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TRITERPENOID SAPONINS AND SAPOGENINS

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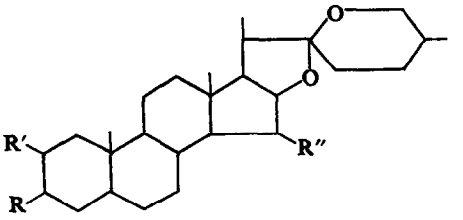
1. INTRODUCTION

THE term saponin is applied to a group of natural products which have in common the property of foaming when shaken with water. They are widely distributed in the vegetable kingdom and have been reported to be present in at least 500 genera of plants. Chemically, saponins are glycosides which yield on hydrolysis (a) one or more sugar units and (b) sugar-free aglycones which are derived from polycyclic ring systems and are commonly referred to as sapogenins.

Classification of saponins into two broad groups is based on the chemical nature of the sapogenins. The insight into the basic carbon skeletons of these genins has been obtained by dehydrogenation with various reagents, e.g. sulphur, palladium-carbon, zinc dust or selenium; the last of these has proved to be a comparatively better dehydrogenating agent. Some of the sapogenins are dehydrogenated to Diel's hydrocarbon (3'-methyl-1,2-cyclopenteno-phenanthrene) which contain a tetracyclic cholane skeleton related to the steroid type of compounds. The second type of sapogenins give on dehydrogenation a mixture of naphthalene and phenanthrene hydrocarbons, mainly sapotalene (1,2,7-trimethylnaphthalene), characterizing these genins as triterpenoids because of the similarity of the pattern of the dehydrogenated products obtained from α- and β-amyrins, lupeol and the tetracyclic triterpenoids.

Thus, the two groups of saponins may be defined as:

(1) *Saponins of cholane group.* These are derived from the same tetracyclic ring system as in sterols, bile acids and cardiac aglycones.[1] Some examples of this class are digitonin (*Digitalis purpurea* and *D. lanata*), gitonin (*D. purpurea*), tigonin (*D. lanata*), sarsasaponin (*Radix sarsaparilla, Yucca schotti*), dioscin (*Dioscorea tokora*), trillarin and trillin (*Trillium erectum*). These sapogenins are C_{27} steroids carrying a spiroketal side-chain which exhibits several characteristic strong i.r. bands[2] in the region of 1350 to 875 cm^{-1}. This group would not be considered in this review but the structures of some typical examples are given in Fig. 1.



Digitogenin,	R, R', R''—OH
Gitogenin,	R, R'—OH; R''—H
Tigogenin,	R—OH; R', R''—H
Sarsaspogenin,	R—OH, R', R''—H

FIG. 1.

[1] L. F. FIESER and M. FIESER, *Steroids*, p. 810. Reinhold, New York (1960).
[2] M. E. WALL *et al.*, *Anal. Chem.* **24**, 1337 (1952); R. N. JONES *et al.*, *J. Am. Chem. Soc.* **75**, 158 (1953).

(2) *Saponins of triterpenoid group.* These are extensively distributed in the plant kingdom and constitute the majority of the saponins found in nature. So far there is only one example of saponins having been isolated from sea-cucumber and star fish and, therefore, having an animal origin.[3] A great variety of these saponins differ only in the number and the type of units in the carbohydrate moiety linked to a particular sapogenin. The triterpenoid sapogenins, with a few exceptions, belong to β-amyrin group and are usually simple alcohols and acids. Occasionally, a sapogenin is encountered having aldehydic and lactone functions.

Triterpenoid saponins have been known for over 100 yr and a few efforts have been made more than a decade ago to review[4] their chemical and biological properties. However, in the last 20 yr a noteworthy progress has been made in this field as a result of the development of improved techniques for the isolation and detection of natural products, and the elucidation of the finer details of triterpenoid chemistry. Therefore, a brief review of the work in this field during the last two decades (as reported in *Chemical Abstracts* up to Volume 62 (1965)) is presented here with a view to presenting a consolidated picture covering the distribution of saponins in nature, their chemistry and biological activity.

2. DETECTION AND ISOLATION

Saponins and their genins are usually detected by means of the characteristic colours they produce with various reagents, e.g. Liebermann-Burchard, thionyl chloride, phosphomolybdic acid, silico-tungstic acid, etc.[5] and the hemolysis of blood.[6] For the purpose of detection on paper chromatograms, some of the above reagents have been modified.[7–11] A quantitative and highly sensitive micro method in which filter paper discs wetted with saponin are embedded in blood gelatin has been devised.[12] Other reagents used for detection are sodium meta-periodate-alkaline potassium permanganate mixture,[13] antimony trichloride/chloroform-chloroform-vanillin/chloroform (5:4:1).[14] Similar reagents for thin layer chromatography (TLC)[15] have also been described. Various solvent systems have been reported to provide satisfactory separations, viz. ethyl acetate:pyridine:water[16] (3:1:3); butanol:acetic

[3] T. MATSUNO *et al.*, *Kyoto Yakka Daigaku Gakuho* **11**, 12 (1963); *Chem. Abstr.* **61**, 889 (1964).

[4] A. M. SOKOLSKAYA and L. N. MANION, *Vestn. Akad. Nauk Kaz. SSR* **11**, 74 (1955); *Chem. Abstr.* **49**, 12779 (1955); CH. SANNIE, *Exposes Ann. Biochem. Med.* **9**, 175 (1948); K. PAECH and M. V. TRACEY, *Modern Methods in Plant Analysis*, Vol. 3, p. 58. Springer, Berlin (1955); R. TSCHESCHE and G. WULFF, *Planta Med.* **12**, 272 (1964); P. BOITEAU, B. PASICH and RATSIMAMANGA RAKOTO, *Les Triterpenoides en Physiologie Vegetale et Animale*, Gautheirs-Villars, Paris (1964).

[5] A. SOSA, *Ann. Pharm. Franc* **20**, 257 (1962); *Chem. Abstr.* **57**, 7383 (1962); G. R. VAN ATTA and J. GUGGOLZ, *J. Agr. Food Chem.* **6**, 849 (1958); *Chem. Abstr.* **53**, 14818 (1959); B. PASICH, *Dissertationes Pharm.* **13**, 1 (1961); *Chem. Abstr.* **55**, 16915 (1961); K. TAKAMURA, M. SATAKE *et al.*, *Yakugaku Kenkyu Hokoku* **2**, 15 (1958); *Chem. Abstr.* **53**, 5590 (1959).

[6] E. KOLOS-PETHES, *Gyogyszereszet* **4**, 339 (1960); *Chem. Abstr.* **60**, 5280 (1964).

[7] CHR. J. K. MINK, *J. Pharm. Pharmacol.* **8**, 1155 (1958).

[8] B. GESTETNER, *et al.*, *Israel J. Chem.* **1**, 460 (1963); *Chem. Abstr.* **60**, 14743 (1964); B. GESTETNER, *J. Chromat.* **13**, 259 (1964).

[9] B. PASICH, *Nature* **190**, 830 (1961).

[10a] G. R. VAN ATTA, *J. Agr. Food Chem.* **10**, 519 (1962); *Chem. Abstr.* **58**, 4975 (1963); A. J. KHORLIN *et al.*, *Izv. Akad. Nauk SSSR* 2008 (1963).

[10b] R. TSCHESCHE and G. WULFF, *Chem. Ber.* **94**, 2019 (1961).

[10c] T. KAWASAKI and K. MIYAHARA, *Chem. Pharm. Bull. (Tokyo)* **11**, 1546 (1963).

[11] E. KOLOS-PETHES, *Gyogyszereszet* **3**, 473 (1959); *Chem. Abstr.* **58**, 2637 (1963).

[12] T. KARTNIG and R. E. HERBST, *Planta Med.* **12**, 428 (1964).

[13] N. L. DUTTA, *Nature* **175**, 85 (1955).

[14] F. SANDBERG and K. H. MICHEL, *Lloydia* **25**, 142 (1962); *Chem. Abstr.* **58**, 7134 (1963).

