibit a very wide variation in the number, configuration and type of carbohydrate units Oleanolic acid-containing saponins, for example, are now known to have a range of 1–10 sugar units. The period has witnessed a noteworthy progress in the isolation of pure saponins and their complete structure elucidation including the configuration of the carbohydrate moieties.

Important advances have also been registered in our understanding of the biogenetic pathways of the synthesis of saponins in plants. The role of squalene as the progenitor of polycyclic triterpenoids is now well established The intermediacy of 2,3-epoxysqualene in lanosterol and cholesterol biogenesis in mammalian tissues and its universal intermediacy in the formation of C_3-oxygenated triterpenes has been amply substantiated. However, in the triterpenoids found in primitive plants, which have no oxygen function at C_3, it has been shown that their biogenesis may involve a direct proton-initiated cyclization of squalene.[4]

DETECTION AND ISOLATION

The techniques reported in the earlier review,[1] have continued to be employed for the detection and isolation of saponins and no significant advance has been made in this area

* Communication No 1940 from Central Drug Research Institute, Lucknow, India For earlier review on this subject, see ref 1

[1] BASU, N and RASTOGI, R P (1967) *Phytochemistry* **6,** 1249

[2] HILLER, K, KEIPERT, M and LINZER, B (1966) *Pharmazie* **21,** 713, WULFF, G (1968) *Deut Apoth-Ztg* **108,** 797, WOITKE, H O, KAYSER, J P and HILLER, K (1970) *Pharmazie* **25,** 212

[3] PETRICIC, J (1970) Bilt Farm Drus Soc Repub *Makedonija,* **16,** 199, CUCU, V and GRECU, L (1971) *Farmacia* **19,** 641, (1972) *Chem Abstr* **76,** 81591, CHEEKE, P R (1971) *Can J Animal Sci* **51,** 621

[4] COREY, E J and ORITZ DE MONTELLANO, P R (1967) *J Am Chem Soc* **89,** 3362, GODFREDSON, W O, LORK, H, VAN TAMELEN, E E, WILLET, J D and CLAYTON, R B (1968) *ibid*, **90,** 208, EPPENBURGER, U, HIRTH, L and OURISSON, G (1969) *European J Biochem* **8,** 180, PONSINET, G and OURISSON, G (1968) *Phytochemistry* **7,** 757, BARTON, D H R, MELLOWS, G and WIDDOWSON, D A (1971) *J Chem Soc* (C) 1110

during the period under review Saponin mixtures have been separated by two dimensional chromatography on silica gel H plates[5] and periodate-alkaline potassium permanganate (Lemeiux reagent)[6] and antimony trichloride–vanillin (5 4) in chloroform have been used for their detection The antimony pentachloride procedure for the colorimetric estimation of saponins has been studied to determine the optimal conditions for the development of colour [7] The saponin content of the plants belonging to the Chenopodiaceae has been estimated by the hemolytic index method [8] The distribution of saponins in *Bupleurum falcatum* roots has been visualized histochemically with 99% EtOH-conc H_2SO_4 (1 1) or Et_2SO_4 [9]

The acidic saponins of *Sapindus mukorossi* have been successfully precipitated as their ammonium salts[10] from crude extracts with $(NH_4)_2SO_4$. For purification, saponins have been separated on silica gel[11] using the solvent system BuOH EtOAc H_2O (1 1 1) and alumina[12] with BuOH·EtOAc.25% NH_4OH (7 2 5) [13]

CHEMICAL STRUCTURE

The aglycone fraction of hydrolysed saponins has been very often found to be a mixture of genins which are produced during drastic conditions of acid hydrolysis. Mild acid hydrolysis of glycosides from *Aegiceras corniculatum* by the Barton procedure, therefore, has been carried out to obtain an improved yield of the genuine sapogenin [14] By varying hydrolytic procedures, artefact and genuine sapogenins have been obtained as in the cases of aescigenin[15] and protoaescigenin[16] from *Aesculus hippocastanum*, cyclamiretins D & A from *Cyclamen* sp.,[17] panaxadiol[18] and protopanaxadiol[19] from the *Ginseng* roots and senegenin[20] (or polygallic acid = senegenic acid)[21] and presenegenin[22] from the *Senega* roots. The genuine sapogenins have been obtained either under mild acidic conditions,[16,17] by chemical degradative procedures such as halogenation in case of protopanaxadiol,[19] periodate oxidation followed by alkaline cleavage in cases of presenegenin[22] and saikogenins [23] A hydrolytic enzyme(s) isolated in a partially purified state from the

[5] KARTNIG, TH and WEGSCHAIDER, O (1972) *Planta Med* **21**, 144, KARTNIG, TH, WEGSCHAIDER, O and RI, C Y (1972) *ibid* **21**, 29

[6] RAMCHANDRA ROW, L and RUKMINI, C (1966) *Indian J Chem* **4**, 149

[7] KISIHARA, S and SIMIZU, T (1967) *Kobe Diagaku Nogakubu Kenkyu Hokoku* **8**, 31, (1969) *Chem Abstr* **70**, 39080 w

[8] MELKUMYAN, KH A, REVAZOVA, L V and SEROBYAN, S E (1969) *Zh Arm* **22**, 94, (1970) *Chem Abstr* **72**, 28844 p

[9] NAGOSHI, K, ODANI, T and HIGASHI, J (1970) *Shoyakugaku Zasshi* **24**, 93, (1971) *Chem Abstr* **75**, 72521

[10] RAMACHANDRA ROW, L and RUCMINI, C (1966) *Indian J Chem* **4**, 36

[11] ISMAILOV, A I and ISKENDROV G B (1969) *Akahmedov Biol Nauki* **11**, 95, (1970) *Chem Abstr* **72**, 63584 a

[12] BUKHAROV V G and KARNELVA L N (1970) *Izv Akad Nauk SSSR Ser Khim* 171, (1970) *Chem Abstr* **73**, 4146 g

[13] MUKHAMEDZIEV, M M and ALIMBAEVA, P K (1970) *Farmatsiya* **19**, 39, (1970) *Chem Abstr* **73**, 117152 z

[14] HENSENS, O D and LEWIS, K G (1965) *Tetrahedron Letters* 4639

[15] CAINELI, G, MELERA, A, ARIGONI, D and JEGER, O (1957) *Helv Chim Acta* **40**, 2390

[16] KUHN, R and LOEW, I (1963) *Liebig's Ann* **669**, 183

[17] TSCHESCHE, R, INCHANRRONDO, F and WULFF, G (1964) *Liebig's Ann* **680**, 107, TSCHESCHE, R, STRIEGLER, H and FEHLHABER, H W (1966) *ibid* **691**, 165

[18] TANAKA, O, NAGAI, M and SHIBATA, S (1964) *Tetrahedron Letters* 2291

[19] SHIBATA, S, TANAKA, O, ANDO, T, SADO, M, TSUSHIMA, S and OHSAWA, T (1966) *Chem Pharm Bull* **14**, 595

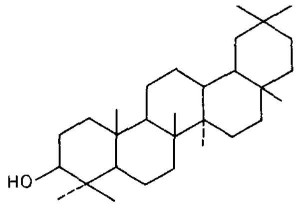
[20] DUGAN, J J, DE MAYO, P and STARRATT, A N (1964) *Can J Chem* **42**, 491

[21] PELLETIER, S W, ADITYACHAUDHURY, N, TOMASZ, M, REYNOLDS, J J and MECHOULAM, R (1964) *Tetrahedron Letters* 3065, *Idem* (1965) *J Org Chem* **30**, 4234

[22] DUGAN, J J and DE MAYO, P (1965) *Can J Chem* **43**, 2033, SHIMIZU, Y and PELLETIER, S W (1966) *J Am Chem Soc* **88**, 1544

[23] KUBOTA, T and HINOH, H (1968) *Tetrahedron* **24**, 675

internal microflora of rat, has been shown to hydrolyse numerous saponins from different plants thereby showing a low degree of specificity, but it is promising enough to be used as a tool for obtaining genuine sapogenins.[24]



Acerotin	22-OAc, 21-OCCH=CHCH=CHBu, Δ^{12}, 28-COOH
Acerocin	22-OAc, 21-OCCH=CHCH=CHSec Bu, Δ^{12}, 28-COOH
Anagalligenone	23-OH, 16-oxo, $13\beta \rightarrow 28$ epoxy
Barringtogenol B	21β, 22α, 28-OH, 16α-anageloyloxy, Δ^{12}
Camelliagenin A	16α, 22α, 28-OH, Δ^{12}
Camelliagenin B	16α, 22α, 28-OH, 23-CHO, Δ^{12}
Camelliagenin C	16α, 22α, 23, 28-OH, Δ^{12}
Caccigenin	2α, 21β, 23-OH, Δ^{12}, 28-COOH
Caccigenin lactone	2α, 23-OH, $21 \rightarrow 28$ lactone, Δ^{12}
16-Desoxy barringtogenol C	21β, 22α, 28-OH, Δ^{12}
Gymnemagenin	16β, 21β, 22α, 23, 28-OH, Δ^{12}
Isothankunic acid	5, 6, 23-OH, Δ^{12}, 28-COOH
Platicodigenin	2β, 16α, 23, 24-OH; Δ^{12}, 28-COOH
Polygalacic acid	2β, 16α, 23-OH, Δ^{12}, 28-COOH
Proceric acid	21β-OH, Δ^{12}, 28-COOH
Protoprimula-genin A	16α-OH, $13 \rightarrow 28$ epoxy
Sapogenin K	2, 21-OH, Δ^{12}, 28-COOH
Spergulagenic acid	Δ^{12}, 28, 30-COOH
Serratagenic acid	Δ^{12}, 28, 29-COOH
Saikogenin A	16β, 23, 28-OH, $\Delta^{11,13(18)}$
Saikogenin B	16β, 28-OH, $\Delta^{9(11),12}$
Saikogenin C	16β, 28-OH, $\Delta^{11,13(18)}$
Saikogenin D	16α, 23, 28-OH, $\Delta^{11,13(18)}$
Saikogenin E	16β,-OH, $13 \rightarrow 28$ epoxy, $\Delta^{11(12)}$
Saikogenin F	16β, 23-OH, $13\beta \rightarrow 28$ epoxy, $\Delta^{11(12)}$
Saikogenin G	16α, 23-OH $13\beta \rightarrow 28$ epoxy, $\Delta^{11(12)}$
Saniculagenin	3,3-dimethyl acrylic ester of R_1 barrigenol
Sapindic acid	$3\xi \rightarrow 23$ epoxy, 28-COOH, Δ^{12}
Sapogenol T-A	15α, 16α, 22α, 28-OH, 21β-anageloxy, Δ^{12}
Sapogenol T-B	16α, 22α, 28-OH, 21β-anageloxy, Δ^{12}
Theasapogenol A	16α, 21β, 22α, 23, 28-OH, Δ^{12}
Theasapogenol E	16α, 21β, 22α, 28-OH, 23-CHO, Δ^{12}

FIG 1 NEW SAPOGENINS OF THE β-AMYRIN GROUP

A novel cleavage method for splitting the glycosidic linkage of triterpene saponins by using soil bacteria giving the genuine sapogenins in good yield, has been reported in the cases of saponins from *Senega* and *Panax*,[25] *Aesculus* (horse chestnut),[26] *Styrax* and *Primula* spp. and *Lysimachia mauritiana*.[27]

[24] GESTETNER, B, BIRK, Y and TENCER, Y (1968) *J Agr Food Chem* **16**, 1031
[25] YOSIOKA I, FUJIO, M, OSAMURA, M and KITAGAWA, I (1966) *Tetrahedron Letters* 6303
[26] YOSIOKA, I, IMAI, K and KITAGAWA, I (1967) *Tetrahedron* **23**, 2577
[27] KITAGAWA, I, MATSUDA, A and YOSIOKA, I (1968) *Tetrahedron Letters* 5377, YOSIOKA, I, SAIJOH, S and KITAGAWA, I (1972) *Chem Pharm Bull* **20**, 564

The structure of the sugar moiety is generally determined by mild acidic or alkaline hydrolysis of the permethylated glycosides The individual methylated sugars are then identified either by direct chromatographic comparison or by gas chromatography (GLC) Mass spectrometry is also emerging as an invaluable tool in these investigations.

