

CHEMICAL CONSTITUENTS AND BIO ACTIVITIES OF GENUS SAPINDUS

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ABSTRACT

The genus Sapindus has been reviewed for its chemical constituents and biological activities together with traditional importances. Trees of genus Sapindus are cultivated in many parts of India for ornamental purposes. The present review is based on chemical constituents and biological activities of known species of Sapindus. The different species of Sapindus are used for curing various diseases and commercially important. Over 103 compounds have been identified from the genus Sapindus and many of them have been evaluated for their biological activities. The overall activity of the extract is based on the interaction between its components. Therefore, the safety and efficacy of the extract cannot be fully imitated by individual constituent. The aim of present review is to summarize the different phytochemical and pharmacological work together.

KEYWORDS: Sapindaceae; Saponins; Triterpenoids; antidiabetic; cytotoxic

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INTRODUCTION

Sapindaceae is one of the important family of plant kingdom consisting about 150 genera and 2000 species¹. The genus Sapindus includes both deciduous and evergreen species widespread over Himalayan range. The soapberry family comprises nearly 2000 species, which are primarily tropical. The soapnut tree commonly known as soapberry (Reetha) by Indians and found over most of the hilly region of Garhwal Himalaya. In China and Japan it has been used as a remedy for centuries. In Japan pericarp is called "enmei-hi", which means "life prolonging pericarp" and In China "wu-huan-zi", the non-illness fruit². The genus sapindus includes two major species *S. mukorossi* and *S. emarginatus* in north and south India. *S. mukorossi* is one of the most important sources for saponins. The pericarps contain 10 - 11% soapnuts and are locally used for protection of pests and micro-organisms. Other species of genus have been investigated for their astringent and pharmacological uses.

The major compounds isolated from genus sapindus are saponins, triterpenoids, fatty acids and flavonoids are well known for their antimicrobial, antidiabetic, cytotoxic, molluscicidal, fungicidal and anti-inflammatory activities. However several other compounds isolated from this genus may contribute important biological activities in their crude extract.

Traditional uses of Sapindus Species

The members of genus sapindus are well known for their folk medicinal values. Pericarps of *S. mukorossi* have been traditionally used as an expectorant as well as a source of natural surfactant³. Due to the presence of saponins, soapnut is well known for its detergent and insecticidal properties and traditionally used for removing lice from the scalp and used in dental carries⁴. The seeds of *S. mukorossi* are used to remove tan and freckles from the skin. The fruits are of considerable importance for its medicinal value for treating a number of diseases like common cold, pimples, epilepsy, constipation, nausea etc⁵. The leaves are used in a bath to relieve joint pain and the roots are used in the treatment of gout and rheumatism.

Since ancient times *S. mukorossi* has been used as a detergent for shawl and silks. The fruit of *S. mukorossi* was utilized by Indian jewelers for restoring the brightness of tarnished ornaments made of gold, silver and other precious metals⁶. The fruit of *S. saponaria* is used by local population as soap for washing clothes, for curing ulcers, and external wounds⁷. Fruits of *Sapindus trifoliatus* have been considered as a tonic, stomachic, alexipharmic, astringent and sedative to the uterus and also useful in chronic dysentery, diarrhoea, cholera, hemicrania, tubercular glands, paralysis and epileptic fits of children. The root of *S. trifoliatus* used as a collyrium in sore eyes and ophthalmia. The seeds of *S. trifoliatus*

are used to stimulate the uterus in childbirth and to increase mensuration⁸. Pericarps of *S. delavayi* are also used as natural surfactants, being exported from China to Japan as a substitute of *Sapindus mukorossi*⁹. Seeds of *S. emarginatus* contains anti inflammatory oil, traditionally used to purify the blood.