[15] A. YA. KHORLIN *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim* 2008 (1963); *Chem. Abstr.* **60**, 8113 (1964); A. J. VAN DUUREN, *J. Am. Soc. Sugar Beet Technologists* **12**, 57 (1962); *Chem. Abstr.* **58**, 5985 (1963).

[16] S. CZYSZEWSKA, *Biul. Inst. Roslin. Lechzniczych* **9**, 12 (1963); *Chem. Abstr.* **60**, 13094 (1964).

acid:water[9] (6:1:3) and butanol:IM NH_4OH:95% alcohol[10a] (60:30·5:13), etc. Chloroform:tetrahydrofuran:pyridine[10b] (10:10:2) saturated with formamide and chloroform:methanol:water[10c] (65:35:10) have proved to be particularly good for paper chromatography, TLC as well as separation of saponins on cellulose and silica gel columns.

A comparative study of the saponin content in *Saponaria, Polymonium, Primula,* etc. has shown that the highest yields are obtained by collecting the plant material just before the flowering time.[17] Several methods have been employed for the isolation of crude saponins and their purification. The water-insoluble saponins generally precipitate out on concentration of the alcoholic extracts. The precipitation of water-soluble saponins has been achieved as stearin or cholesterol addition complexes[18–20] from which the saponin may be liberated quantitatively. The use of paper electrophoresis for the purification of saponins, using aqueous borate buffers,[21] and of genins using butanol:acetic acid:water (1:1:1·25) has been reported[22] but more fruitful results have been obtained by employing ion exchangers. Thus, araloside A is absorbed over Dowex 1 and eluted with 10% acetic acid followed by 90% alcohol;[23] the saponins of *Hedera helix,* horse chestnut and *Glycyrrhiza glabra* are absorbed by anion exchangers from the solution of saponin-Et_3N salts and then eluted by displacement with Cl^- ion;[24] alfalfa saponins are purified by ion-exchange chromatography prior to precipitation with cholesterol.[25] In the case of acidic saponins advantage has been taken of the precipitation of the crude saponins as sodium or ammonium salts[26] or esterification of the carboxyl group with diazomethane prior to partition chromatography.[27] Although some reports on the chromatography of saponins over acid-washed alumina[28] are available, generally the purification is best achieved by partition chromatography over cellulose[29] or silica gel.[30] Processes have also been patented for the large-scale extraction of saponins from beet[31] (*Beta vulgaris*) and licorice[199] (*Glycyrrhiza glabra*).

3. CHEMICAL CONSTITUENTS

(a) *Sugars*

The ease with which saponins are hydrolysed into sapogenins and sugars (of which there may be up to 12 units) varies from case to case; usually refluxing with 5–10 per cent mineral acid is necessary for a complete breakdown. Sometimes hydrolysis can be carried out with

[17] I. L. Stecka, *Dissertations Pharm.* **15**, 327 (1963); *Chem. Abstr.* **61**, 5450 (1964); B. Drozdz, *Pharmazie* **19**, 538 (1964).
[18] W. Schwabe, *Ger. Patent* 1045597; *Chem. Abstr.* **54**, 23211 (1960).
[19] F. A. Klinge, *Brit. Patent* 820788; *Chem. Abstr.* **54**, 6041 (1960).
[20] W. Winkler and P. Patt, *Naturwissenschaften* **47**, 83 (1960); *Chem. Abstr.* **54**, 15830 (1960).
[21] C. B. Coulson, *J. Sci. Food Agr.* **9**, 281 (1958); *Chem. Abstr.* **52**, 15662 (1958).
[22] T. Shimano *et al., Gifu Yakka Daigaku Kiyo* **6**, 35 (1956); *Chem. Abstr.* **51**, 5366 (1957).
[23] G. B. Elyakov *et al., Izv. Akad. Nauk. SSSR Otd. Khim. Nauk* 1605 (1962); C.A. **58**, 4604 (1963).
[24] H. Sander, M. Alkemeyer *et al., Pharm. Acta Helv.* **35**, 30 (1960); *Chem. Abstr.* **54**, 15830 (1960).
[25] H. D. Jackson and R. A. Shaw, *Arch. Biochem. Biophys.* **84**, 411 (1959).
[26a] S. Hohnjec-Mihalijinac and F. Benzinger, *Sci. Pharm.* **30**, 3 (1962); *Chem. Abstr.* **57**, 12632 (1962); N. K. Kochetkov *et al., Zhur Obshchei Khim.* **31**, 658 (1961); *Chem. Abstr.* **55**, 22367 (1961).
[26b] R. Tschesche and G. Wulff, *Planta Med.* **12**, 281 (1964).
[27] B. Gestetner *et al., Israel J. Chem.* **1**, 460 (1963); *Chem. Abstr.* **60**, 14743 (1964).
[28] F. Sandberg *et al., Svensk Farm. Tidskr.* **62**, 541 (1958); *Chem. Abstr.* **53**, 2538 (1959); S. Czyszewska, *Biul. Inst. Roslin. Lecniczych* **6**, 192 (1960); *Chem. Abstr.* **55**, 7567 (1961); F. Sandberg and A. F. Shalaby, *Svensk Farm. Tidskr.* **64**, 677 (1960); *Chem. Abstr.* **55**, 2817 (1961).
[29] R. P. Rastogi and M. L. Dhar, *J. Sci. Ind. Res. (India)* **19B**, 252 (1960).
[30] T. Shiga, *Japan Patent 1940* ('64) *Chem. Abstr.* **61**, 819 (1964).
[31] T. Bernstein *et al., Israeli Patent* 16340; *Chem. Abstr.* **61**, 5964 (1964).

enzymes, e.g. hydrolysis of alfalfa saponin has been achieved with a fungus preparation (*Aspergillus*).[32]

The sugar components have been usually identified by the conventional method of paper chromatography in various solvent systems. The sugar units are linked to the genin by glycosidic linkages; an ester linkage is rarely encountered and only D-glucose has so far been found in such a combination.[33] The following eight sugars have almost exclusively been found to be involved in glycosidation: D-glucose, D-galactose, D-galacturonic acid, D-glucoronic acid, D-xylose, L-arabinose, L-fucose and L-rhamnose. The structure of the sugar chains in a few cases have been elucidated by the usual method of methylation followed by hydrolysis and the identification of the inidividual methylated units (see Section A). It has been found that the sugar moiety is very often linked at C-3 OH of the aglycone but in some this linkage is at other positions, e.g. in musennin at C-16 OH and in asiaticoside at C-28 COOH. Gypsoside A has two sugar chains, one linked at C-3 OH and the other C-28 COOH. Further, the nature of the sugar chain generally seems to be branched although there are some exceptions, e.g. asiaticoside.

Although the configuration of the glycosidic linkages in saponins has been rarely worked out, the general composition of the glycosidic chains is such that the pentoses and methyl pentoses are "on the outside", i.e. as shown in Fig. 2.

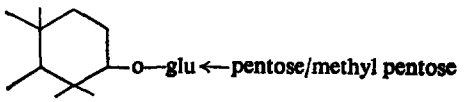


FIG. 2.