Some unusual and interesting features found in certain saponins are the presence of glucose on C_2 and C_6 of genins, in addition to C_3, in *Bassia* and *Dianthus* saponins respectively, identification of 3-*O*-methylglucose from stychoposides A and C, 3-*O*-acetylglucose in sanguisorbin E, α-D-glucose in calenduloside and glucose in the furanose form in patrinosides C and D

Measurements of UV, IR, NMR and MS are being used now as routine techniques in stereochemical and structural determination studies These aspects have been covered in a recent review on the triterpenoids.[27a] By far the largest number of newly reported sapogenins belong to β-amyrin group, as was also found in the earlier survey [1] Thus, out of the 54 new genins, 32 belong to this group, two to the hopane group and 19 to lanostane group amongst which are included 15 holothurinogenins of animal origin The new sapogenins characterized during this period are given in Figs 1 4

It may be mentioned that the structure of platicodigenin has been determined by X-ray crystallography of its bromolactone and it is the first example of a naturally-occurring triterpene having geminal hydroxymethyl groups at C-4 in ring A

The hopane group of genins were not encountered in nature so far and its first representatives, mollugogenol A (3β, 6α, 16β, 22-tetrahydroxy isohopane), and Mollugogenol B (3β, 6α dihydroxy-hop-15,17 (21) diene) have been reported. An interesting C_{30}-Nortriterpenoid, eupteleogenin has also been found during this period (Fig 2)

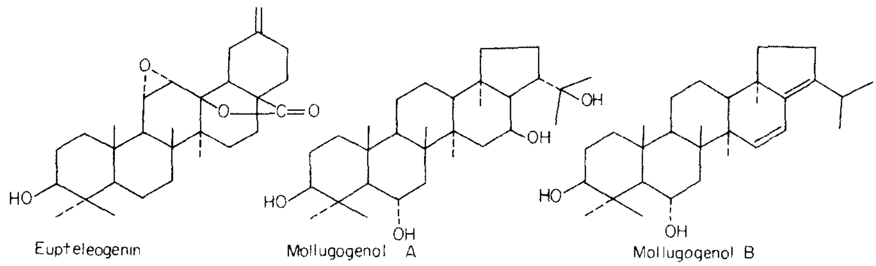
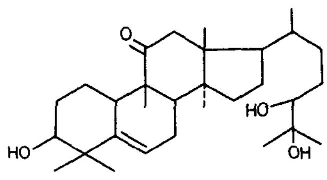


FIG. 2 HOPANE AND NORTRITERPENOID SAPOGENINS

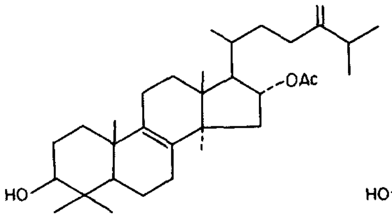
In the tetracyclic triterpenoid group, only four genins, aglycon-I, 16-acetyl tumulosic acid, its dehydroproduct and dahurinol have been obtained (Fig 3)

Sea cucumbers secrete, presumably as a defence mechanism, water-soluble glycosides, holothurins, which possess greater hemolytic activity than saponins of plant origin. Holothurin itself is a mixture of glycoside sulphates and under varying conditions of hydrolysis, more than twelve genins have been isolated The genins containing 7 8, 9·11 heteroannular diene system and methoxyl group are artefacts because these groups are absent in parent holothurin and the structure of genuine aglycone moiety is still to be elaborated These genins contain an unusual lactone ring (18 → 20) and belong to lanostane group Stichopogenins A_2 and A_4 differ from holothurinogenin in the position of double bonds (Fig 4)

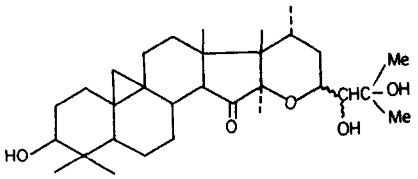
[27] KULSHRESHTHA, M J, KULSHRESHTHA, D K and RASTOGI, R P (1972) *Phytochemistry* **11**, 2369



Aglycon – I



16–Acetyl tumulosic acid
16–Acetyl dehydro($\Delta^{7(8),9(11)}$) tumulosic acid



Dahurinol
16ξ → 23ξ Epoxy, 9→19 cyclo, 2β lanostan–3β, 24ξ, 25 triol, 15– one

FIG 3 SAPOGENINS OF THE TETRACYCLIC TRITERPANOID GROUP

LIST OF SAPONINS CHARACTERIZED FROM 1966–72

The survey has been divided into five 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 1 A–E).

TABLE 1A SAPONINS WHOSE CHEMISTRY HAS BEEN COMPLETELY ELABORATED INCLUDING THE CONFIGURATION OF THE CARBOHYDRATE CHAIN

Plant	Saponin m p °C	Structure	Ref.
1 *Achyranthes aspera*	Saponin A	Oleanolic acid, α-L-Rha(1 → 4)β-D-glu (1 → 4)β-D-glu.A–C_3	28
	Saponin B	β-D-Gal-C_{28} ester of saponin A	
2 *Akebia quinata* Decne	Saponin A 228–9 d	Same as scabioside A	29
	Saponin B 249–50 d	Hederagenin, β-D-Xyl(1 → 2)-α-L-ara-C_3	
	Saponin C 248–50 d	Hederagenin, β-D-Glu(1 → 2)-α-L-ara-C_3	
3 *Bassia latifolia* Roxb	Saponin A	Bassic acid, β-D-Glu-C_2; β-D-Glu-C_3	30
	Saponin B	Rha(1 → 4)xyl(1 → 2)-ara-C_{28} ester of saponin A	
4 *Beta vulgaris*	Glycoside A 248–50	Methyl oleanolate, β-D-Glu-C_3	31
	Glycoside B 242–4	Oleanolic acid, β-D-Glu-C_3	
	Glycoside C	Oleanolic acid, β-D-Glu A–C_3	

TABLE 1A (*cont*)

Plant	Saponin mp °C	Structure	Ref
5 *Bupleurum falcatum* L	Saikosaponin A 225–32	Saikogenin F β-D-Glu(1 → 3)β-D-fuc-C_3	32
	Saikosaponin C 202–10	Saikogenin E β-D-Glu(1 → 6)-[α-L-rha(1 → 4)]-β-D-glu-C_3	
	Saikosaponin D 212–18	Saikogenin G β-D-Glu(1 → 3)-β-D-fuc-C_3	
6 *Calendula officinalis*	Calenduloside A	Oleanolic acid β-D-Gal(1 → 4)-β-D-glu-C_3	33
	Calenduloside B	Oleanolic acid β-D-Gal (1 → 4)-β-D-glu-C_3, α-D-Glu-C_{28}	
7 *Caltha silvestris*	Calcoside D 248–53	Hederagenin β-D-Glu(1 → 2)α-L-ara-C_3	34
8 *Caulophyllum robustum*	Saponin I 224–6 d	Hederagenin α-L-Ara-C_3	35
	Saponin II 252–5 d	Same as Calcoside D	
9 *Chenopodium anthelminticum*	Saponin I	Echinocystic acid β-D-Xyl(1 → 6)β-D-glu (1 → 2)α-L-ara-C_3	36
	Saponin II	β-D-Glu(1 → 4)α-L-rha-C_{28} ester of saponin I	
10 *Clematis mandschurica*	Clematoside A	Oleanolic acid D-Glu(1 → 4)-D-xyl (1 → 2)-L-ara(1 → 2)-L-ara-(1 → 4)-L-rha-C_3, L-Rha-(1 → 4)-D-glu (1 → 4)-D-glu(1 → 6)-D-glu C_{28}	37
	Clematoside A	Oleanolic acid, D-Glu(1 → 4)-D-xyl(1 → 2)-L-ara(1 → 4)-L-rha-C_3	
	Clematoside B	Oleanolic acid D-Glu(1 → 4)-D-glu(1 → 4) D-xyl-(1 → 2)-L-ara(1 → 2) L-ara-(1 → 4)-L-rha-C_3 L-Rha(1 → 4)-D-glu(1 → 4)-D glu(1 → 6)-D-glu-C_{28}	
	Clematoside C	Oleanolic acid L-Rha(1 → 6)-D-glu(1 → 6)-D-glu(1 → 4)-D-xyl(1 → 2)-L-ara(1 → 4)-L-rha-C_3 L-Rha(1 → 4)-D-glu(1 → 4)-D-glu(1 → 6)-D-glu-C_{28}	
11 *Dianthus deltoides*	Dianthoside A 220–5	Gypsogenic acid β-D-Glu-C_3	38
	Dianthoside B 229–34	Gypsogenic acid β-D-Glu-C_3 β-D-Glu-C[illegible]	
12 *Dipsacus azureus*	Dipsacoside B	Hederagenin α-L-Rha(1 → 2)α-L-ara-C_3, β-D-Glu(1 → 6) β-D-glu-C_{28}	39

TABLE 1A (*cont*)

Plant	Saponin m p °C	Structure	Ref
13 *Gypsophylla trichotoma*	Trichoside A	Gypsogenin, β-D-Glu(1 → 3)-β-D-glu A-C_3, β-D-Gal-C_{28}	40
14 *Hedera caucasigena*	Hedera-caucaside B	Oleanolic acid, L-Rha(1 → 4)β-D-glu (1 → 6)β-D-glu-C_3	41
15 *H colchica*	Hedera-colchiside E	Oleanolic acid, L-Rha-L-ara(D-glu)-C_3, L-Rha(1 → 4)β-D-glu (1 → 6)β-D-glu-C_{28}	42
	Saponin	Oleanolic acid D-Glu(1 → 4)[L-rha(1 → 5)]-*2 deoxyhex?-C_3, *3-Deoxyhex?(1 → 4) β-D-glu(1 → 6)-β-D-glu-C_{28}	
16 *H pastuchovii*	Pastuchoside B	Hederagenin, α-D-Glu(1 → 4)-α-D-glu(1 → 3)-α-L-rha-C_3	43
	Pastuchoside C	Hederagenin, α-L-Rha-C_3	
17 *Helianthus annuus* (Sun flower)	Helianthoside B	Cochalic acid, D-Xyl-(1 → 4)-L-rha-C_3, D-Glu(1 → 4)-L-rha(1 → 2) L-ara-C_{28}	44
	Helianthoside C	Cochalic acid, L-Rha(1 → 4)-L-rha(1 → 3) [D-xyl(1 → 6)]-D-glu-C_3, D-Glu(1 → 4)-L-rha(1 → 2)-L-ara-C_{28}	
18 *Herniaria glabra*	Saponin I	Medicagenic acid, β-D-Glu(1 → 6)-β-D-glu-C_{28}	45
	Saponin II	Medicagenic acid, β-D-Glu(1 → 4)[β-D-fuc (1 → 2)]-α-L-rha-C_{28}	
19 *Koelreuteria paniculata* Laxm	Saponin A	Same as scabioside A	46
	Saponin B	Gypsogenin, α-L-Rha(1 → 3)α-L-ara (1 → 4)[β-D-gal(1 → 3)]-D-gal A-C_3	
20 *Leontice eversmanni*	Leontoside A 276-8	Hederagenin, α-L-Ara-C_3	47
	Leontoside B 242-4	Hederagenin, β-D-Glu(1 → 4)α-L-ara-C_3	
	Leontoside C 222-4	Hederagenin, β-D-Glu(1 → 3) [β-D-glu(1 → 4)]-α-L-ara-C_3	
	Leontoside D 202-4	Hederagenin, β-D-Glu(1 → 4) α-L-ara-C_3, α-L-Rha(1 → 4)β-D-glu(1 → 6)-β-D-glu-C_{28}	