SOLUBILIZING PROPERTIES OF SAPONINS ISOLATED FROM SAPINDUS

Mukurozi - saponins [8, 9] and bisdesmoside from pericarps of *Sapindus mukorossi*, greatly increased the water solubilities of the co-occurring monodesmosides. The mode of solubilizing properties of these saponins was investigated. These bisdesmosides also increased the solubilities of yellow OB and progesterone in phosphate buffer⁹. Kimata and coworkers was observed the solubilising properties of monodesmosides [15-17] and bisdesmosides [11,12,14] isolated from pericarps of *S.mukorossi*. It was observed that the monodesmosides [15-17] were sparingly soluble in water in pure state with tremendous yield and these monodesmoside [15-17] showed remarkable promotion of absorption of an antibiotic, sodium ampicin, from rat intestine or rectum, while the bisdesmoside 5-7 did not¹⁸

BIOLOGICAL ACTIVITIES

Anti-Inflammatory Activity

Takagi and coworkers examined the anti-inflammatory activity of hederagenin and crude saponin isolated from *S. mukorossi*, utilising carrageenin-induced edema, granuloma pouch and adjuvant arthritis in rats. The effects of these agents on vascular permeability and acetic-acid-induced writhing in mice were also examined. Anti-inflammatory activity on carrageenin edema was observed after intraperitoneal and oral administration of crude saponin, whether hederagenin and the other agents showed activity only when administered¹⁰. The aqueous extract of *S.emarginatus* leaves for four different solvents such as Aqueous, 1,4-dioxan, methanol and acetone showed antibacterial activity against *Pseudomonas testosteroni* NCIM5098 and *Proteus morgani* NCIM2040. The maximum inhibitory activity was shown by TDi (1,4-dioxan extract) where as minimum activity was shown by TMe (methanol extract) and TAc (acetone extract) and TAq (water extract)⁹.

Cytotoxic Activity

Kuo and co workers tested the cytotoxic effect of saponins isolated from the galls of *S.mukorossi*. The preliminary bioassay data revealed that saponins [39, 41-43] showed moderate cytotoxic activity (ED₅₀~9-18µg/ml) against human tumor cell lines (Hepa59T/VGH, NCI, HeLa and Med)²²

Molluscicidal Activity

Huang and coworkers checked the molluscicidal activity of hederagenin saponins [6,19,20,43-45] isolated from *S. mukorossi* against golden apple snails including bacteria like Pomacea and Canaliculata²³.

Anti-Platelet-Aggregation Activity

Huang and coworkers demonstrated that five new tirucallane type saponins, saponinmusaponins [66-70] from the galls of *S. mukorossi* showed moderate activity in a 12-*O*-tetradecanoylphorbol- 13-acetate (TPA)-induced Epstein- Barr virus early antigen (EBV-EA) activation assay²⁷.

Anti-diabetic Activity

In 2009 S. Jeyabalan and coworkers studied the antihyperglycemic effects of alcoholic extract of *S.emarginatus* at different doses in glucose-loaded hyperglycemic and normal fasted rats. The study also showed that the level of total hemoglobin, glycosylated-hemoglobin, serum urea, serum creatinine, and lipid profiles measured in alloxan induced diabetic rats which show Antidiabetic activity³⁸.

Anti-hyperalgesic activity

S. trifoliatum had studied the effect of aqueous pericarps extract of fruits in an *in vivo* migraine hyperalgesic model. They suggested that antagonism to dopamine D₂ might underlie the mechanism involved in the anti-hyperalgesic activity of the plant extract³⁹.

CONCLUSION

The main objective of this review is to present the whole research carried out with species of the genus *Sapindus*, in order to organize the data produced. Many species of this genus have been used as traditional medicines for various ailments. The earlier reports on chemical investigation and pharmacological evaluation showed that the members of genus *Sapindus* contain a number of bio-active novel compounds of different nature like saponins and sesquiterpene oligoglycosides etc. As literature illustrates that, many biological and pharmacological activities were shown by fractions of crude extracts and isolated substances. Furthermore, the chemically unknown species may have become a source of novel drugs; therefore detail chemical analysis is required to isolate bio-active constituents from genus *Sapindus* and to trace out their biological activities. Thus, it can be concluded that the genus *Sapindus* can play an important role in modern medicinal system in near future.

REFERENCES

1. Evans WC, Trease, Evans. Pharmacogony. 13th edition. Balliere Tindall. 1989; 9:7020-1357.
2. Tanaka O, Tamura Y, Masuda H, Mizutani K. Application of saponins in foods and cosmetics: saponins of Mohova Yucca and *S.mukorossi* gaertn, saponin used in food and agriculture. Waller and Yamasaki, plenum press, New York. 1996.