It would be interesting to postulate on the preferential incorporation of the sugars, listed above, into these glycosides, The sugars are biogenetically related, probably in such a manner that the other seven originate from D-glucose. Thymidine diphospho-D-glucose gives rise to L-rhamnose[34] whereas guanosine diphospho-D-mannose(GDP-Man) has been proved to be the biosynthetic precursor of L-fucose.[35] A pathway for the conversion of glucose to GDP-Man is also known.[36] The conversion of D-glucose into the other sugars is well known and can occur by way of UDP derivatives.[37]

Thus, the new sugars are formed as nucleotide derivatives of the type which are especially suited for transglycosidation to a genin. The free sugars are not incorporated. This makes the preferential formation of glycosides of these sugars understandable if it is assumed that other sugars, such as pentoses and deoxy-hexoses, do not originate in plants in an exactly corresponding manner. Some evidence that this is in fact the case has already been obtained.[38]

(b) *Sapogenins*

Intensive investigations on the chemistry of triterpenes commenced around 1930 but until 1950 these were mainly confined to establishing the gross structures and relationship of members of this group. The problem of the stereochemistry of this group was indeed very complex as the parent hydrocarbon contains eight centres of asymmetry giving rise to 256 possible

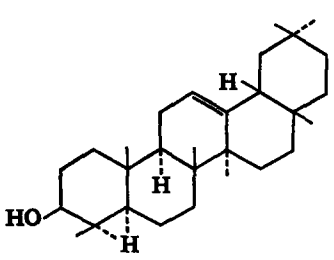
[32] W. A. LOURENS and M. B. O'DONOVAN, *S. African J. Agr. Sci.* **4**, 293 (1961); *Chem. Abstr.* **56**, 10196 (1962).
[33] N. K. KOCHETKOV *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1398 (1963); *Chem. Abstr.* **60**, 5620 (1964).
[34] W. Z. HASSID *et al.*, *Proc. Natl Acad. Sci. U.S.* **45**, 905 (1959).
[35] W. Z. HASSID, *Biochem. Soc. Symp.* **21**, 63 (1962).
[36] J. E. WATKIN and A. C. NEISH, *Phytochem.* **1**, 52 (1961).
[37] T. REICHSTEIN, *Angew. Chem., Intern. Ed.* **1**, 572 (1962).
[38] S. BARBAN and H. O. SCHULZE, *J. Biol. Chem.* **236**, 1887 (1961); *Idem, Ibid.* **237**, 291 (1962).

configurations which would be further augmented when substituents were introduced in the alicyclic system. Some simplification of the problem became apparent with the realization that the mode of locking of rings A to D was common to α,β-amyrins and lupane derivatives. The situation was, however, resolved by the exposition of the principles of conformational analysis[39] and by the application of rules to the shifts of the molecular optical rotations of polycyclic compounds.[40]

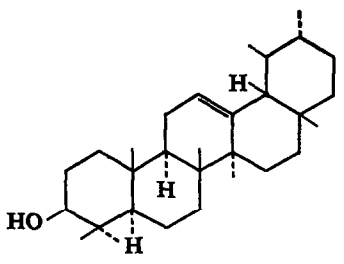
The stereochemistry of β-amyrin was derived from the chemical[41] and X-ray[42] evidence; that of the lupeol family followed from its relationship with β-amyrin family by interconversion.[43]

The gross structure of the α-amyrin group was determined[44] in 1949, and the first direct interconversion between the two amyrin groups was accomplished in 1955 with the conversion of ursa-11:13(18)-dienyl acetate to olean-11:13(18)dienyl acetate.[45] Almost simultaneously the complete stereostructure of α-amyrin was established on the basis of extensive chemical and physical data.[46] The unambiguous configuration of this expression was obtained by the synthesis of α-amyrin from glycyrrhetic acid (a β-amyrin derivative with functionality at C_{20}) by a series of stereospecific reactions.[47]

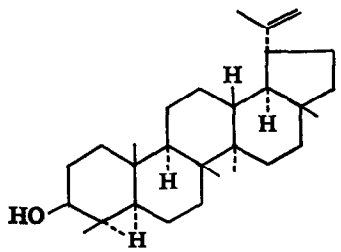
Both α and β-amyrins possess trans-anti-trans-trans-syn-cis arrangement of the rings A, B, C, D and E and the formulae are given in Fig. 3.



β-Amyrin



α-Amyrin



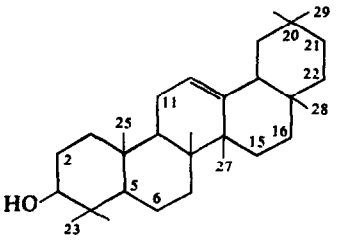
Lupeol

FIG. 3.

[39] D. H. R. BARTON, *Experientia* **6**, 316 (1950).
[40] W. KLYNE, *J. Chem. Soc.* 2916 (1952); J. A. MILLS and W. KLYNE, *Progress in Stereochemistry*, Vol. 1, p. 177. Butterworths, London (1954).
[41] D. H. R. BARTON and N. J. HOLNESS, *J. Chem. Soc.* 78 (1952).
[42] A. M. ABD EL RAHIM and C. H. CARLISLE, *Chem. Ind.* 279 (1954).
[43] T. R. AMES, T. G. HALSALL *et al.*, *J. Chem. Soc.* 450 (1951).
[44] L. RUZICKA, O. JEGER *et al.*, *Helv. Chim. Acta* **32**, 1075 (1949).
[45] G. G. ALLAN *et al.*, *Chem. Ind.* 281 (1955).
[46] E. J. COREY and J. J. URSPRUNG, *Chem. Ind.* 1387 (1954); *Idem, J. Am. Chem. Soc.* **78**, 183 (1956); L. RUZICKA *et al.*, *Helv. Chim. Acta* **39**, 441 (1956).
[47] E. J. COREY *et al.*, *J. Am. Chem. Soc.* **81**, 1745 (1959).

It is also worthwhile to note some leading recent applications of physical data, e.g. u.v.,[48] i.r.,[49] ORD,[50] cricular dichroism,[51] and especially NMR[52] and mass spectroscopy[53] to stereochemical and conformational problems as well as to structural determinations in the triterpenoids.

This review shows that the genins derived from β-amyrin outnumber, both in variety and frequency, any other types, and that oleanolic acid seems to be the predominant compound of this type found in nature. The genins which have been characterized are recorded in Figs. 4 and 5



Acacic acid,	16, 21-OH; 28-COOH
Arjunolic acid,	2-OH; 23-CH_2OH; 28-COOH
R_1-Barrigenol,	15, 16-OH; 27,28-CH_2OH
Barringtogenol, (= R_2 barrigenol)	2-OH; 23,28-CH_2OH
Barringtogenic acid,	2-OH; 23,28-COOH
Barringtogenol C,	16, 21, 22-OH; 28-CH_2OH
Barringtogenol D,	22-OH; 16 → 21 OXO; 28-CH_2OH
Bassic acid	2-OH; 23-CH_2OH; 28-COOH; $\Delta^{5(6)}$
Cincholic acid	27, 28-COOH
Cyclamiretin D,	16-OH; 25-CHO; 28-CH_2OH
Echinocystic acid,	16-OH; 28-COOH
Escigenin,	22-OH, 16 → 21 OXO; 23, 28-CH_2OH
Glycyrrhetic acid	11-CO; 29-COOH
Gypsogenin,	23-CHO; 28-COOH
Hederagenin,	23-CH_2OH; 29-COOH
Medicagenic acid,	2-OH; 23, 28-COOH
Oleanolic acid,	28-COOH
Protoescigenin,	16, 21, 22-OH; 23, 29-CH_2OH
Polygalacic acid	2, 16-OH; 23-CH_2OH; 28-COOH
Phytolaccagenin,	2-OH; 23-CH_2OH; 28-COOH; 29-$COOCH_3$
Soyasapogenol A,	21, 22-OH; 23-CH_2OH
Soyasapogenol B,	21-OH; 23-CH_2OH
Soyasapogenol C,	23-CH_2OH; $\Delta^{21(22)}$
Styphnodendron genin B,	21 → 28 lactone
Styphnodendron genin F,	2-OH; 20 → 28 lactone.

FIG. 4.

[48] D. W. TURNER, *J. Chem. Soc.* 30 (1959); R. A. MICHELI and T. H. APPLEWHITE, *J. Org. Chem.* **27**, 345 (1962); G. SNATZKE and H. FEHLHABAR, *Ann. Chem.* **663**, 123 (1963).

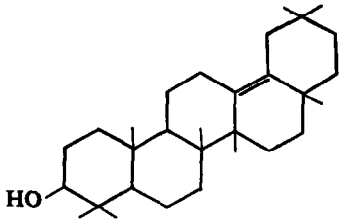
[49] A. R. H. COLE *et al.*, *J. Chem. Soc.* 4868 (1956); *Idem, ibid.* 1212, 1218, 1222 (1959); G. SNATZKE *et al.*, *Tetrahedron* **18**, 1417 (1962).