TABLE 1A (cont)

Plant	Saponin mp C	Structure	Ref
	Leontoside E 202 4	Hederagenin, at C-3 As in leontoside C at C-28 As in leontoside D	
21 *Medicago sativa*	Saponin	Medicagenic acid β-D-Glu(1 → 6)-β-D-glu(1 → 3)-β-D-glu-C_3	48
22 *Patrinia intermedia*	Patrinoside D	Oleanolic acid β-D-Glu(1 → 3)-[β-D-xyl (1 → 2)]-α-L-rha(1 → 4) β-D-xyl-C_3 β-D-Glu(1 → 2) β-D-glucofuranosyl(1 → 4) β-D-glu-C_{28}	49
	Patrinoside C	Oleanolic acid β-D-Xyl(1 → 2)-α-D-glucofuranosyl(1 → 3)rha-C_3, at C-28 As in Patrinoside D	
23 *Patrinia scabiosofolia* Link	Scabioside A 216–9	Hederagenin, α-L-Ara-C_3	50
	Scabioside B 210–2	Oleanolic acid, β-D-Glu(1 → 4)α-L-ara-C_3	
	Scabioside C 216–8	Hederagenin, β-D-Glu(1 → 4)α-L-ara-C_3	
	Scabioside D 224 6	Oleanolic acid, β-D-Glu(1 → 4)α-L-ara-C_3, β-D-Xyl-C_{28}	
	Scabioside E	Oleanolic acid, β-D-Glu(1 → 4)α-L-ara-C_3, α-L-Rha(1 → 4)-β-D-xyl-C_{28}	
	Scabioside G 235–6	Oleanolic acid, β-D-Glu(1 → 4)α-L-ara-C_3, β-D-Glu(1 → 4)α-L-ara (1 → 3)α-L-rha(1 → 4)β-D-xyl-C_{28}	
24 *Patrinia sibirica*	Sibiroside A 245 50	Hederagenin β-D-Glu-C_3 α-L-Ara-C_{28}	51
	Sibiroside C 245 8	Hederagenin, β-D-Glu(1 → 4)α-L-ara(1 → 4)-β-D-glu-C_3, D-Glu(1 → 4)-β-D-glu (1 → 4)α-L-ara-C_{28}	
25 *Phaseolus vulgaris* L (Broad bean)	Phaseoloside D	Genin?*, β-D-3-Deoxyhex*?(1 → 2) β-D-glu(1 → 4)[α-L-rha-(1 → 6)]β-D-gal(1 → 2)α-L-ara(1 → 3)β-D-glu A-C_3	52
	Phaseoloside E	Genin?*, β-D-glu(1 → 4)β-D-glu (1 → 4)-β-D-3-deoxyhex?* (1 → 2)β-D-glu(1 → 4) [α-L-rha(1 → 6)]β-D-gal(1 → 2)α-L-ara(1 → 3) β-D-glu A C_3	

TABLE 1A (*cont*)

Plant	Saponin m p °C	Structure	Ref
26. *Putranjiva roxburghii*	Saponin A	Oleanolic acid, α-L-Rha(1 → 2)β-D-glu(1 → 3)β-D-glu A–C_3	53
	Saponin B	Oleanolic acid, α-L-Rha(1 → 2)-β-D-glu(1 → 3)[β-D-xyl(1 → 4)] β-D-glu A–C_3	
	Saponin C	β-D-Glu-C_{28} ester of saponin A	
	Saponin D	β-D-Glu-C_{28} ester of saponin B	
27. *Sanguisorba officinalis*	Sanguisorbin B 266–7	Ursolic acid, β-L-Ara-C_3	54
	Sanguisorbin E 190–2	Ursolic acid, β-L-Ara-C_3, β-D-3-Acetyl-glu-C_{28}	
28 *Sapindus mukorassi* (Chinese soap berry)	Sapindoside A 214–16	Hederagenin, α-L-Rha(1 → 2) α-L-ara-C_3	55
	Sapindoside B 276–8	Hederagenin, β-D-Xyl(1 → 3)α-L-rha(1 → 2)α-L-ara-C_3	
	Sapindoside C 235	Hederagenin, β-D-Glu(1 → 4)β-D-xyl (1 → 3)α-L-rha(1 → 2) α-L-ara-C_3	
	Sapindoside E	Hederagenin, D-Xyl(1 → 3)-L-rha(1 → 2) L-ara-C_3, β-D-Glu(1 → 2) β-D-glu(1 → 4)[α-L-rha (1 → 6)]β-D-xyl(1 → 3) α-L-rha(1 → 2)α-L-ara-C_{28}	
29 *Saponaria officinalis*	Saponaside A 132–4	Gypsogenin, β-D-Glu A-C_3, β-D-Glu(1 → 6)β-D-glu(1 → 3)β-D-glu-C_{28}	56
	Saponaside D 241–4	Gypsogenin, α-L-Ara(1 → 4)[β-D-gal (1 → 2)]β-D-xyl(1 → 3) [α-L-rha(1 → 4)]β-D-glu A–C_3, β-D-Gal (1 → 4)[β-D-glu(1 → 2)] β-D-xyl(1 → 3)[α-L-rha(1 → 4)]β-D-fuc-C_{28}	
30 *Xanthoceras spp*	Saponin	Gypsogenin, β-D-Ara(1 → 4)β-D-gal (1 → 6)[β-D-glu A(1 → 3)] β-D-glu-C_3	57

Note All the reported sugars are present in pyranose form, unless otherwise mentioned

Abbreviations used Glu = glucose, Fru = fructose, Gal = galactose, Ara = arabinose, Fuc = fucose, Xyl = xylose, Rha = rhamnose, Glu A = glucuronic acid, gal A = galacturonic acid.

* As printed in *Chem Abstr* but could not be confirmed due to non-availability of the relevant journals and contact with concerned authors could not be established

[28] HARIHARAN, V and RANGASWAMI, S (1970) *Phytochemistry* **9**, 409

[29] HIGUCHI, R, MIYAHARA, K and KAWASAKI, T (1972) *Chem Pharm Bull* **20**, 1935

[30] HARIHARAN, V, RANGASWAMI, S and SARANGAN, S (1972) *Phytochemistry* **11**, 1791

[31] KRETSU, L G and LAZUR'EVSKII, G V (1970) *Khim Prir Soedin* **6**, 272, (1970) *Chem Abstr* **73**, 63200

[32] KUBOTA, T and HINOH, H (1968) *Tetrahedron Letters* 303

[33] VECHERKO, L P, ZINKEVICH, E P, LIBIZOV, N I and BAN'KOVSKII, A I (1971) *Khim Prir Soedin* **7**, 22, (1971) *Chem Abstr* **74**, 112385 p, VECHERKO, L P, KABANOV, V S and ZINKEVICH, E P (1971) *Khim Prir Soedin* **7**, 533, (1971) *Chem Abstr* **75**, 152042 b

[34] STRIGINA, L I, REMENNIKOVA, T M, SHCHEDRIN, A P and ELYAKOV G B (1972) *Khim Prir Soedin* **8**, 303, (1972) *Chem Abstr* **77**, 161938

[35] MURAKAMI, T, NAGASAWA, M, URAYAMA, S and SATAKE, T (1968) *Yakugaku Zasshi* **88**, 321, (1968) *Chem Abstr* **69**, 67661

[36] CHIRVA, V YA, CHEBAN, P L, KINTYA, P K and BOBEIKO, V A (1971) *Khim Prir Soedin* **7**, 27, (1971) *Chem Abstr* **74**, 112384

[37] KHORLIN, A YA, CHIRVA, V YA and KOCHETKOV, N K (1967) *Izv Akad Nauk SSSR, Ser Khim* 1306, (1967) *Chem Abstr* **67**, 117188 CHIRVA, V YA and KONYUKHOV, V P (1967) *Izv Akad Nauk Mold SSSR Ser Biol Khim Nauki*, 43, (1969) *Chem Abstr* **71**, 70851 t, CHIRVA, V YA KONYUKHOV, V P, CHEBAN, P L and LAZUR'EVSKII, G V (1967) *Khim Biokhim Uglevodov, Mater Vses Konf 4th* 98, (1970) *Chem Abstr* **73**, 88099

[38] BUKHAROV, V G and SHCHERBAK, S P (1970) *Mater Nauch Konf, Inst Org Fiz Khim, Akad Nauk SSSR* **20**, (1972) *Chem Abstr* **76**, 70100

[39] MUKHAMEDZIEV, M M, ALIMBAEVA, P K, GOROVITS, T T and ABUBAKIROV N K (1971) *Khim Prir Soedin* **7**, 153, (1971) *Chem Abstr* **75**, 49494

[40] LUCHANSKAYA, V N, KONDRATENKO, E S, GOROVITS, T T and ABUBAKIROV, N K (1971) *Khim Prir Soedin* **7**, 151, (1971) *Chem Abstr* **75**, 49495

[41] DEKANOSIDZE, G E, PKHEIDZE, T A and KEMERTELIDZE, E P (1970) *Khim Prir Soedin* **6**, 491, (1971) *Chem Abstr* **74**, 23091

[42] DEKANOSIDZE, G E, PKHEIDZE, T A, GOROVITS, T T and KEMERTELIDZE, E P (1970) *Khim Prir Soedin* **6**, 484, (1971) *Chem Abstr* **74**, 10352 DEKANOSIDZE, G E PKHEIDZE, T A KEMERTELIDZE, E P, MIKHAI-LOVA, L I TOLOKNEVA, A Z and FRUENTOV N K (1971) *Soobshch Akad Nauk Gruz SSR*, **61**, 609 (1971) *Chem Abstr* **75**, 45630

[43] ISKENDEROV, G B (1971) *Khim Prir Soedin* **7**, 425, (1971) *Chem Abstr* **75**, 152041 a ISKENDEROV G B (1970) *Khim Prir Soedin* **6**, 486, (1970) *Chem Abstr* **73**, 127741

[44] CHEBAN, P L, CHIRVA, V YA and LAZUR'EVSKII, G V (1969) *Khim Prir Soedin* **5**, 129, (1969) *Chem Abstr* **71**, 70889 m, CHEBAN, P L and CHIRVA, V YA (1969) *Khim Prir Soedin* **5**, 327, (1970) *Chem Abstr* **73**, 45777 g

[45] BUKHAROV, V G and SHCHERBAK, S P (1970) *Khim Prir Soedin* **6**, 307, (1970) *Chem Abstr* **73**, 110070 n