3. Kasai R, Fujino H, Kuzuki T, Wong WH, Goto C, Yata N, Tanaka O, Yasuhara F, Yamaguchi S. Acyclic sesquiterpene oligoglycosides from pericarps of *S.mukorossi*. *Phytochemistry*. 1986; 25: 871-876.
4. *Sapindus vitiensis* Gray A. Germplasm Resources Information Network. United States Department of Agriculture. 2007-04-30.
5. Kirtikar and Basu. *Indian Medicinal Plants*. 2004; 1: 632-35.
6. Singh N, Kaur A, Yadav K. A reliable *in vitro* protocol for rapid mass propagation of *S.mukorossi* Gaertn. *Nature and Science*. 2010; 8:41-47.
7. Anonymous, the useful plants of India, Publications and Information Directorate. CSIR. New Delhi. 1992.
8. Pelegrini DD, Tsuzuki JK, Amado CAB, Cortez DA.G, Ferreira ICP. Biological activity and isolated compounds in *S.saponaria* L. and other Plants of the Genus *Sapindus*. *Lat. Am. J. Pharm.* 2008; 27:922.
9. Nakayama K, Fujino H, Kasai R, Mitoma Y, Yata N, Tanaka O. Solubilizing properties of saponins from *S.mukorossi*, gaertn. *Chem.Pharm.Bull.* 1986; 34:279.
10. Takagi K., Park E-H., Kato H., Anti-inflammatory activities of hederagenin and crude saponin isolated from *S.mukorossi* gaertn. *Chem. Pharm. Bull.* 1980; 28:1183.
11. Chirva VY, Kintya PK, Sosnovskii VA, Krivenchuk PE, Zykova NYa. Tri terpene glycosides of *S.mukorossi*-D part 2 structure of sapindoside A and sapindoside B. *Khim Prir Soedn (Tashk)*. 1970; 6:218-221.
12. Chirva VY, Kintya PK, Sosnovskii VA, Zolotarev BM. Tri terpene glycosides of *S.mukorossi* part 3 structure of sapindoside C. *Chemistry of Natural Compounds (English Translition of Khim. Prir. Soedn)*. 1973; 6:380-381.
13. Chirva VY, Kintya PK, Sosnovskii VA, Zolotarev BM. Tri terpene glycosides of *S.mukorossi* part 5 structure of sapindoside D *Khim. Prir. Soedn. (Tashk)* 1973; 6:316-319.
14. Chirva VY, Kintya PK, Sosnovskii VA, Zolotarev BM. Tri terpene glycosides of *S.mukorossi* part 5 structure of sapindoside E. *Chemistry of Natural Compounds (English Translition of Khim. Prir. Soedn)*. 1973; 6:440-442.
15. Linde H. Uberinhaltsstoffe der perikarpein von *S.mukorossi* gaertn. *Arch. Pharm.* 1979; 312:416-425.
16. Triterpenoid saponin (I-III) isolated from peels of *S.mukorossi*. *Jpn.* 1982; 20:299.
17. Kimata H, Nakashima T, Kokubun S, Nakayama K, Mitima Y, Kitahara T, Tanaka O. Saponins of pericarps of *Sapindus mukorossi* Gaertn. and solubilisation of monodesmosides by bisdesmosides. *Chem..Pharm.Bull.* 1983; 31:1998-2005.
18. Azhar I, Usmanghani K, Perveen S, Ali MS, Ahmad VU. Two triterpenoidal saponins from *S.mukorossi* Gaertn. *Pak Jour of Pharma Sci.* 1993; 6:71.
19. Azhar I, Usmanghani K, Perveen S, Ali MS, Ahmad VU. Chemical constituents of *S.mukorossi* gaertn. *Pak Jour. of Pharma Sci.* 1994; 7:33.
20. Huang C, Liao SC, Chang FR, Kuo YH, Wu YC. Molluscicidal Saponins from *Sapindus mukorossi*. *J. Agric. Food Chem.* 2003; 51:4916-4919.