[50] C. DJERASSI *et al.*, *J. Am. Chem. Soc.* **81**, 4587 (1959); *Idem, Tetrahedron* **13**, 13 (1961); *Idem, J. Am. Chem. Soc.* **84**, 4929 (1962); G. OURISSON *et al.*, *Bull. Soc. Chim. France* 1938 (1960); J. S. E. HOLKER and W. B. WHALLEY, *Proc. Chem. Soc.* 464 (1961).

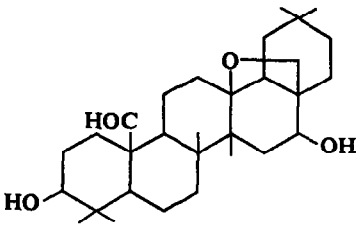
[51] G. OURISSON *et al.*, *Bull. Soc. Chim. France* 1101 (1963).

[52] J. M. LEHN *et al.*, *Bull. Soc. Chim. France* 1702 (1963); *Idem, Tetrahedron* **19**, 1733 (1963); M. SHAMMA *et al.*, *J. Org. Chem.* **27**, 4512 (1962); D. LAVIE *et al.*, *Tetrahedron* **19**, 2255 (1963); A. K. BOSE *et al.*, *J. Am. Chem. Soc.* **85**, 2795 (1963).

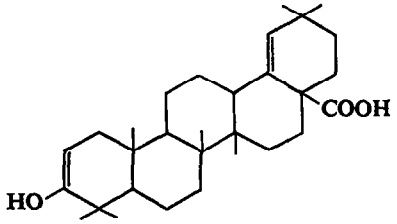
[53] C. DJERASSI *et al.*, *Tetrahedron Letters* 263 (1962); *Idem, J. Am. Chem. Soc.* **85**, 3688 (1963); J. L. COURTNEY and J. S. SHANNON, *Tetrahedron Letters* 13, 173 (1963); W. VETTER, *Bull. Soc. Chim. France* 415 (1964).



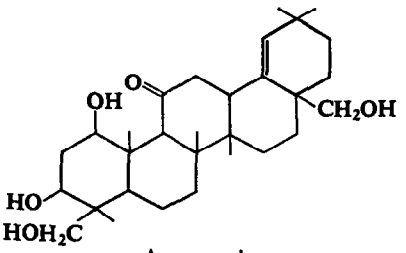
Albigenin 16-CO
Albigenic acid, 16-OH; 28-COOH



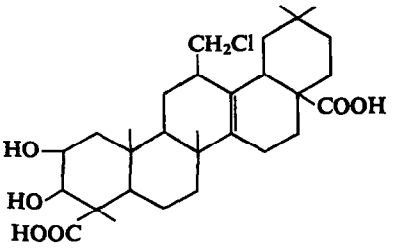
Cyclamiretin A



Morolic acid

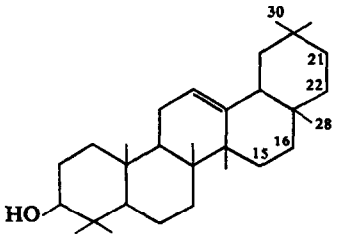


Avenagenin



Senegenin

FIG. 5.



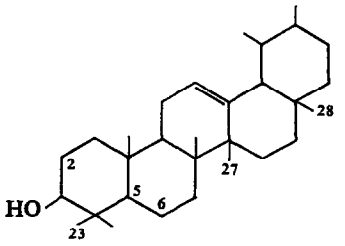
Erythrodiol,	28-CH_2OH
Maniladiol,	16-OH
Cochalic acid,	16-OH; 28-COOH
Gummosogenin,	16-OH; 28-CHO
Longispinogenin,	16-OH; 28-CH_2OH
Machaerinic acid,	21-OH; 28-COOH
Machaeric acid,	21-CO; 28-COOH
Queretaroic acid,	30-CH_2OH; 28-COOH
Dumortierigenin,	22-OH; 15 → 28 lactone
Myrtillogenic acid,	16-OH; 28-CH_2OH; 30-COOH
Chichipegenin,	16, 22-OH; 28-CH_2OH
Treleasegenic acid,	21-OH; 28-COOH; 30-CH_2OH

FIG. 6.

in a classified form and the references pertaining to them are given in relevant Sections A to E. Recent investigations have shown that occasionally alterations take place in the genins during the acid hydrolysis of the glycosides, with the result that either more than one aglycone is obtained or the isolated aglycone is not genuine.

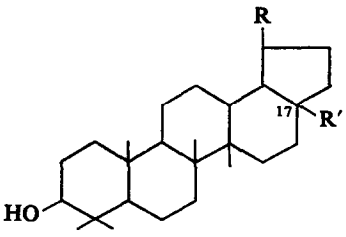
Mention must also be made of the extensive investigations[54] on 40 species belonging to 12 genera of the subtribe *Cereanae* of the giant cactii, which have yielded interesting results. All these genins, except thurberogenin and stellatogenin (Section E—*vide infra*), belong to β-amyrin series and are given Fig. 6.

Apart from machaerinic acid (in certain species of *Albizzia* only), erythrodiol and manil-adiol, these genins have so far been encountered amongst cactii only. An interesting fact emerges that besides the ubiquitous 3β—OH group, oxygenation is only limited to six other carbon atoms (positions 15, 16, 21, 22, 28 and 30) which form virtually a continuous chain. Oxygenation at 15, 21, 22, and 30—as found in cactus genins—is rare in the triterpene field.



Quinovic acid,	27, 28-COOH
Asiatic acid,	2-OH; 23-CH_2OH; 28-COOH
Centoic acid	5,6-OH; 23-CH_2OH; 28-COOH
Brahmic acid	2,6-OH; 28-COOH; 23-CH_2OH

FIG. 7.



Betulin,	R'—CH_2OH; R—$\overset{CH_2}{\underset{CH_3}{<}}$
Betulinic acid,	R'—COOH; R—$\overset{CH_2}{\underset{CH_3}{<}}$
Thurberogenin,	17 → 19 lactone; R—$\overset{CH_2}{\underset{CH_3}{<}}$
Stellatogenin,	17 → 19 lactone: R—$\overset{CH_3}{\underset{CH_3}{<}}$OH

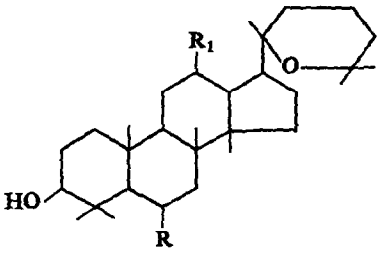
FIG. 8.

[54] C. DJERASSI, *Festschrift Prof. Dr. Arthur Stoll*, p. 330. Birkhauser, Basel (1957).

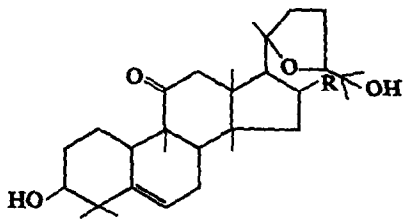
Examples of saponins having genins of α-amyrin group have so far been encountered in two cases. These genins are quinovic acid[55] and asiatic acid (Fig. 7).

The lupeol group of genins are very rare in nature. The following types have been reported and the last two genins have been found only in cactii (Fig. 8).

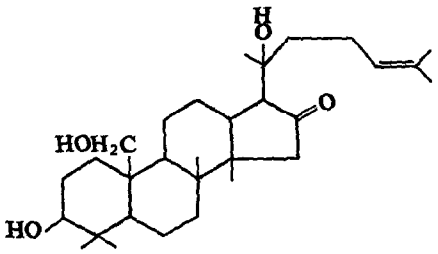
In the tetracyclic triterpenoid group, there are five examples, namely panaxadiol, bryogenin, bacogenins, gratiogenin and the cucurbitacins shown in Fig. 9.