[46] CHIRVA, V YA, KINTYA, P K and SOSNOVSKII, V A (1970) *Khim Prir Soedin* **6**, 328, (1970) *Chem Abstr* **73**, 110063 n

[47] MZHEL'SKAYA, L G and ABUBAKIROV, N K (1967) *Khim Prir Soedin* **3**, 101, (1967) *Chem Abstr* **67**, 100383 d, *Idem* (1967) *Khim Biokhim Uglevodov Mater Vses Konf 4th* 106, (1970) *Chem Abstr* **73**, 99168 c, *Idem* (1968) *Khim Prir Soedin* **4**, 216, (1969) *Chem Abstr* **70**, 88199 a, *Idem* (1968) *Khim Prir Soedin* **4**, 153, (1968) *Chem Abstr* **69**, 77678 j

[48] GESTETNER, B (1971) *Phytochemistry* **10**, 2221

[49] BUKHAROV V G, KARLIN, V V and TALAN, V A (1967) *Khim Prir Soedin* **3**, 17, (1967) *Chem Abstr* **67**, 82363 r, *Idem* (1969) *Khim Prir Soedin* **5**, 84, (1969) *Chem Abstr* **71**, 70878, *Idem* (1969) *Khim Prir Soedin* **5**, 22, (1969) *Chem Abstr* **71**, 30644

[50] BUKHAROV, V G and KARLIN, V V (1970) *Khim Prir Soedin* **6**, 211, 373, (1970) *Chem Abstr* **73**, 66857, 110059, BUKHAROV, V G, KARLIN, V V and SIDOROVICH, T N (1970) *Khim Prir Soedin* **6**, 69, (1970) *Chem Abstr* **73**, 99162 w

[51] BUKHAROV, V G and KARLIN, V V (1970) *Khim Prir Soedin* **6**, 60 64, (1970) *Chem Abstr* **73**, 56361, 56359

[52] LAZUR'EVSKII, G V, CHIRVA, V YA, KINTYA, P K and KRETSU L G (1971) *Dokl Akad Nauk SSSR* **199**, 226, (1971) *Chem Abstr* **75**, 115903 n

[53] RANGASWAMI, S and SESHADRI, T R (1971) *Indian J Chem* **9**, 189

[54] BUKHAROV, V G and KARNEEVA, L N (1970) *Izv Akad Nauk SSSR Ser Khim* 2402, (1971) *Chem Abstr* **74**, 121340

[55] CHIRVA, V YA, KINTYA, P K and SOSNOVSKII, V A (1969) *Khim Prir Soedin* **5**, 450 (1970) *Chem Abstr* **72**, 75669 v, CHIRVA, V YA, KINTYA, P K, SOSNOVSKII, V A, KRIVENCHUK, P E and ZYKOVA, N YA (1970) *Khim Prir Soedin* **6**, 218, (1970) *Chem Abstr* **73**, 77544, CHIRVA, V YA KINTYA, P K and SOSNOVSKII V A (1970) *Khim Prir Soedin* **6**, 374 (1970) *Chem Abstr* **73**, 110062 m, *Idem* (1970) *Khim Prir Soedin* **6**, 431, (1971) *Chem Abstr* **74**, 13384

[56] CHIRVA, V YA and KINTYA, P K (1969) *Khim Prir Soedin* **5**, 188, (1970) *Chem Abstr* **72**, 13007, *Idem* (1970) *Khim Prir Soedin* **6**, 214, (1970) *Chem Abstr* **73**, 88123

[57] CHIRVA, V YA, KINTYA, P K and SOSNOVSKII, V A (1971) *Khim Prir Soedin* **7**, 442, (1971) *Chem Abstr* **75**, 152047 g

TABLE 1B SAPONINS STATED TO BE PURE, WHOSE GENINS HAVE BEEN CHARACTERIZED

	Plant	Saponin m p °C	Genins and Sugars	Ref
1	*Acacia concinna*	Acacinine 260–64	Acacic acid + glu + ara + rha	58
2	*Acer negundo*	Saponin P	Acerotin + acerocin + glu + ara	59
3	*Albizzia lebbek*	Lebbekanin A	Echinocystic acid + glu + ara + xyl + rha	60
		Lebbekanin B	Oleanolic acid + glu + ara + xyl + rha	
4	*A procera*	Proceranin A	Proceric acid + glu + gal + ara + xyl + fuc + rha	61
5	*Bassia longifolia*	Brassianin	Brassic acid + glu + ara + xyl + rha	62
6	*Calendula officinalis*	Calenduloside A 260–62	Oleanolic acid + glu + gal	63
7	*Caulophyllum robustum*	Caulosides A, B	Hederagenin + glu + rha + ara	64
		Cauloside C	Hederagenin + glu + ara	
		Cauloside D	Hederagenin (?) + ara	
		Cauloside E	Hederagenin + ara	
8	*Centella asiatica*	Isothank-uniside	Isothankunic acid + glu + rha	65
9	*Chenopodium ambrosioides*	Chenopodo-side B 213–16	Echinocystic acid + rha + xyl + ara + glu A	66
10	*Dianthus deloides*	Dianthoside C 270–5	Gypsogenic acid + ara + fuc + glu A + gal + xyl + rha	38
11	*D superbus* var *longicalycinus*	Saponin D	Gypsogenin + glu	67
12	*Dipsacus azureus*	Dipsacoside A	Hederagenin + ara + rha	68
		Dipsacoside B	Hederagenin + glu + ara + rha	
13	*Eleutherococcus senticosus*	Senticosides A, B	Oleanolic acid + ara + rha	69
		Senticosides C, D, E, F	Oleanolic acid	
14	*Empetrum sibiricum*	Empetroside A 209–11	Ursolic acid + glu	12
		Empetroside B 293–5	Ursolic acid + glu	
		Empetroside C 185–8	Ursolic acid + glu + ara	
15	*Entada phaseoloides*	—	Entagenic acid + ara + xyl	70
16	*Euptelea polyandra*	Eupteleoside A	Eupteleogenin + glu + rha + ara	71
		Eupteleoside B	Monoacetate of eupteleoside A	
17	*Gleditschia triacanthos*	Triacanthoside C	Oleanolic acid + glu + ara + rha + xyl	72
18	*Glycyrrhiza echinata*	Saponin A	Macedonic acid + rha + glu A	73
		Saponin B	Echinatic acid + rha + glu A	
19	*Gypsophila acutifolia*	Acutifolioside	Gypsogenin + Glu A + gal + ara + xyl + rha	74
20	*G trichotoma*	Trichoside B	Gypsogenin + glu + gal + glu A	75
		Trichoside D	Gypsogenin + gal + ara + xyl + glu A + glu + rha + fuc	

TABLE 1B (*cont*)

Plant	Saponin m p °C	Genins and Sugars	Ref
21 *Hedera caucasigena* (Caucasian ivy)	Hederacaucaside B	Hederagenin + oleanolic acid + glu + rha	76
	Hederacaucasides A, C D	Hederagenin + oleanolic acid	
22 *H pastuchovii*	Pastuchoside A (=Calopanax-saponin B)	Hederagenin + 2 glu + 2 rha + ara	77
	Pastuchosides B D, E, F, G, H, I	Oleanolic acid + hederagenin + glu + ara + rha	
23 *Ladygınia bucharica*	Ladyginoside C	Oleanolic acid + glu + ara + glu A	78
	Ladyginoside D	Hederagenin + glu + glu A	
24 *Myrsine africana*		Primulagenin A + glu + 2 rha + gal + glu A	79
25 *Olax subscorpioides*	–	Oleanolic acid + glu + xyl + rha	80
26 *Panax japonicum*	Saponin I 196 7	Panaxadiol + glu + xyl	81
	Saponin II 235 d	Oleanolic acid + glu + ara + glu A	
	Saponin III 230 d	Oleanolic acid + glu + glu A	
27 *Phaseolus vulgaris*	Phaseoloside E 130	Soyasapogenol + glu + gal + ara + rha + glu A	82
28 *Platycodon grandiflorum*	Platycodoside C	Platycodogenin ($C_{30}H_{46}O_6$) + polygallic acid	83
29 *Polygala senega*	Senegin II 247 8	Presenegenin + glu + gal + rha + xyl + fuc + 3,4 dimethoxy cinnamic acid	84
30 *Pulsatilla nigricans*	Pulsatoside	Hederagenin + ara + gal + glu + rha	85
31 *Putranjiva roxburghii*	Putranjivoside 215 7	Oleanolic acid + ara + rha + glu	86
32 *Sapindus emarginatus*	Emarginatoside 220 2	Hederagenin + glu + xyl + rha	87
33 *S mukorossi*		Hederagenin + ara + xyl + glu A	88
	Mukorosside 155 6	Hederagenin + glu + xyl + ara + rha	10
	Saponoside D	Hederagenin + glu + xyl + rha + ara	89
34 *Saponaria officinalis*	Saponaroside 202 2	Gypsogenic acid + xyl	90
	Saponarosides B, C	Gypsogenin	
35 *Spergularia arbuscula*	Espergularin 235 8 d	Oleanolic and echinocystic acids + gal + rha + xyl	91
36 *Ternstroemia japonica*	Saponin D	A_1 – barrigenol + 2 rha + glu + gal + glu A	92
	Saponin C_1	Octadienoic acid ester of saponin D	

Note Saponin[93] from *Primula macrocalyx* Bunge (calyx primrose) is identical to primula-saponin from *P turkestanica*

[58] VARSHNEY, I P and SHARMA, S C (1969) *Indian J Appl Chem* **32**, 69
[59] KUPCHAN, S M, TAKASUGI, M, SMITH, R M and STEYN, P S (1970) *J Chem Soc* (D) 969
[60] VARSHNEY, I P and BADHWAR, G (1970) *J Indian Chem Soc* **47**, 907