21. Kuo YH, Huang HC, Kuo LMY, Hsu YW, Lee KH, Chang FR, Wu YC. New demmarane-type saponins from galls of *S.mukorossi*. *J. Agric. Food Chem.* 2005; 53:4722.
22. Sengupta A, Basu SP, Saha S. Triglyceride composition of *S.mukorossi* seed oil. *Lipids*. 1975; 10:33-40.
23. Zikova NI, Krivenchuk PE. Chemical study of the flavonoids from the leaves of *S.mukorossi* gaertn. *Farm. Zh.* 1970; 25:43-45.
24. Ni W, Hua Y, Liu HY, Teng RW, Kong YC, Hu XY, Chen CX. Tirucallane-Type Triterpenoid Saponins from the Roots of *S. mukorossi*. *Chem. Pharm. Bull.* 2006; 54:1443.
25. Huang HC, Wu MD, Tsai WJ, Liao SC, Liaw CC, Hsu LC, Kuo YH. Triterpenoids saponins from the fruits and gallsof *S. mukorossi*. *Phytochemistry*. 2008; 69:1609.
26. Huang HC, Sai WJ, Natschke LM, Tokuda H, Lee KS, Wu YC, Kuo YH. Sapnmsaponins F-J Bioactive Tirucallane – Type Saponins from the Galls of *S. Mukorossi*. *J.Nat.Prod.* 2006; 69:763.
27. Ni W, Hua Y, Teng RW, Kong YC, Chen CX. New tirucallane-type triterpenoid saponins from *S.mukorossi* Gaetn. *J of Nat. Prod. Res.* 2004; 6:205.
28. Huang HC, Tsai WJ, Liaw CC, Wu SH, Wu YC, Kuo YH. Anti-platelet Aggregation Triterpene Saponins from the galls of *Sapindus mukorossi*. *Chem. Pharm. Bull.* 2007; 55:1412.
29. Wong WH, Kasai R, Choshi W, Nakagawa Y, Mizutani K, Ohtani K, Tanaka O. Acyclic sesquiterpene oligoglycosides from pericarps of *Sapindus delavayi*. *Phytochemistry* .1991; 30:2699-2702.
30. Lemos TLG, Mendes AL, Sousa MP, Braz Filho R. *Fitoterapia*. 1992; 6:515-517.
31. Lemos TLG, Mendes AI, Sousa MP, Braz-Filho R. *Fitoterapia*. 1994; 65:557.
32. Ribeiro A, Zani CL, Alves TMA, Mendes NM, Hamburger M, Hostettmann K. *Int. J. Pharmacogn.* 1995; 33:177.
33. Gupta DR, Ahamad B. Emarginatosides B and C Two new Saponins from *S. emarginatus*. *Ind. J. of Chem.* 1990; 29B:268-270.
34. Mahabusarakam W, Towers GHN, Tuntiwachwuttikul P, Wiriyachitra P. Pesticidal triterpenoid saponins of the pericarps of *S. emarginatus*. *J. of the Sc. Soc. of Thialand.* 1990; 16:187.
35. Jain SC. Isolation of flavonoids from soap nut of *S.emarginatus*. *Vahl. Indian J Pharm.* 1976; 38:141.
36. Kasai R, Nishi M, Mizutani K, Miyahara I, Moriya T, Miyahara K, Tanaka O. Trifolioside II an acyclic sesquiterpene oligoglycoside from Pericarps *S. trifoliatus*. *Phytochemistry*. 1988; 27:2209.
37. Morikawa T, Xie Y, Asao Y, Okamoto M, Yamashita C, Muraoka O, Matsuda H, Pongpiriyadacha Y, Yuan D, Yoshikawa M. Oleanane type triterpene oligoglycosides with pancreatic lipase inhibitory activity from the pericarps of *S. rarak*. *Phytochemistry*. 2009; 70:1166-1172.
38. Jeyabalan S, Palayan M. Antihyperglycemic and antidiabetic activity of leaves extracts of *S.emarginatus* Vahl. *Asian Biomedicine*. 2009; 3:313.
39. Arulmozhi DK, Veeranjanyulu A, Bodhankar SL, Arora SK. Effect of *Sapindus trifoliatus* on hyperalgesic *in vivo* migraine models. *Braz. J. of Med. and Bio. Res.* 2009; 38:469.