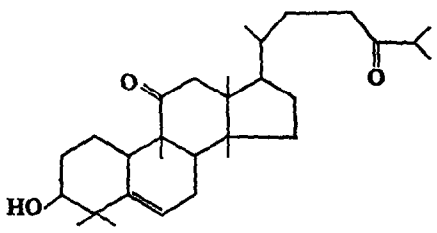
Panaxadiol R—H, R_1—OH
Panaxatriol R—OH, R_1—OH



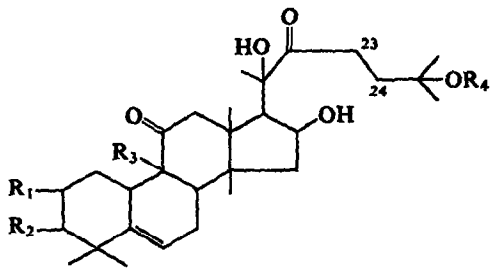
Gratiogenin R—H
Hydroxygratiogenin R—OH



Bacogenin A_1



Bryogenin



Cucurbitacin A,	R_1—OH,	R_2—CO,	R_3—CH_2OH,	R_4—Ac,	$\Delta^{23(24)}$
B,	OH,	CO,	CH_3,	Ac,	$\Delta^{23(24)}$
C,	H,	OH,	CH_2OH,	Ac,	$\Delta^{23(24)}$
D,	OH,	CO,	CH_3,	H,	$\Delta^{23(24)}$
E,	OH,	CO,	CH_3,	Ac,	$\Delta^{23(24)}$, $\Delta^{1(2)}$
F,	OH,	OH,	CH_3,	H,	$\Delta^{23(24)}$
I,	OH,	CO,	CH_3	H,	$\Delta^{23(24)}$, $\Delta^{1(2)}$
J,*	OH,	CO,	CH_3,	H,	$\Delta^{1(2)}$, C_{24}—OH
K,*	OH,	CO,	CH_3,	H,	$\Delta^{1(2)}$, C_{24}—OH
L,	OH,	CO,	CH_3,	H,	$\Delta^{1(2)}$

* C_{24}—OH isomers

FIG. 9.

[55] K. PAECH and M. V. TRACEY, *Modern Methods in Plant Analysis*, Vol. 3, p. 123. Springer, Berlin (1955).

4. CLASSIFICATION OF AVAILABLE DATA

This survey has been divided into five sections based on the isolation of the saponins and the characterisation of their genins. The sugar components wherever identified have also been incorporated. This survey does not, however, include those plants in which the presence of saponin has been reported but no further work has been done. The following abbreviations have been used: glc. = glucose, fru. = fructose, gal. = galactose, ara. = arabinose, fuc. = fucose, xyl. = xylose, rha. = rhamnose, glc. UA = glucuronic acid, gal. UA = galacturonic acid, amorph. = amorphous, cryst. = crystalline.

SECTION A. PURE SAPONINS WHOSE CHEMISTRY HAS BEEN COMPLETELY ELABORATED, INCLUDING THE CONFIGURATION OF THE CARBOHYDRATE CHAIN

Plant	Saponin	Genins and sugars	Ref.
Aesculus hippocastanum (horse chestnut)	Escin, cryst., m.p. 224°	Prosapogenin → escigenin	56, 57, 58
	Cryptoescins A and B	(Mixture of escin, methyl ester of escin and cholesterol)	59, 60
	Escin	Protoescigenin + escigenin + escinidin (present as angelic or tiglic acid salts) + D-glc. + D-xyl. + D-glc. UA	61
Aralia manschurica *Aralia elata*	Araloside A m.p. 195°	Oleanolic acid + glc. UA + D-glc. + L-ara.	62
	Araloside B m.p. 230°	Oleanolic acid + glc. UA + glc. + 2 ara.	
	Araloside C	Oleanolic acid + glc. UA + glc. + xyl + gal	
Centella asiatica Syn., *Hydrocotyle asiatica* (Madagascar variety)	Asiaticoside	Asiatic acid + 2 glc. + rha.	63
Cinchona Calisaya	Glycoside A (quinovin)	Quinovic acid + 6 deoxy-glucose (quinovose)	64
	Glycoside B	Quinovic acid + D-glc.	
	Glycoside C	Cincholic acid + 6 deoxy-glucose	
Glycyrrhiza glabra and other spp.	Glycyrrhizin (Glycyrrhizic acid)	Glycyrrhetic acid + 2 glc. UA	65
Gypsophila pacifica	Gyposide	Gypsogenin + D-glc. + D-gal. + D-ara. + L-rha. + D-fuc. + D-glc. Ua + 3 D-xyl.	66

[56] *Idem, ibid.*, Vol. 3, p. 117. Springer, Berlin (1955).

[57] O. JEGER *et al.*, *Helv. Chim. Acta* **40**, 2390 (1957).

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[61] R. TSCHESCHE, *Ann. Chem.* **669**, 171 (1963); R. KUHN and I. LOW, *Ann. Chem.* **669**, 183 (1963); *Idem, Tetrahedron Letters* 891 (1964).

[62] A. YA. KHORLIN *et al.*, *Zh. Obshch. Khim.* **31**, 658 (1961); *Chem. Abstr.* **55**, 22367 (1961); *Idem, Izv. Akad. Nauk. SSSR, Ser. Khim.* 1398 (1963); *Chem. Abstr.* **60**, 5620 (1964); *Idem, ibid.* 1338 (1964); *Chem. Abstr.* **61**, 16344 (1964); *Idem, Ref. Zh. Khim.* 1963, Abstr. No. 17 Zh 336; *Chem. Abstr.* **61**, 1930 (1964).

[63] J. POLONSKY *et al.*, *Bull. Soc. Chim. France* 880, (1959); *ibid.* 1586 (1961).

[64] R. DUPHORN, G. SNATZKE *et al.*, *Ann. Chem.* **667**, 151 (1963).

[65] B. LYTHGOE and S. TRIPPET, *J. Chem. Soc.* 1983 (1950); C. A. MARSH and G. A. LEVY, *Biochem. J.* **63**, 9 (1956).

[66] A. YA. KHORLIN *et al.*, *Zh. Obshch. Khim.* **32**, 782 (1962); *Chem. Abstr.* **58**, 4636 (1963); *Idem, Izv. Akad. Nauk SSSR, Ser. Khim.* 83 (1964); *Idem, ibid.* 90 (1964); *Chem. Abstr.* **60**, 10776 (1964); *Idem, Tetrahedron Letters* 477 (1963).

SECTION A—*continued*

Plant	Saponin	Genins and sugars	Ref.
Kalopanax septemlobus	Saponin A m.p. 230°	Oleanolic acid + L-ara. + L-rha.	67
	Saponin B	Oleanolic acid + D-ara. + D-rha.	
	Saponin	Oleanolic acid + 2 glc. + 2 ara.	68
Primula elatior	Saponin A	Neutral genins (Primula genins A, B, C, D, E, F, G) + acidic genins (Primula genins SG, SF, SD, SC). D-glc. + D-gal. + D-gal. UA + L-rha.	69

SECTION B. SAPONINS, STATED TO BE PURE, WHOSE GENINS HAVE BEEN CHARACTERISED

Plant	Saponin	Genins and sugars	Ref.
Albizzia amara	Amorph.	Echinocystic acid + neutral genin	70
A. anthelmintica	Musennin	Echinocystic acid + D-glc. + 3 L-ara.	71
A. odoratissima (from U.P., India)	Odoratissimin m.p. 227–8°	Echinocystic acid + glc. + arab. + rha. + xyl.	72
A. procera	Proceranin m.p. 156–8°	Machaerinic acid + ethyl machaerinate + D-glc. + ara. + D-xyl. + D-rha.	73
Avena sativa	Avenacin	Avanagenin + *O*-monomethylamino benzoic acid + 2 glc. + pentose	74
Bacopa monniera	Monnierin	Glc. + ara. + genin	75
	Bacosides A, B	Glc. + ara. + bacogenins A_1, A_2, A_3, A_4	76
Centella asiatica (Syn. *Hydrocotyle asiatica*)	Brahmoside	Brahmic acid + glc. + ara. + rha.	29, 77, 77a
Indian variety	Brahminoside	Brahmic acid + 2 glc. + ara. + rha.	
	Thankuniside	Thankunic acid* + 2 glc. + rha.	78
	Indocentelloside†	Indocentoic* acid	79
(Ceylonese variety)	Centelloside†	Centellic acid (isomer of centoic acid) + 10 glu. + 2 fru.	80
Cyclamen europaeum	Cyclamin m.p. 254° d	Cyclamiretins A, B, C, D + 3 glc. + D-xyl. + L-ara.	81
Elvira biflora	Amorph.	Echinocystic acid + gal. + xyl. + ara. + rha.	82

* Structures not assigned.
† Saponins not isolated.