[61] VARSHNEY, I P and BADHWAR, G (1972) *Arch Pharm Ber Deut Pharm Ges* **305,** 280
[62] VARSHNEY, I P and BADHWAR, G (1971) *Proc Nat Acad Sci, India Sect A* **41,** 21
[63] VECHERKO, L P, ZINKEVICH, E P, LIBIZOV, N I and BAN'KOVSKII, A I (1969) *Khim Prir Soedin* **5,** 58, (1969) *Chem Abstr* **71,** 773 v
[64] STRIGINA, L I, CHETYRINA, N S and ELYAKOV, G B (1970) *Khim Prir Soedin* **6,** 552, (1971) *Chem Abstr* **74,** 50520 t, STRIGINA, L I, CHETYRINA, N S, LEPSHKINA, M K, KOL'CHUK, E M, REMENNIKOVA, T M and ELYAKOV, G B (1970) *Aktual Probl Izuch Efirnomaslich Rest Efirm* **166,** (1972) *Chem Abstr* **76,** 83537
[65] DUTTA, T and BASU, U P (1968) *Bull Nat Inst Sci India* 178
[66] BOGACHEVA, N G, KOGAN, L M and LIBIZOV, N I (1972) *Khim Prir Soedin* **8,** 395, (1972) *Chem Abstr* **77,** 162003 v
[67] SHIMIZU, M and TAKEMOTO, T (1967) *Yakugaku Zasshi* **87,** 250, (1967) *Chem Abstr* **67,** 8716
[68] MUKHAMEDZIEV, M M and ALIMBAEVA, P K (1969) *Khim Prir Soedin* **5,** 451, (1970) *Chem Abstr* **72,** 129407, *Idem* (1970) *Farmatsiya (Moscow)* **19,** 39, (1970) *Chem Abstr* **73,** 117152
[69] SUPRUNOV, N I (1970) *Khim Prir Soedin* **6,** 486, (1970) *Chem Abstr* **73,** 127741, FROLOVA, G M, OVODOV, YU S and SUPRUNOV, N I (1971) *Khim Prir Soedin* **7,** 614, (1972) *Chem Abstr* **76,** 70053
[70] LIU, W C, KUGELMAN, M, WILSON, R A and RAO, K V (1972) *Phytochemistry* **11,** 171
[71] GOTO, M, IMAI, S, MURATA, T, NOGUCHI, T and FUJIOKA, S (1970) *Yakugaku Zasshi* **90,** 736, (1970) *Chem Abstr* **73,** 84655, MURATA, T, IMAI, S, IMANISHI, M and GOTO, M (1970) *Yakugaku Zasshi* **90,** 744, (1970) *Chem Abstr* **73,** 66754
[72] ALI-ZADE, T A, KONDRATENKO, E S and ABUBAKIROV, N K (1970) *Khim Prir Soedin* **6,** 482, (1970) *Chem Abstr* **73,** 127740
[73] SEMENCHENKO, V F and MURAVEV, I A (1968) *Rast Resur* **4,** 62, (1968) *Chem Abstr* **69,** 21864, *Idem* (1969) *Khim Prir Soedin* **5,** 17, (1969) *Chem Abstr* **71,** 3507
[74] CHIRVA, V YA, KINTYA, P K and CHEBAN, P L (1970) *Khim Prir Soedin* **6,** 487, (1971) *Chem Abstr* **74,** 10355 m.
[75] LUCHANSKAYA, V N, KONDRATENKO, E S and ABUBAKIROV, N K (1970) *Khim Prir Soedin* **6,** 434, (1971) *Chem Abstr* **74,** 1041 d, *Idem* (1971) *Khim Prir Soedin* **7,** 431, (1971) *Chem Abstr* **75,** 152039 f
[76] DEKANOSIDZE, G E, PKHEIDZE, T A and KEMERTELIDZE, E P (1970) *Khim Prir Soedin* **6,** 376, (1970) *Chem Abstr* **73,** 127732 c, *Idem* (1970) *Soobshch Akad Nauk Gruz SSSR* **60,** 349, (1971) *Chem Abstr* **74,** 84026 b
[77] DEKANOSIDZE, G E, PKHEIDZE, T A and KEMERTELIDZE, E P (1970) *Khim Prir Soedin* **6,** 375, (1970) *Chem Abstr* **73,** 127731 b, ISKENDEROV, G B (1971) *Farmatsiya* **20,** 27, (1971) *Chem Abstr* **75,** 106045
[78] PAKHULLAEVA, M, MZHEL'SKAYA, L G and ABUBAKIROV, N K (1970) *Khim Prir Soedin* **6,** 485, (1971) *Chem Abstr* **74,** 10353
[79] KUPCHAN, S M, STEYN, P S, GROVE, M D, HORSFIELD, S M and MEITNER, S (1969) *J Med Chem* **12,** 167
[80] DAVREUX, M, DELAUDE, C and HULS, R (1971) *Bull Soc Roy Sci, Liege* **40,** 493, (1972) *Chem Abstr* **76,** 138146
[81] KONDO, N and SHOJI, J (1968) *Yakugaku Zasshi* **88,** 325, (1968) *Chem Abstr* **69,** 77689
[82] CHIRVA, V YA, KRETSU, L G and KINTYA, P K (1970) *Khim Prir Soedin* **6,** 377, (1970) *Chem Abstr* **73,** 99161
[83] ELYAKOV, G B and ALAD'INA, N G (1970) *Izv Sib Otd Akad Nauk SSSR Ser Biol Nauk* 148, (1971) *Chem Abstr* **75,** 59778 m
[84] SHOJI, J, KAWANISHI, S and TSUKITANI, Y (1971) *Chem Pharm Bull* **19,** 1740
[85] KURILENKO, M I (1968) *Farm Zh (Kiev)* **23,** 75, (1969) *Chem Abstr* **70,** 99583 x
[86] GARG, H S and MITRA, C R (1968) *Planta Med* **16,** 17
[87] ROW, L R and RUKMINI, C (1966) *Indian J Chem* **4,** 149
[88] ZIKOVA, N YA (1966) *Farmatsevt Zh (Kiev)* **21,** 51, (1966) *Chem Abstr* **65,** 14013
[89] CHIRVA, V YA, KINTYA, P K and SOSNOVSKII, V A (1969) *Khim Prir Soedin* **5,** 450, (1970) *Chem Abstr* **72,** 75669 v
[90] BUKHAROV, V G and SHCHERBAK, S P (1969) *Izv Akad Nauk SSSR Ser Khim* 137, (1969) *Chem Abstr* **71,** 3620 d CHIRVA, V YA, KINTYA, P K and LAZUR'EVSKII, G V (1969) *Khim Prir Soedin* **5,** 59, (1969) *Chem Abstr* **71,** 10281 x
[91] APPEL, H H and HALEBY, A. (1965) *Scientia* **32,** 17, (1967) *Chem Abstr* **66,** 38202 t
[92] SAEKI, I, SUMIMOTO, M and KONDO, T (1968) *Mokuzai Gakkaishi* **14,** 110, (1969) *Chem Abstr* **70,** 30214
[93] ZAKHAROV, A M, ZAKHAROVA, O I, PAKALNS, D and SOKOL'SKII, I N (1971) *Khim Prir Soedin* **8,** 672, (1972) *Chem Abstr* **76,** 83518 t ASOEVA, E Z, DAUKSHA, A D, DENISOVA, E K and MURAVEVA, D A (1967) *Uch Zap Pyatigorsk Farm Inst* **6,** 8, From Ref *Zh Biol Khim* (1968) Abstract No 18F 1049, (1969) *Chem Abstr* **70,** 10719

TABLE 1C. SAPONINS ISOLATED AS IMPURE POWDERS WHOSE GENINS HAVE BEEN CHARACTERIZED

	Plant	Crude saponin m.p. °C	Genins (m.p. °C) and sugars	Ref.
1	*Acanthophyllum adenophorum*	212–18	Gypsogenin + gal + xyl + rha + ara + fuc	94
2	*Adina pilulifera*	Mixed saponins	Morolic, betulinic, quinovic and chincholic acids + an unidentified triterpene acid + glu + glu A	95
3	*Aegiceras corniculatum*	Mixed glycosides	Primulagenin + aegiceradienol + aegiceradiol	96
4	*Aesculus turbinata* Blume		Protoaescigenin + barringtogenol C (=aescinidin) + 16-desoxybarringtogenol C	97
5	*Albizzia anthelmintica*	Musennin	Echinocystic acid + ara + 3 glu	98
6	*A. procera* Benth		Proceric, machaerinic acids + ethyl machaerinate + machaerinic acid (28 → 21) lactone + Proceragenin A, m.p. 294, $C_{30}H_{46}O_4$ + Proceragenin B, m.p. 255–8, $C_{30}H_{46}O_4$	99
7	*Anagallis arvensis*	Hetroside I	Anagalligenone	100
8	*Barringtonia acutangula* Gaertn	–	Barringtogenols B, C and D	101
9	*Blepharis edulis*	–	Lupeol	102
10	*Bryonia dioica*	Two glycosides	Aglycon-I + $C_{30}H_{48}O_3$ + glu + rha	103
11	*Bupleurum falcatum* L		Saikogenins A, B, C, D	104
	Bupleurum species	Saikoside Ib 213–17	Saikogenin A	
12	*Caccinia glauca*	230–57	Caccigenin + glu + rha	105
13	*Camellia japonica* L.	–	Camelliagenins A, B and C	106
14	*C. sasanqua* Thumb	–	Camellia sapogenols I and II + theasapogenols A, B & E (thea sapogenol B = barringtogenol C)	107
15	*Cimicifuga dahurica*		Dahurinol	108
16	*Clerodendron serratum*		Oleanolic, queretaroic and serratagenic acids	109
17	*Eryngium bieberstemianum* *E. octophyllum*		Barringerols R_1, A_1	110
18	*Fagonia cretica*	Fagonin	Oleanolic acid	111
19	*Gleditschia fera*		Oleanolic, cochalic acids + glu + rha + xyl + ara	112
20	*Gymnema sylvestre* R. Br	–	Gymnemagenin	113
21	*Hedera colchica*		Oleanolic acid + hederagenin	114
22	*H. helix*	amorph 195–200	Hederagenin	115
		Saponin lactone 225	Hederagenin	

TABLE 1C (*cont*)

Plant	Crude saponin m p °C	Genins (m p °C) and sugars	Ref
23 *Helianthus annuus*	Fraction A	Oleanolic, albigenic and echinocystic acids + glu + ara + rha + xyl (COOH of genin not free)	116
	Fraction B	Same as above (COOH of genin free)	
24 *Lysimachia clethroides* *L japonica*	—	Primulagenin A + dihydropriverogenin A	117
25 *L mauritiana*	—	Dihydropriverogenin A (=camelliagenin A) + Priverogenin B	118
26 *Medicago sativa* (Lucerne)	Lucerne saponin	Medicagenic acid + soyasapogenol A + aglycone + glu + xyl + ara	119
27 *Melianthus comosis*	—	Ellagic acid	120
28 *Mimusops elengi*	—	β-Amyrin + bassic acid + neutral genin	121
29 *Mollugo hirta*	—	Mollugogenols A and B	
30 *M spergula*	—	Spergulagenic acid + neutral genin, $C_{30}H_{50}O_4$	123
31 *Patrinia scabiosaefolia*	Patrinosides mix	Oleanolic acid + xyl + ara	124
32 *Platycodon grandiflorum* A De candolle	—	Polygalacic acid + platicodigenin	125
33 *Pithecolobium dulce*	—	Oleanolic and echinocystic acids + xyl + ara + glu	126
34 *Pittosporum tobira* Ait	—	Barrigenol R_1 + 21-*O*-anageloyl barrigenol-R_1 (=sapogenol T–A) + 21-*O*-anageloyl barringtogenol C (=sapogenol T–B)	127
35 *Polygala senega*	Saponins, A, B, C, D	Presenegenin + glu + rha + xyl + gal + fuc	128
36 *Primula sieboldi*	—	Protoprimulagenin A	129
37 *P japonica*	—	Camelliagenin A (=dihydropriverogenin A)	129
38 *Sanicula europaea*	Saponins, A, B, C, D	Saniculagenin + genin B, m p 160–70 + genin C, m p 276–9 + glu + ara	130
39 *Sapindus laurifolius*	—	Methyl hederagenate + sapindic acid + methyl oleanolate + two triterpenes	131
40 *Stryphnodendron coriaceum*	—	Maslinic and machaerinic acids + sapogenin K	132
41 *Thea sinensis* L	—	Barringtogenol C (=theasapogenol B), theasapogenol A, camelliagenin C (=theasapogenol C), dihydropriverogenin A (=camelliagenin A = theasapogenol D), theasapogenol E	133
42 *Trametes dickinsii*	Mix of two trametosides	16-Acetyl tumulosic acid + 16-acetyl dehydrotumulosic acid + glu	134