TABLE 1: ISOLATED COMPOUNDS FROM GENUS SAPINDUS

Name of species	Plant part used	Chemical constituents	Ref
<i>S.mukorossi</i>	Fruit husk	Hederagenin[1]; platycodigenin [2]; saikogenin [3]; oleanolic acid [4]	10
	Pericarps	Hederagenin3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranoside [5]; Hederagenin3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl(1 \rightarrow 2)- β -D-xylopyranoside [6];	11
	Fruits	hederagenin3- <i>O</i> - α -L-arabinopyranosyl(2 \rightarrow 1)- α -L-rhamnopyranosyl(3 \rightarrow 1)- β -D-xylopyranosyl(4 \rightarrow 1)glucopyranoside [7];	12
	Pericarps	hederagenin3- <i>O</i> - α -L-arabinopyranosyl(2 \rightarrow 1)- α -L-rhamnopyranosyl(3 \rightarrow 1)- β -D-xylopyranosyl(4 \rightarrow 1)glucopyranosyl(2 \rightarrow 1)gluco-pyranoside [5 \rightarrow 1]rhamnopyranoside [8];	13
	Fruits	hederagenin3- <i>O</i> - α -L-arabinopyranosyl(2 \rightarrow 1)- α -L-rhamnopyranosyl(3 \rightarrow 1)- β -D-xylopyranosyl,28-arabinopyranosyl(2 \rightarrow 1)- α -L-rhamnopyranosyl(3 \rightarrow 1)xylopyranosyl(4 \rightarrow 1)glucopyranosyl[(6 \rightarrow 1)rhamnopyranosyl](2 \rightarrow 1)glucopyranoside [9];	14
	Fruits and galls	stigmasterol [10],	15
	Peels	hederagenin3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl(1 \rightarrow 2)- α -L-arabinopyranoside,28-di- <i>O</i> -glycoside [11]; hederagenin3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl(1 \rightarrow 2)- β -D-xylopyranosyl,28-di- <i>O</i> -glycoside [12]; hederagenin3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl(1 \rightarrow 2)- α -L-arabinofuranosyl,28-di- <i>O</i> -glycosides [13]; hederagenin3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl,28-di- <i>O</i> -glycoside [14]	16
	Pericarps	hederagenin3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl(1 \rightarrow 2)- α -L-arabinopyranoside [15]; hederagenin3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl(1 \rightarrow 2)- α -L-arabinofuranosyl [16]; hederagenin3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl(1 \rightarrow 2)- β -D-xylopyranosyl-4-acetyl [17]; Hederagenin3- <i>O</i> -(3,4-di- <i>O</i> -acetyl- β -D-xylopyranosyl)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [18]; Hederagenin,28-di- <i>O</i> -glycosides [19]	17
	Pericarps	1- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranoside-12- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [20]; hederagenin12- <i>O</i> - α -rhamnopyranosyl-(1 \rightarrow 2)- β -glucopyranoside-1- <i>O</i> - α -rhamnopyranosyl-(1 \rightarrow 2)-[α -rhamnopyranosyl-(1 \rightarrow 3)]- β -glucopyranoside [21]; hederagenin1,12-bisglycoside- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranoside [22]; hederagenin 1,12-bisglycoside- <i>O</i> - α -rhamnopyranosyl-(1 \rightarrow 2)-[α -rhamnopyranosyl-(1 \rightarrow 3)]- β -glucopyranoside [23]; 1- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -rhamnopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranoside-12-hydroxy-all-trans-farnesol [24]; 1- <i>O</i> - α -rhamnopyranosyl-(1 \rightarrow 2)-[α -rhamnopyranosyl-(1 \rightarrow 3)]- β -glucopyranoside-12-hydroxyfarnesol [25]; 12-hydroxy-all-trans-farnesol [26]; 1-hydroxylinalool [27]; GoshonosideF1 [28]; 8-hydroxygeraniol [29]; β -glucosidegeraniol [30]; 11(S)(E,E)-2,6-dodecadiene-3,7,11-trimethyl-1,12-diol [31]	18
	Fruits	3- <i>O</i> -{ α -L-arabinopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranosyl(3 \rightarrow 1)- α -L-rhamnopyranosyl}-hederagenin [32]; 3- <i>O</i> -{ β -D-xylopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranosyl(3 \rightarrow 1)- α -L-rhamnopyranosyl}hederagenin[33]	19