[67] A. YA. KHORLIN *et al.*, *Dokl. Akad. Nauk SSSR* **155**, 619 (1964); *Chem. Abstr.* **60**, 15964 (1964).
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[70] I. P. VARSHNEY and K. M. SHAMSHUDDIN, *J. Sci. Ind. Res.* (*India*) **21B**, 347 (1962).
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[72] I. P. VARSHNEY and M. S. Y. KHAN, *J. Sci. Ind. Res.* (*India*) **21B**, 30 (1962).
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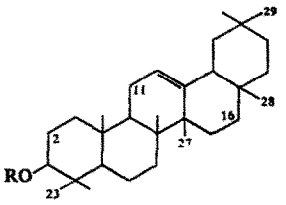
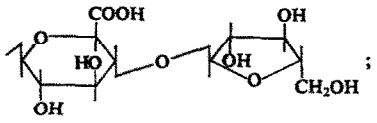
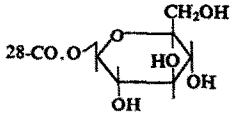
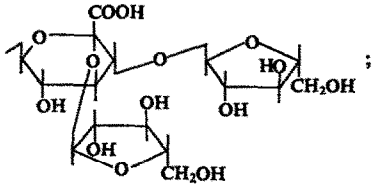
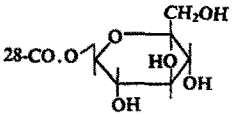
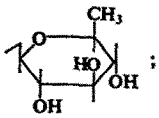
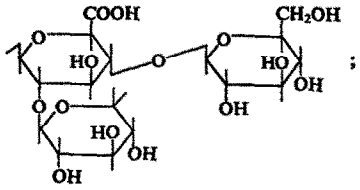
[77] R. P. RASTOGI and M. L. DHAR, *Indian J. Chem.* **1**, 267 (1963).
[77a] Unpublished work of the authors.
[78] U. P. BASU and T. DUTTA, *J. Sci. Ind. Res.* (*India*) **21B**, 239 (1962).
[79] S. C. BHATTACHARYA, *J. Indian Chem. Soc.* **33**, 893 (1956).
[80] S. C. BHATTACHARYA, *J. Indian Chem. Soc.* **33**, 579, 630 (1956).
[81] D. H. R. BARTON *et al.*, *J. Chem. Soc.* 5176 (1962); R. TSCHESCHE *et al.*, *Ann. Chem.* **680**, 107 (1964).
[82] M. M. OLIVEIRA and S. O. ANDRADE, *J. Pharm. Sci.* **50**, 780 (1961).

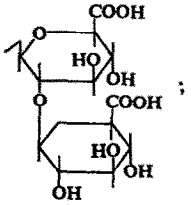


Araloside A, R,  ; 

Araloside B, R,  ; 

Cinchona glycoside C, R,  ; 27,28-COOH

Escin R,  ; 16 — 21 OXO; 23-CH_2OH; 22-OH; 28-CH_2OCOCH—$CHCH_3$ (CH_3, $OCOCH_3$)

Glycyrrhizin, (glycyrrhizic acid) R,  ; 11-CO; 29-COOH

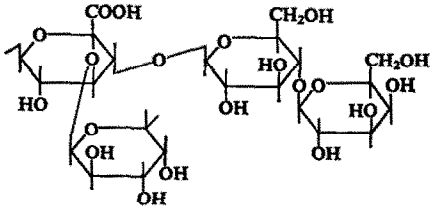
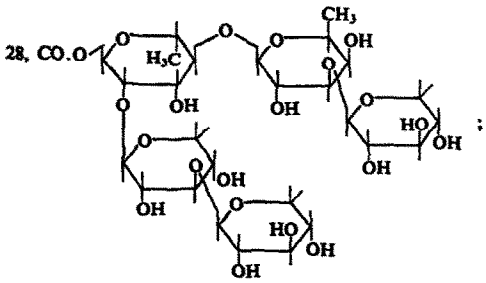
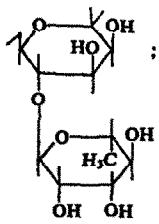
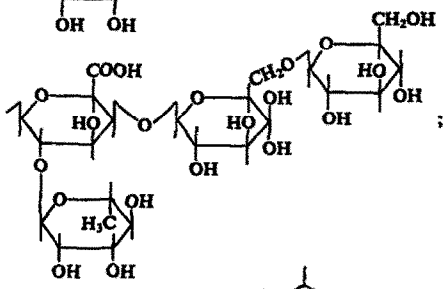
Gypsoside A, R, 

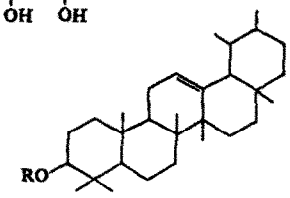
FIG. 10.

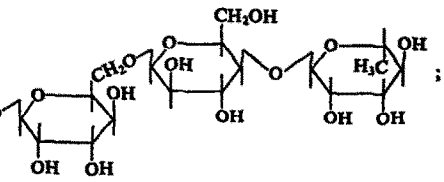


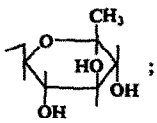
28, CO.O ; 23-CHO

Kalopanax saponin A, R,  ; 23-CH_2OH; 28-COOH

Primula saponin A, R,  ; 16-OH; 28-CH_2OH



Asiaticoside, 28, CO.O  ; 2-OH; R—H; 23-CH_2OH

Cinchona glycoside A, (quinovin) R,  ; 27,28-COOH

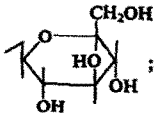
Cinchona glycoside B, R,  ; 27,28-COOH

FIG. 10 (*continued*).

SECTION B—*continued*

Plant	Saponin	Genins and sugars	Ref.
Glinus lotoides	m.p. 248°	Oleanolic acid	83
Gratiola officinalis	Gratioside m.p. 268–74°	Gratiogenin + 2 glc.	84
Hedera helix	Hederacoside A Hederacosides B, C	Hederagenin + D-glc. + L-ara.	85
Helianthus annus	Amorph.	Echinocystic acid	86
Leontice leontopetalum	Cryst. m.p. 236°	Hederagenin + glc. + ara.	87
Luffa echinata	Amorph.	Oleanolic acid + glc. + rha.	88
L. graveolens	Amorph.	Oleanolic acid + glc. + ara. + rha.	89
Medicago sativa (alfalfa)	Cryst. m.p. 255°	Medicagenic acid + D-glc.	90
Mora excelsa	Amorph	Morolic acid + glc. + ara.	91
Patrinia intermedia	Patrinin	Sapogenin + fru. + pentose	92
	Patrinosides A, B, C, D	Oleanolic acid + glc. + xyl.	93
	Patrizid A m.p. 229°	Oleanolic acid + glc. + xyl.	94
Panax ginseng	Ginsenosides R_x X = a, b, c, d, e, f, g-1, g-2, g-3 and h		
	Ginsenosides R_x X = b, c, d, e, f,	Protopanaxadiol → Panaxadiol	95
	Ginesenoside R_{g-1}	Panaxatriol	96
Polygala senega	Senegin	Senegenin‡	97
Phaseolus radiatus	Cryst. m.p. 215° d	Soyasapogenol c + glc. + rha. + ara. + glc. UA	98
Phytolacca americana	Phytolacca toxin	Phytolaccagenin + glc. + xyl.	99
Sapindus laurifolius	Amorph. m.p. 145°	Hederagenin	100

‡ Chlorine incorporated in the molecule during hydrolysis.