[94] Amanmuradov, K and Tanyurcheva, T N (1969) *Khim Prir Soedin* **5**, 326, (1970) *Chem Abstr* **72**, 55829
[95] Hui, W H and Yee, C W (1968) *Australian J Chem* **21**, 543
[96] Hensens, O D and Lewis, K G (1965) *Tetrahedron Letters* 4639
[97] Yosioka, I, Imai, K and Kitagawa, I (1967) *Tetrahedron Letters* 2577
[98] Tschesche, R, Kammerer, F J and Wulff G (1966) *Z Naturforsch* **21**, 596
[99] Roy S and Roy A K (1967) *Experientia* **23**, 182
[100] Heitz, S, Billet, D Staron, T and Raulais D (1969) *C R Acad Sci Paris Ser D* **268**, 2279
[101] Barua, A K, Dutta, S P and Das, B C (1968) *Tetrahedron* **24**, 1113
[102] Varshney I P and Logani M (1969) *Indian J Appl Chem* **32**, 72
[103] Biglino, G and Nano G M (1967) *Farmaco Ed Sci* **22**, 140, (1967) *Chem Abstr* **67**, 32785 j *Idem* (1968) *Corsi Semin Chim* **11**, 78 (1970) *Chem Abstr* **72**, 32076 g
[104] Kubota T and Tonami, F (1967) *Tetrahedron* **23**, 3353 Kubota, T Tonami, F and Hinoh, H (1967) *ibid* **23**, 3333, Wolters, B (1968) *Planta* **79**, 77
[105] Ayengar, K N N and Rangaswami S (1966) *Tetrahedron Letters* 1947
[106] Ito, S, Kodama, M and Konoike M (1967) *Tetrahedron Letters* 591
[107] Yosioka, I, Matsuda A and Kitagawa, I (1967) *Chem Pharm Bull* **15**, 547
[108] Sakurai, N, Inoue T and Nagai, M (1972) *Yakugaku Zasshi* **92**, 724 (1972) *Chem Abstr* **77**, 101932
[109] Rangaswami, S and Sarangan, S (1969) *Tetrahedron* **25**, 3701
[110] Ikramov M T, Khazanovich R L and Khalmatov Kh Kh (1971) *Khim Prir Soedin* **7**, 843 (1972) *Chem Abstr* **76**, 110304
[111] Rimpler H and Rizk A M (1969) *Phytochemistry* **8**, 2269
[112] Nguyen Dangtam, M (1967) *C R Acad Sci, Paris, Ser C* **264**, 121, (1967) *Chem Abstr* **67**, 73750
[113] Rao G S and Sinsheimer, J E (1970) *J Pharm Sci* **59**, 622 629, *Idem* (1970) *J Chem Soc (C)* 1823, *Idem* (1968) *Chem Comm* 1681, Stocklin, W (1969) *Helv Chim Acta* **52**, 365
[114] Dekanosidze G E and Pkheidze, T A (1968) *Khim Prir Soedin*, **4**, 253, (1969) *Chem Abstr* **70**, 35047 t
[115] Julius J T B and Pierre J L B Neth Appl 6513 079 (Cl A 61K) April 12, 1966 Fr Appl Oct 9 1964, (1967) *Chem Abstr* **66**, 14034
[116] Kasprzyk, Z, Wojciechowski, Z and Kuczewska-Jamkowska I (1966) *Bull Acad Pol Sci Ser Sci Biol* **14**, 747
[117] Kitagawa, I, Matsuda A, Nishimura, T, Hirai, S and Yosioka I (1967) *Chem Pharm Bull* **15**, 1435, Kitagawa, I, Matsuda, A and Yosioka I (1972) *Chem Pharm Bull* **20**, 2226
[118] Kitagawa, I Matsuda, A Nishimura T, Hirai S and Yosioka, I (1967) *Chem Pharm Bull* **15**, 1435, Kitagawa I Matsuda A and Yosioka I (1968) *Tetrahedron Letters* 5377
[119] Gestetner B, Shany, S, Tencer, Y, Birk, Y and Bondi A (1970) *J Sci Food Agr* **21**, 502
[120] Anderson, L A P (1968) *J S Afr Chem Inst* **21**, 91
[121] Varshney, I P and Badhwar G (1971) *Proc Nat Acad Sci (India) Sect A* **41**, 21
[122] Chakrabarti, P, Sanyal, P K and Barua, A K (1969) *J Indian Chem Soc* **46**, 96 Chakrabarti, P (1969) *Tetrahedron* **25**, 3301
[123] Chakrabarti P, Mukherjee D and Barua, A K (1968) *Bull Nat Inst Sci India* 74
[124] Sidorovich T N (1966) *Aptech Delo* **15**, 38, (1967) *Chem Abstr* **66**, 73217
[125] Akiyama, T, Iitaka, Y and Tanaka, O (1968) *Tetrahedron Letters* 5577, Akiyama, T, Tanaka, O and Shibata S (1968) *Chem Pharm Bull* **16**, 2300
[126] Nigam, S K and Mitra, C R (1969) *Planta Med* **18**, 44
[127] Yosioka I Hino K, Matsuda, A and Kitagawa I (1972) *Chem Pharm Bull* **20**, 1499, Yosioka I Kitagawa I, Hino, K, Matsuda, A and Nakagawa Y (1968) *ibid* **16**, 190
[128] Akada, Y, Yuki H and Takiura, K (1971) *Yakugaku Zasshi* **91**, 1178 (1972) *Chem Abstr* **76**, 56647
[129] Kitagawa I Matsuda, A and Yosioka, I (1968) *Tetrahedron Letters* 5377, Kitagawa, I, Matsuda A Nishimura T, Hirai Shinichi H and Yosioka, I (1967) *Chem Pharm Bull* **15**, 1435
[130] Hiller K Linzer, B and Pfeifer, S (1966) *Pharmazie* **21**, 182 Hiller, K Linzer, B Pfeifer S Tokes, L and Murphy J (1968) *ibid* **23**, 376
[131] Maiti, P C Roy, S and Roy, A (1968) *Experientia* **24**, 1091
[132] Tursch B Daloze, Z, Tursch F and Chiurdoglu, G (1966) *Bull Soc Chim Belges* **75**, 26 (1966) *Chem Abstr* **64**, 19692
[133] Yosioka I Nishimura T Matsuda A and Kitagawa, I (1970) *Chem Pharm Bull* **18**, 1610 1621 *Idem* (1971) *ibid* **19**, 1186
[134] Inouye, H Tokura, K and Hayashi T (1970) *Tetrahedron Letters* 2811

TABLE 1D SAPONINS, PURE OR CRUDE, WHOSE GENINS HAVE NOT BEEN CHARACTERIZED

	Plant	Work done	Ref
1	*Acacia concinna*	Pure saponin, m p 252° → genin, $C_{30}H_{48}O_5$ + glu	135
2	*Cucumaria fraudatrix*	Cucumarioside C → genin A_3 ($C_{30}H_{44}O_5$) + glu + xyl + rha	136
3	*Cyclamen vernum* *C ibericum* *C adzharicum* *C abchasicum*	Saponin, m p 252 → Aglycone + glu + ara	137
4	*C pseudoibericum*	Saponin, m p 270 → $C_{30}H_{45}O_6$ + glu + xyl + ara	138
5	*Fagonia cretica*	Saponin → Fagogenin, m p 307° + $C_{30}H_{46}O_5$, m p 326° + glu + rha + ara	139
6	*Gleditschia spp* (Honey locust)	Pure saponin, m p 190° → aglycone + glu + fru	140
7	*G australis*	Saponin, $C_{30}H_{48}O_4$, m p 296°	141
8	*G triacanthos*	Triacanthosides, A, B and D	142
9	*Gypsophilla trichotoma*	Trichosides A and C	143
10	*Hedera pastuchovii*	Pastuchoside C, m p 254° → $C_{30}H_{48}O_4$ + hederagenin + rha	144
11	*Hydrocotyle vulgaris*	Saponin → Cotylegenins A, B, C, D & E + glu + ara	145
12	*Ladyginia bucharica*	Ladyginosides A, B & E	78
13	*Lyonia ovalifolia* var *elliptica*	Ovalifolioside, $C_{35}H_{58}O_7$ → ovalifoliogenin, $C_{30}H_{50}O_3$ + ara	146
14	*Panax ginseng*	Panaxoside B′ → 3 glu Panaxoside C → 2 glu + rha	147
15	*Polemonium coeruleum*	Polemonioside B, m p 232° → Gal Polemonioside C, m p 241° → Ara + gal	148
16	*Polemonium acutifolium* *P pauciflorum* *P occidentale*	Three saponins → 2 aglycones + gal + ara	149
17	*Sanguisorba officinalis*	Sanguisorbin A, m p 272° → genin, m p 242° + ara Waremokonin, m p. 204° → genin + ara + glu + acetic acid	150
18	*Securigera securidaca*	Crude saponin → glu + gal + rha	151
19	*Sophora prodani*	Saponin, m p 220°	152
20	*Valeriana officinalis*	Valeroside A, m p 298° → genin + glu	153
21	*Zygophyllum fabago*	Zygophylosides A, B, C, D & E → genin, m p 305° + gal + glu + ara	154

[135] GUPTA, G L and NIGAM, S S (1971) *Planta Med* **19**, 55

[136] ELYAKOV, G B and PERETOLCHIN, N V (1970) *Khim Prir Soedin* **6**, 637, (1970) *Chem Abstr* **74**, 39765 f

[137] KHVEDELIDZE, T A (1967) *Tr Inst Farmakokhim Akad Nauk Gruz SSR Ser* 212, (1968) *Chem Abstr* **69**, 16799 c

[138] TANKER, N (1965) *Istanbul Univ Eczacilik Fak Mecmuasi* **1**, 61, (1967) *Chem Abstr* **67**, 93926 c

[139] ALI, M A and AHMED, Z (1966) *Pakistan J Sci Ind Res* **9**, 41

[140] ASOEVA, E Z, DENISOVA, E K, DAUKSHA, A D and MURAV'EVA, D A (1967) *Uch Zap Pyatigorsk Farm Inst* **6**, 11, (1969) *Chem Abstr* **71**, 806 h

[141] GH MATEESCU, I C and GH HERMAN (1966) *Farmacia* **14**, 663

[142] ALI-ZADE, T A, KONDRATENKO, E S and ABUBAKIROV, N K (1970) *Khim Prir Soedin* **6**, 482; (1970) *Chem Abstr* **73**, 127740 d, PANOVA, D and GEORGIEVA, E (1971) *Farmatsiya* **21**, 34

[143] LUCHANSKAYA, V N, KONDRATENKO, E S and ABUBAKIROV, N K (1970) *Khim Prir Soedin* **6**, 434, (1971) *Chem Abstr* **74**, 1041 d