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SECTION B—*continued*

Plant	Saponin	Genins and sugars	Ref.
Soja hispida (Soya bean)	Cryst. m.p. 220–22°	Soyasapogenols A, B, C and D (structure of Soyasapogenol D not known)	101
Terminalia arjuna	Amorph. m.p. 216–20°	Arjunolic acid + glc.	102

SECTION C. SAPONINS ISOLATED AS IMPURE POWDERS WHOSE GENINS HAVE BEEN CHARACTERISED

Plant	Crude Saponins	Genins and sugars	Ref.
Acacia concinna	Amorph.	Acacic acid	103
Achyranthes aspera	Amorph.	Oleanolic acid + glc. + gal. + xyl. + rha.	104
A. bidentata	Amorph.	Oleanolic acid	105
Albizzia lucida	Amorph.	Echinocystic acid + neutral genin + oleanolic acid	106
Albizzia lebbek (seed, U.P., India)	m.p. 200–5°	Oleanolic acid + echinocystic acid	107a
(bark) (seeds, Bengal, India)	Amorph.	Acacic acid	107b, 103
	—	Albigenic acid + oleanolic acid + echinocystic acid + albigenin	107c
Albizzia odoratissima (Maharashtra, India)	Amorph.	Machaerinic acid + acid genin	107d
Aster tartaricus	—		
	Amorph. m.p. 212–14°	Hederagenin + glc.	108
Atriplex canescens	—	Oleanolic acid	109
Barringtonia racemosa	Amorph.	Barringtogenol + barringtogenic acid	110a
		Barrigenol R_1 + barrigenol R_2 (= barringtogenol)	110b
Barringtonia acutangula		Barringtogenols B, C, D + barringtogenic acid	110c
Bryonia dioica	Bryonin	Bryogenin	111
Calendula officinalis	—	Oleanolic acid + glc. UA	112
Clematis panniculata	Amorph.	Hederagenin	113

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SECTION C—*continued*

Plant	Crude saponins	Genins and sugars	Ref.
Diospyros peregrina	Amorph.	Oleanolic acid + glc.	114
Lotus corniculatus	—	Soyasapogenol B	115
Luffa aegyptica	—	Oleanolic acid + neutral genin	116a
Mimusops heckelii	Amorph.	Bassic acid + glc. + L-rha. + D-xyl.	116b
Prunella vulgaris, *P. grandiflora*	Amorph.	Oleanolic acid	117
Randia dumetorum	Amorph.	Oleanolic acid + glc. + fru. + xyl. + glc. UA	118
Saponaria vaccaria	Vaccaroside m.p. 204° d	Gypsogenin + glc.	119
Polygala paenea	—	Polygalacic acid	119a
Sesbania aculeata	—	Oleanolic acid + neutral genin	120
Sideroxylon tomentosum	Amorph.	Gypsogenin	105
Styphonodendron coriaceum	—	Sapogenins B and F	121
Trifolium repens	m.p. 225°	Soyasapogenols A, B, C + glc. + gal. + xyl. + rha.	122
Zizypus xylopyrus	—	Oleanolic acid	123

SECTION D. SAPONINS, PURE OR CRUDE, WHOSE GENINS HAVE NOT BEEN CHARACTERISED

Plant	Work done	Ref.
Asculus turbinata	Amorph. saponin (Japoaescin) → 2 glc. Ua + xyl. + tiglic acid + japoescigenin (hydroxy-escigenin)	124
Albizzia adianthifolia	Amorph. saponin → acid genin + rha. + ara. + glc. Ua	125
A. gummifera	Albitocin, amorph., m.p. 220–25° → glc. + ara. + xyl. + rha. + acid genin, $C_{30}H_{48}O_5$	126
A. procera (Maharashtra, India)	Pure saponin → Proceric acid	127
Anabasis articulata	Pure Saponins, A, B, C, D, → genins A, B, C, D, + glc. + glc. UA (sugars identical in each case)	128
	Saponin B → anabasic acid glucuronate + numerous fission products	

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SECTION D—*continued*

Plant	Work done	Ref.
Anemone chinensis	Glc.+rha.+an unidentified sugar +anemosapogenin (Pentacyclic, 2-CHOH, 1 hindered COOH, nonhydrogenable Δ).	129
Anemone nemorosa	Amorph. saponin → genin, $C_{30}H_{48}O_4$+glc.+rha.+ara.	130
Blighia unijugata	Amorph. Saponin → genin, $C_{16}H_{26}O_2$+ara.+rha.	131
Bredemeyera floribunda	Brademolic acid, $C_{30}H_{48}O_4$ (1-COOH, 2-OH)+tenuifolic acid (2-OH, 2-COOH)+glc.	132
Bupleurum falcatum	Saponin	133
Cestrum diurnum	Cryst. saponin, m.p. 269° → genin, m.o. 204°	134
Caccinia glauca	Amorph. saponin, m.p. 230–50° d	135
Caldeonium majus	Saponin → glc.	136
Camellia japonica	Saponin, m.p. 206° → Camellia sapogenol, $C_{30}H_{50}O_4$+ara.+gal.+glc.+uronic acid+tiglic acid.	137
Coronillus emerus	Neutral saponin → xyl.+sapogenin Acidic saponin → xyl.+gal. UA+genin. Saponinic acid → gal. UA+resinous genin	138
Cyclamen elegans	Saponin, m.p. 240–8° d	139
Doryanthes palmeri	Two sapogenins	140
Entada scandens	Saponin A, m.p. 116° and saponin B, m.p. 150° → genin, m.p. 306° (entagenic acid)+glc.+gal.+xyl.+ara.	141
E. pursaetha	Saponin → entagenic acid	142
Eupteleа polyandra	Eupteleosides A and B → eupteleogenin	143
Heloniopsis orientalis	Amorph. saponin → pennogenin+isochiapagenin+heloniogenin	144
Hepatica triloba (syn: *Anemone Hepatica*)	Hepatisaponin, m.p. 225° → ara.+cryst. prosapogenin → hepatigenin+glc.	145
Herniaria hirsuta, H. glabra	20% neutral+60% acidic saponins → two genins, m.p. 310° and m.p. 343°	146
Hydrocotyle vulgaris	Saponins A, A_2, B and S_4	147
Leonurus quinquelobatus	Saponin, pure	148
Mahonia pubescens	Amorph. saponin	149

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SECTION D—*continued*

Plant	Work done	Ref.
Mollugo nudicaulis	Cryst. saponin A, m.p. 269° → genin, $C_{30}H_{50}O_5$ + glc. + rha. + gal.	150
Mollugo spergula	Amorph. saponin → spergulagenin, $C_{30}H_{50}O_4$	151
Pachyrrhizus erosus	2 amorph. saponins → cryst. pachysapogenin A, $C_{30}H_{38}O_6$, m.p. 196°, and pachysapogenin B, $C_{23}H_{18}O_7$, m.p. 176°	152
Pithecolobium dulce	Saponin, m.p. 175–81° → Pithecogenin, $C_{28}H_{44}O_4$, m.p. 207°	153
Polygala major	Pure saponin → sapogenin, $C_{27}H_{46}O_8$, m.p. 208° + D-glc. + L-ara. + L-rha.	154
Primula vulgaris	Pure saponin, m.p. 233° → 2 genins + 3 glc. + rha. + gal.	155
Silene brahuica	Saponin, m.p. 104–6° (from roots); saponin, m.p. 208–10° (from stem)	156
Sophora japonica	Saponin m.p. 210–20° → betulin + sophoradiol $C_{30}H_{50}O_2$, m.p. 219° + glc. + glc. UA + glucurono-lactone	157
Solidago canadensis	Amorph. saponin → sapogenin, $C_{30}H_{50}O_5$, m.p. 310–15°	158
Styrax japonica	jegosaponin → jegosapogenol, $C_{30}H_{50}O_5$, probably β-amyradiene with axial OH at C_{19}	159
S. officinalis	Cryst. saponin, m.p. 242° → benzoic acid. + glc. + gal. + rha. + glc. UA + genin, $C_{27}H_{44}O_5$ (not steroidal, probably new type)	160
Swartzia madagascariensis	Pure saponins A and B → Swartziagenin, $C_{30}H_{48}O_4$ + glc. + xyl. + rha. + glc. UA	161
Trifoleum fragiferum	Cryst. saponin mixture → soyasapogenols B and C + a sapogenin, m.p. 227°	162
Thymus vulgaris	Acidic saponin (thymunic acid), m.p. 198° → thymuninic acid + reducing sugars. Neutral saponin (thymusaponin), m.p. 232° → thymusapogenin + reducing sugars	143, 163
Xanthocephalum spp. (Broom weed)	Amorph. saponins → genin, m.p. 305–7°	164