[144] ISMAILOV, A I, ISKENDEROV, G B and AKHMEDOV, V KH (1969) *Biol Nauki* **95**, (1970) *Chem Abstr* **72**, 63584 a
[145] HILLER, K, KLIPERT, M and PFEIFER, S (1971) *Pharmazie* **26**, 780
[146] IASUE, M, SAKAKIBARA, I and KATO, T (1971) *Yakugaku Zasshi* **91**, 194, (1971) *Chem Abstr* **75**, 20900
[147] UVAROVA, N I, FERENS, N A SHAPOSHNIKOVA, G I and ELYAKOV, G B (1970) *Khim Prir Soedin* **6**, 312, (1970) *Chem Abstr* **73**, 99157 y
[148] BUKHAROV, V G, SHAIKHUTDINOV, V A and KOMLEVA, L N (1969) *Khim Prir Soedin* **5**, 498, (1970) *Chem Abstr* **73**, 15163 m
[149] LOEKADIA, S (1968) *Acta Pol Pharm* **25**, 463, (1969) *Chem Abstr* **70**, 88197
[150] KUSUMOTO, S, FUJIWARA, T, OHSUKA, A and KOTAKE, M (1968) *Nippon Kagaku Zasshi* **89**, 1118, BUKHAROV, V G and KARNELVA, L N (1970) *Izv Akad Nauk SSSR Ser Khim* 2402, (1971) *Chem Abstr* **74**, 121340 x
[151] MOITRA, S K, GANGULY, A N, CHAKRAVARTI, N N and ADHYA, R N (1969) *Bull Calcutta Sch Trop Med* **17**, 80
[152] PISLARASU, N (1969) *Farmacia* **17**, 733
[153] NIKUL'SHINA, N I, TALAN, V A, BUKHAROV, V G and IVANOVA, V M (1969) *Farmatsiya* **18**, 44 (1970) *Chem Abstr* **72**, 96784 u
[154] KERIMOVA, KH M, PKHEIDZE, T A and GOROVITS, T T (1971) *Khim Prir Soedin* **7**, 536, (1971) *Chem Abstr* **751**, 17443 q

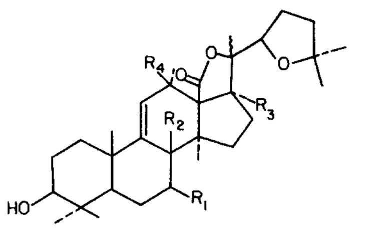
TABLE 1E SAPONINS OF ANIMAL ORIGIN FROM HOLOTHURIANS (SEA-CUCUMBERS)—PHYLUM *Echinodermata*

Name	Saponin m p C	Genins and sugars	Ref
1 *Cucumaria frandatrix*	Cucumarioside C	Genin A_3 ($C_{30}H_{44}O_5$) + glu + xyl + rha	155
2 *Actinopyga agassizi* 3 *Holothuria vagabunda* *H lubrica* *H leucospilota*	Holothurin A	22,25-oxidoholothurinogenin*, 17-deoxy-22,25-oxidoholothurinogenin + xyl + quinovose + H_2SO_4 as Na-salt	155a
	Holothurin B 213–23 d	12β-methoxy-7,8 dihydroholothurinogenin (neo-holothurinogenins)	
H polii 4 *Bohadschia koellikeri*		Griseogenin, praslinogenin, ternaygenin, seychellogenin, koellikerigenin	155b
5 *Stichopus japonicus* Selenka	Stichoposide A 215–17	Stichopogenin A_2 and A_1 + glu + xyl + 3-*O*-methyl glu	156
	Stichoposide C	Stichopogenins + glu + gal + xyl + 3-*O*-methyl glu	

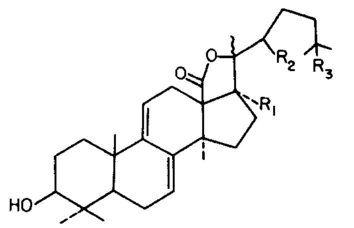
* The various holothurinogenins are artefacts produced during hydrolysis of the saponins

It may be of interest to mention that asteroids (sea stars), another class of phylum *Echinodermata*, also elaborate saponins which belong to steroid group and are highly toxic [156]

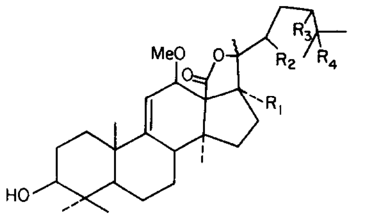
[155] ELYAKOV, G B and PERETOLCHIN, N V (1971) *Khim Prir Soedin* **6**, 637, (1971) *Chem Abstr* **74**, 39765 f, 155a YASUMOTO, T, NAKAMURA, K and HASHIMOTO, Y (1967) *Agr Biol Chem* **31**, 7, MATSUNO, T and IBA J (1966) *Yakugaku Zasshi* **86**, 637, (1966) *Chem Abstr* **65**, 12613, CHANLEY, J D and ROSSI, C (1969) *Tetrahedron* **25**, 1897, 1911, 155b HABERMEHL, G and VOLKWEIN, G (1970) *Ann* **731**, 53, ROLLER, P, DJERASSI, C, CLOETENS, R and TURSCH, B (1969) *J Am Soc* **91**, 4918, TURSCH, B, CLOETENS, R and DJERASSI, C (1970) *Tetrahedron Letters* 467, ROLLER, P, TURSCH, B and DJERASSI, C (1970) *J Org Chem* **35**, 2585
[156] ELYAKOV, G B, KUZNETSOVA, T A and VASKOVSKII V E (1968) *Khim Prir Soedin* **4**, 253, (1969) *Chem Abstr* **70**, 45173 v ELYAKOV, G B, KUZNETSOVA, T A, DZIZENKO, A K and ELKIN, YU N (1969) *Tetrahedron Letters* 1151, 156a GROSSERT J S (1972) *Chem Soc Rev* **1**, 1



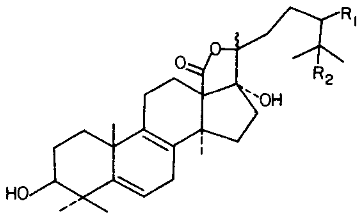
R_1	R_2	R_3	R_4	
Double bond		OH	H	22,25 Oxido-holothurinogenin (A)
Double bond		H	H	17 Deoxy-A
H	H	OH	OMe	12β Methoxy 7,8 dihydro-A
H	H	H	OMe	12β Methoxy 7,8 dihydro 17, deoxy-A



R_1	R_2	R_3	
OH	H	H	Holothurinogenin (B)
OH	OH	H	22 Hydroxy-B (griseogenin)
OH	H	OMe	25 Methoxy-B
H	H	H	17 Deoxy-B (scychellogenin)
H	H	OH	17 Deoxy, 25 hydroxy-B
H	H	OMe	17 Deoxy, 25 methoxy-B



R_1	R_2	R_3	R_4	
OH	H	Double bond		$\Delta^{24(25)}$ 7,8 dihydro holothurinogenin
OH	H	H	OMe	25 Methoxy 7,8 dihydro holothurinogenin
OH	OAc	H	H	22 Acetoxy 7,8 dihydro holothurinogenin



R_1	R_2	
Double bond		Stichopogenin A_2
H	OH	Stichopogenin A_4

FIG 4 SAPOGENINS OF THE SEACUCUMBERS

BIOLOGICAL ACTION AND USES

The significance of saponins in pharmacy with special reference to surface activity, complex formation, hemolysis, toxicity and various therapeutic effects has been reviewed.[157] The relationship between the presence of saponins in leguminous plants and the appearance of tympanites in ruminants and the present knowledge of the depressive action of leguminous saponins on the growth of chicks and egg laying have also been reviewed.[158]

The hemolytic activity of the saponins have been found to be very variable. The water soluble saponin from *Hedera helix* leaves is devoid of hemolytic properties whereas water-insoluble saponin lactone from the same source and the magnesium salt of its corresponding hydroxy acid showed a potent activity.[115] The hemolytic index of pure saponin from *Calyx primrose* was found to be 20.[159]

[157] GERLACH, I H (1967) *Pharm Zentralh Deut* **106**, 573; (1967) *Chem Abstr* **67**, 111362 x; ZVAVING, J H. (1971) *Pharm Weekbl* **106**, 629

[158] MAYMORE, B (1962) *Ann Ist Sper Zootec Roma* **9**, 429, (1966) *Chem Abstr* **65**, 20575 f

[159] ASOEVA, E Z, DAUKSHA, A D, DENISOVA, E K and MURAV'EVA, D A (1967) *Vch Zap Pyatigorsk Farm Inst* **6**, 8, From Ref *Zh Biol Khim* (1968) Abstract No 18F 1049, (1969) *Chem Abstr.* **70**, 103719 r

Lucerne saponin showed strong hemolytic activity and depressed growth of the beetle (*Tribolium castaneum*) larvae but its inhibitory effect could be reversed when cholesterol was incorporated in diet. Germination of cotton seeds was inhibited in soils on which lucerne has been grown or on soils supplemented with lucerne meal from tops and roots[160]

The structural specificity of saponin hemolysis has been studied by testing a large number of saponins and triterpene aglycones using cattle erythrocytes *in vitro* It has been shown that the requirements for optimum activity are a polar grouping in ring A and a moderately polar grouping in ring D or E. The compounds containing 16α-OH or 16-keto group together with 3β-OH had the highest hemolytic index The distance of 10 5 Å between 3β-OH and 16α-OH is of special significance Acylation of the either hydroxyl group resulted in loss of activity The sugar chains (in glycosides) had a certain influence on the hemolytic activity. A polar group in ring D and/or E, such as sugar chain or a number of OH groups, induced inactivation[161]

A significant antimitotic activity has been observed in the glycosides and their magnesium salts from *Hedera helix*. These substances inhibited the growth of cells without destroying them and can be used for inhibiting the growth of benign or malignant tumors and for combating protozoa, in particular *Trichomones* Although they widely differ in hemolytic activity, they are relatively non-toxic for mice, rats and guinea pigs and a process patent has been taken for their production.[115] The saponin fraction of *Acer negundo* and *Cyclamen persieum* showed inhibitory activity against Walker 256 tumor in rats[162] The saponins isolated from *Myrsine africana* and *Entada phaseoloides*, have shown significant inhibitory activity against the Walker 256 in rats.[70-79]

Some saponins have shown prominent anti-inflammatory activity The mixture of saikosides from *Bupleurum falcatum* is effective (400 mg/kg) for treatment of rat edema[104] The crude saponin of *Thea sinensis* showed pronounced antiexudative and anti-inflammatory properties It normalized the capillary permeability which is disturbed in the initial stage of inflammation[163] The saponins from *Mimusops manikara* and *Pithecolobium dulce*, hederagenin and sodium nimbinate showed anti-inflammatory activity against carrageenin-induced edema and formaldehyde-induced arthritis in rats; ED_{50}, LD_{50} and structure activity relations have been described[164] A gypsogenin saponin from *Momordica cochinchinensis* had LD_{50} 37 mg/kg in mice, inhibited rat paw edema and intestinal mobility of rabbit duodenum The saponin at 3×10^{-4} g/ml potentiated the contractile response of guinea pig ileum to acetyl choline (10^{-9} g/ml) and abolished the anti-acetylcholine action of papavarine (2×10^{-5} g/ml)[165]

The antifungal and antimicrobial effects of escin, *Gypsophylla* saponin, *Quillaja* saponin, primulic acid and ammonium glycyrrhizate upon the hyphal growth of *Claviceps purpurea*,

[160] Shany, S, Birk, Y, Gestetner, B and Bondi, A (1970) *J Sci Food Agr* **21**, 131 Gestetner B Shany S, Tencer, Y, Birk Y and Bondi, A (1970) *ibid* **21**, 502

[161] Schloesser, E and Wulff, G (1969) *Z Naturforsch B* **24**, 1284

[162] Kupchan, S M, Hemingway, R J, Knox, J R Barboutis, S J Werner, D and Barboutis M A (1967) *J Pharm Sci* **56**, 603

[163] Vogel, G Marek, M L and Oertner, R (1968) *Arzneim-Forsch* **18**, 1466, (1969) *Chem Abstr* **70**, 36279 g