SECTION E. SAPONINS WERE NOT ISOLATED BUT THE PURIFIED PLANT EXTRACTS WERE DIRECTLY HYDROLYSED FOR THE IDENTIFICATION OF THE GENINS

Plant	Genin	Ref.
Giant cactii (subtribe—Cereanae)		
(i) *Lemaireocerus* spp.	Oleanolic acid, erythrodiol, betulinic acid, longispinogenin, chichipegenin, stellatogenin, thurberogenin, oxyallobetulin, treleasegenic acid, queretaroic acid, dumortierigenin	165

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SECTION E—*continued*

Plant	Genin	Ref.
(ii) *Machaerocereus* spp.	gummosogenin, machaeric acid, machaerinic acid, betulinic acid, stellatogenin	166
(iii) *Myrtillocactus* spp.	Cochalic acid, chichipegenin, myrtillogenic acid, oleanolic acid, stellatogenin	167
Heliabravoa chende	Oleanolic acid + Oleanolic aldehyde	168
Mimusops globosa (Syn: Manilkara bidentata)	Bassic acid + glc. + rha. + xyl.	169
Pittosporum undulatum	A_1-barrigenol + Pittosapogenin, $C_{30}H_{50}O_6$	170
Pittosporum phillyraeoides	Pittosapogenin + Phillyrigenin, $C_{30}H_{48}O_4$	171
Cucurbitaceae plants: *Bryonia* spp., *Citrullus* spp., *Cucurbita* spp., *Coccinia* spp., *Ecballium elaterium*, *Echinocystis* spp., *Peponium mackenii*, etc.	Cucurbitacins A, B, C, D, E, F, I, J, K, L	171a
Luffa operculata	Gypsogenin	171b

5. BIOLOGICAL ACTIONS AND USES

The wide occurrence of saponins in nature has evoked considerable interest in their use and considerable data has accumulated concerning their physiological action and other properties.[171c] Saponins, in general, lower surface tension and possess emulsifying properties. They tend to alter the permeability of the cell-wall and, therefore, exert a general toxicity on all organised tissues. Their hemolytic and antilipemic activities and capacity to lower the serum cholesterol levels can be considered to be their important characteristics.

Saponins produce hemolysis in very dilute solutions but amongst them there is a very great variation in their hemolytic activity.[171d] An attempt has been made to correlate the physical, chemical and biological properties of *Gypsophila* (I), *Saponaria* (II), *Quillaja* (III) saponins and quillaja acid (IV); foam number, reduction in surface tension of liquids, hemolytic activity and LD_{50} in rats were found to diminish in the order I, II, IV and III, but some other properties could not be correlated.[172] The saponins of *Gypsophila* and *Saponaria*, when administered subcutaneously in subhemolytic doses, cause an intense stress reaction

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[171c] G. VOGEL, *Planta Med.* **11**, 362 (1963).

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accompanied by a greatly increased excretion of the neutral, reducing lipids and a lesser increase of the 17-ketosteroids.[173] They cause a significant decrease in the ascorbic acid content of the adrenals.[174] It has been demonstrated that individual erythrocytes differ in resistance to lysis by individual saponins and their statistical distribution has been reported to be different in a normal cell population.[175] It is likely that different saponins may produce quite different structural alterations in cell-membrane lipids which in fact has been indicated by recent electron micrographs,[176] but the exact relation of these structural changes to hemolysis remains to be elucidated. When normal organs of rat and slices of fibrosarcosoma were placed in saponin solution, changes in nuclei were observed leading to their fragmentation and complete disruption. There was no indication of a differential behaviour towards the normal and neoplastic cells.[177]

The elevation of cholesterol lipid P ratio of serum which was obtained in rats by cholesterol, lard or cotton seed oil feeding, was prevented by saponins. Saponins also prevented the rise of lipids in serum and liver.[178] Similar results were obtained on chicks fed on a diet containing 0·6 per cent saponins. It is suggested that complexing of saponin with cholesterol found (either by ingestion or by secretion) in the intestinal lumen makes less cholesterol available for reabsorption.[179] However, no correlation between hemolytic activity and cholesterol depletion has been found.

Alteration in the structure of the natural saponins by sulphonation with cholorosulphonic acid or oleum with a view to obtain physiologically active products has also been tried.[180] The antilipemic, anticoagulant and antiproteolytic activities of various saponins (*Primula*, *Gypsophila*, etc.) and their sulphonated products have been compared with heparin and other antiheparinoids.[181] It was observed that the antilipemic activity of these products varied from 10 to 70 per cent of heparin and that these were weak anticoagulants.[182] The data tend to confirm the hypothesis of non-specificity of antilipemic action and its independence of the anticoagulant activity.

General pharmacological behaviour of saponins has been studied in various animals.[180, 183] The effects of ingested saponins of alfalfa on cardiovascular, central nervous systems and various parts of the digestive tract have been studied.[184]

Aralosides A, B and C caused increase in motor activity (stimulation) at 5–10 mg/kg and depression at 20–100 mg/kg for 30–40 min in mice.[183] A saponin which is a respiratory inhibitor has been isolated from alfalfa.[185] Another saponin which inhibited hyaluronidase edema in intact rats subcutaneously or orally has been reported and the curative effect was

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seen even in adrenalectomised rats.[186] An oxytocic saponin has been reported from *Albizzia gummifera*.[187]

Although most saponins are poorly absorbed from alimentary tract it is apparently established that the administration of at least some of them simultaneously with drugs would increase the absorption of the latter from the intestines. There is a reported adjuvant effect of saponins on vaccine against foot and mouth disease (virus of types 4, O and C).[188] However, the significance of saponins in therapeutics seems at present to be uncertain.

Certain saponins exhibit specific properties. Some have been tried as insecticides and being non-toxic to human beings and animals, these can be used as powders, emulsion or in solution form.[189] The *in vitro* anthelmintic effects of certain saponins were good, but these could not be used due to their marked irritation of the mucosa.[190] The saponin of *Kalopanax* has remarkable termiticidal action and is responsible for the termite resistance of the wood.[191] The saponin of *Altriplex* promotes germination of seeds at a concentration of 0·1 per cent but acts as an inhibitor at the level of 1–5 per cent.[192] *Pittosporum* saponin depressed yeast proliferation.[193]

The ability of saponins to reduce surface tension has been utilised in making emulsion stabilizers,[194] and the results have been compared with fatty acid salts. Saponin of *Ruscus aculeatus* has been shown to be useful as foaming agent or as a detergent.[195] Their wetting power and detergent action has been compared with commercial detergents and favourable results have been obtained.[196] Their use as protective colloids in spray drying of powdered flavouring materials has been investigated and found to be equal to that of gum arabic.[197] Some saponins have been employed in beverages to produce a frothy effect.

Finally, reference must be made to the saponins which have been evaluated clinically. Asiaticoside has been reported to have remarkable curative effect against leprosy,[198] and glycyrrhizin (glycyrrhizic acid), the saponin of licorice root, has shown varied and interesting biological activity. Many patents have been taken on the preparation of glycyrrhizin as such or as its ammonium, sodium, potassium and cholchicine salts.[199] Glycyrrhizin has been used in the treatment of gastric ulcers[200] and dermatitis.[201] It reduces hypercholesteraemia[202]

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[202] N. SHIBATA, *Med. J. Osaka Univ.* **12**, 297 (1961).

and its mineralocorticoid and glucocorticoid[203] actions and anti-inflammatory[204] effects have been established beyond doubt. It shows hypertensive[205] properties and detoxifying effects in mice poisoned with strychnine nitrate.[206] The metabolism[207] of the orally administered tritium labelled ammonium glycyrrhizate and glycyrrhetic acid has been studied in rat as well as in human beings.

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