[164] Bhargava, K P, Gupta, M B Gupta, G P and Mitra, C R (1970) *Indian J Med Res* **58**, 724

[165] Kubota, K, Sato M, Murakami T and Yamagishi, T (1971) *Yakugaku Zasshi* **91**, 174 (1971) *Chem Abstr* **74**, 139209

Piricularia oryzae, *Trichothecium roseum* and *Polyporus versicolor* were determined *in vitro*. Only escin and primulic acid at 50–400 μg/ml inhibited hyphal growth.[166]

The fungistatic action of 19 saponins and saponin fractions were tested on 15 species of fungi, mostly plant pathogens. *Sclerotinia fructicola*, *C. purpurea*, *T. roseum*, *P. oryzae* and *Fomes officinalis* were most sensitive to the saponins, whereas *Botrytis allii*, *Alternaria solani*, *Coniophora cerebella*, *Rhizoctonia solani*, *Schizophyllum commune* and 3 *Fusarium* species were quite resistant. *T. roseum* was sensitive to saponins but was resistant to steroid saponins with double bond at C-5 as in α-solanine etc. *Polystictus* was completely inhibited by steroid saponins but only weakly effected by triterpene saponins whereas the reverse was true for *Coniophora* and *Aspergillus*.[167] The glycoside of *Anagallis arvensis* revealed antifungal action and inhibited germination of linseed. Its LD_{50} in mice was 675 mg/kg *per os* and 30·4 mg/kg by *s.c.*[168] Eupteleoside A and B from *Euptelea polyandra* also possess intense anti-microbial activity[169] against *Saccharomyces cerevisiae* and *Piricularia oryzae* as well as some phytopathogenic fungi. A synergistic effect of A and B is also described. In another study avenacin, the resistance factor in oat roots, and escin were found to inhibit the growth of various fungi including *Ophiobolus graminis* and *Neurospora crassa*. These saponins were found to cause a rapid loss of inorganic ions—K from the mycelium of the former and Mg from latter—in the phosphate buffer Similar action was noted from the mycelia suspended in acetate buffer. The saponins also inhibited the uptake of K and Mg in fungal mycelium both in phosphate and succinate buffers.[170]

The effect of *Sapindus mukorossi* saponins (a mixture of five glycosides of hederagenin) on blood pressure and cholesterol content in mice has been studied The saponins showed LD_{50} (mg/kg) *per os* 1625, *s.c.* 650, *i v* and *i.p* 276 in mice. In normal rabbits saponins administered *per os* (0·04 mg/kg) did not change arterial pressure. If injected (*s c.*) at the same dose they decreased blood pressure by 25% during first 2–3 hr but blood cholesterol content remained unchanged. In rabbits with experimental atherosclerosis induced by feeding cholesterol rich diet, saponins administered *per os* for 30–50 days, beginning from the 40th day decreased the cholesterol level from 292–248 to 53–110 mg%.[171]

The action of *Cyclamen ibericum* saponin in tests on cats, frogs, isolated frog hearts, rabbits and monkeys, showed positive inotropic and negative chromotropic action but no significant effect on arterial pressure and respiration. It also exhibited vasoconstrictive effect in isolated rabbit ears and increased permeability of dermal capillaries in rats.[172] The effect of *Leontice eversmanni* saponin and glycyrrhizic acid on experimental atherosclerosis was evaluated on three groups of rabbits which were given 0·3 g/kg of cholesterol daily for 60 days. In addition, group 2 received 10 mg/kg saponin and group 3 received 15 mg/kg of K-glycyrrhizate. After 60 days animals were killed and the degree of atherosclerosis was evaluated. The protective action against atherosclerotic changes was more pronounced with saponin than with glycyrrhizic acid. The cholesterol blood levels in the respective

[166] WOLTERS, B (1966) *Naturwiss* **53,** 253
[167] WOLTERS, B (1968) *Planta* **79,** 77
[168] STARON, T, ALLARD, C, HEITZ, S and BILLET, D (1969) *Phytiat-Phytopharm* **18,** 161, (1971) *Chem Abstr* **75,** 59769 j
[169] GOTO, M, MURATA, T, IMAI, S and FUJIOKA, S (1970) *Yakugaku Zasshi* **90,** 736, (1970) *Chem Abstr* **73,** 84655 k
[170] OLSEN, R A (1971) *Physiol Plant*, **24,** 534, (1971) *ibid* **25,** 204, 503
[171] EFIMOVA, T G, PIVNENKO, G P, KUTSEVICH, V A and ZIKOVA, N YA (1966) *Farm Zh* (*Kiev*) **21,** 45, (1967) *Chem Abstr* **66,** 93780 e
[172] GLADKIKH, A S (1966) *Farmakol Toksikol* **29,** 559, (1966) *Chem Abstr* **66,** 9774 s

groups were as follows: Group (1) 600–775, (2) 400–500; (3) 500–600 mg%. In addition the cholesterol: lecithin ratio was reduced by saponin and glycyrrhizic acid [173]

Aralosides A, B and C of *Aralia manschurica* upon intravenous injection at 10 mg/kg markedly stimulated the electrical activity of the rabbit brain and increased the processes of nerve cell excitability and lability [174]

The acid and neutral saponins of *Patrinia intermedia* when administered *s.c.* to mice at 10–100 mg/kg, reduced the spontaneous motor (CNS depressant) activity, prolonged hexanal (70 mg/kg, *i p*) induced sleep and in rats, at the same dose, inhibited conditioned reflex reaction. Prior administration of the glycoside (0·2–0·3 g/kg) reduced the convulsive action of strychnine (1 mg/kg *s c*) and increased the life span.[175] The saponins of *Centella asiatica* exhibited sedative action in rat and mice and the mode of action appeared to be mainly on the cholinergic mechanism in CNS.[176]

The comparative study of pharmacological properties of *Bupleurum longeradiatum* var *breviradiatum* and *B falcatum* saponins has been made. *Per os* administration of 1·0–3·0 g/kg of the saponins was not toxic and the analgesic effect of the former was twice that of the latter. Both the saponins (500 mg/kg *per os*) prolonged sleeping time induced by hexabarbital sodium in mice. They also decreased the blood pressure of rabbit (10–25 mg/kg), caused cardiac inhibition of isolated frog heart and guinea pig arterial preparations and increased the peristalsis of isolated rabbit intestine ($1–2 \times 10^{-4}$ g/ml). Rat paw edema induced by dextran, 5-HT and croton oil was suppressed by *per os* administration of 600 mg/kg of both the saponins whereas inhibition of pleural exudation after 0·1% Evans blue and 0·2% gum arabic, was only slight. Thus, there was no difference in the actions of the two saponins except in the analgesic effect [177]

The termite and fungal resistance of the ancient woods in temples have been found to be due to the presence of saponins.[178] Saponins, aglycones have been found to strongly inhibit the voracity of the termites.[179] The antitermitic behaviour of the *Ternstroemia japonica* wood was shown to be due to saponins C_1, C_2 and D which were active in the order $C > D > C_2$ [92]

A process has been patented for an antigenic vaccine with a saponin adjuvant for immunizing vertebrates against protozoal diseases. The antigenicity of an antigen preparation obtained from the trypanosomes of protozoa of *Trypanosoma* species, has been enhanced by admixture with the aqueous solution of a saponin preparation, obtained from the bark of *Quillaja saponaria* or the root of *Saponaria officinalis*. The resulting antigen preparation was to immunize against diseases caused by pathogenic protozoa as Chagas' disease and trypanosmiasis [180]

An improved process for the commercial production of three active glycosides, m p 260–270°, 215–220° and a syrup respectively, from *Panax ginseng*, has been developed and

173 EVODOKIMOVA, N I and KANILOV I K (1967) *Farmakol Alkaloidov Glikozidov* 222, (1969) *Chem Abstr* **70**, 22304 u

174 SOKOLOV, S YA (1965) *Byul Eksperim Biol Med* **60**, 73, (1966) *Chem Abstr* **64**, 3616

175 LAPIK A S BUKHAROV V G TALAN V A and KARLIN, V V (1968) *Farmakol Toksikol* **3**, 650 (1969) *Chem Abstr* **70**, 56100 v

176 RAMASWAMY, A S, PERIYASAMY S M and BASU, N K (1970) *J Res Indian Med* **4**, 160

177 IMAOKA, I (1970) *Shioku Igaku Zasshi* **26**, 1, (1970) *Chem Abstr* **73**, 43769

178 SANDERMANN, W and FUNKE, H (1970) *Naturwiss* **57**, 407

179 TSCHESCHE R, WULFF, G, WEBER, A and SCHMIDT, H (1970) *Z Naturforsch B* **25**, 999

180 RALPH A N Brit 1 083 815 (Cl A61 K) Sept 20 1967, Appl Oct 1, 1963 (1968) *Chem Abstr* **68**, 33197

their action on the rectal and abdominal muscles of frog have been determined.[181] Recently two saponins have been isolated from *Gleditschia horrida* which show antifertility effect in female mice.[182]

The saponins from sea-cucumbers exhibit varied types of biological activities. Holotoxin, a crystalline saponin m.p. 250°d, isolated from the body-wall tissues of *Stichopus japonicus* showed high activity against various fungi including vegetable pathogens (*in vitro* MIC = 2–16 μg/ml) but it was almost inactive against Gram negative and Gram positive bacteria and mycobacteria. The IR spectrum of holotoxin is similar to that of holothurin but it is not sulphate. Holothurin did not exhibit antifungal activity.[183] Holothurin A caused almost complete inhibition of protein synthesis in rat bone marrow cell cultures at 10 mg/ml, stichoposides A_1, A and cucumarioside C produced 90, 70 and 50% inhibition but plant saponins, panaxosides B and C, were found to be almost completely inactive at this dose level.[184] Holothurin B at a concentration of $2{\cdot}5 \times 10^{-5}$ M, produced irreversible blockade of the responses both to indirect electrical stimulation via the nerve in the rat phrenic nerve diaphragm preparation and direct electric stimulation of muscle.[185] The toxic effects of stichoposide A have been studied and it was found to arrest the division of eggs of sea urchin, *Stronglylocentrotus intermedius* with cytolysis of blastomeres.[186]

[181] BELLET, P and CEREDE, J ROUSSEL—UCLAF Fr 1,477,421, April 21, 1967, Appl July 20, 1964; (1967) *Chem Abstr* **67,** 102775

[182] CHOU, S C, RAMANATHAN, S, MATUI, A, ROGERS, J and CUTTING, W C (1971) *Indian J Exp Biol* **9,** 503

[183] SCHIMADA, S (1969) *Science* **163,** 1462.

[184] ANISINOV, M M, PROKOFEVA, N G, KUZNETSOVA, T A and PERETOLCHIN, N V (1971) *Izv Akad Nauk SSR, Ser, Biol* 137, (1971) *Chem Abstr* **74,** 73825 k, ELYAKOV, G B, ANISINOV, M M, PROKOFEVA, N G., KUZNETSOVA, T A and FRONERT, E B (1972) *Toxicon* **10,** 299, (1972) *Chem Abstr* **77,** 57344

[185] FRIESS, S L, DURANT, R C and CHANLEY, J D (1968) *Toxicon* **6,** 21, (1969) *Chem Abstr* **69,** 104786 b

[186] ANISINOV, M M, KUZNETSOVA, T A, SHIROKOV, V P, PROKOFEVA, N G and ELYAKOV, G B (1972) *Toxicon* **10,** 187, (1972) *Chem Abstr* **76,** 136599