	Fruits	Eupha 7,24-dien-3-tetradecanoate[34]; eupha 7,24-dien-3-pentadecanoate [35]; eupha 7,24-dien-3-hexadecanoate [36]; eupha,7,24-dien-3-heptadecanoate [37]; eupha,7,24-dien-3-nonadecanoate [38]; eupha,7,24-dien-3-heneicosanoate [39];	20
	Pericarps	11(S)-2,6(E,E)-dodecadiene-3,7,11-trimethyl-1,12-diol-1,12-bis- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 3)]-6- <i>O</i> -acetyl- β -D-glucopyranoside [40]	21
	Pericarps	Hederagenin3- <i>O</i> -(2,4- <i>O</i> -Di-acetyl- α -L-arabinopyranoside)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [41]; Hederagenin3- <i>O</i> -(3,4- <i>O</i> -Di-acetyl- α -L-arabinopyranoside)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [42]; Hederagenin3- <i>O</i> - α -L-Arabinopyranoside [43]	22
	Galls	3 β ,7 β ,20(S),22-tetrahydroxydammar-24-ene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [44]; 3 β ,7 β ,20(S),22,23-pentahydroxydammar-24-ene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [45]; 3 β ,7 β ,20(S),22,25-pentahydroxydammar-23-ene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [46]; 25-methoxy-3 β ,7 β ,20(S),22-tetrahydroxydammar-23-ene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [47]; 25-methoxy-3 β ,7 β ,20(R)-trihydroxydammar-23-ene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [48]; 4-Allyl-2-methoxyphenyl-6- <i>O</i> - α -L-arabinopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside [50]	23
	Leaves	4-Allyl-2-methoxyphenyl-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside [49];	24
	Roots	3- <i>O</i> - α -L-arabinopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-arabinopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-21,23R-epoxyl tirucalla-7,24-diene-21 β -ethoxy-3 β -ol [51]; 3- <i>O</i> - β -D-xylopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[β -L-arabinopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-21,23R-epoxyl tirucalla-7,24-diene-21 β -ethoxy-3 β -ol [52]; 3- <i>O</i> - β -D-xylopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-arabinopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-21,23R-epoxyl tirucalla-7,24-diene-21 β -methoxy-3 β -ol [53]; 3- <i>O</i> - α -L-arabinopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-21,23R-epoxyl tirucalla-7,24-diene-21 β -ethoxy-3 β -ol [54]; 3- <i>O</i> - α -L-arabinopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-21,23R-epoxyltirucalla-7,24-diene-21 β -methoxy-3 β -ol [55]; 3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl-21,23R-epoxyl tirucalla-7,24-diene-21 β -ethoxy-3 β -ol [56]	25
	Fruits and Galls	hederagenin-3- <i>O</i> -(3- <i>O</i> -acetyl- α -L-arabinopyranosyl)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [57]; hederagenin-3- <i>O</i> -(4- <i>O</i> -acetyl- α -L-arabinopyranosyl)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [58]; hederagenin-3- <i>O</i> -(2,3- <i>O</i> -diacetyl- β -D-xylopyranosyl)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [59]; hederagenin-3- <i>O</i> -(2,4- <i>O</i> -diacetyl- β -D-xylopyranosyl)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [60]; hederagenin3,7,20(S)-trihydroxydammar-24-ene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [61]; 3,7,20(R)-trihydroxydammar-24-ene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-	26

		glucopyranoside [62]	
	Galls	21 β -methoxy-3 β ,21(<i>S</i>),23-(<i>R</i>)-epoxytirucalla-7,24-diene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside [63]; 21 α -methoxy-3 β ,21(<i>R</i>),23-(<i>R</i>)-epoxytirucalla-7,24-diene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside [64]; 21 α -methoxy-3 β ,21-(<i>R</i>),23(<i>R</i>)-epoxytirucalla-7,24-diene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [65]; 21 β -methoxy-3 β ,21(<i>S</i>),23(<i>R</i>)-epoxytirucalla-7,24-diene-3- <i>O</i> - α -L-dirhamnopyranosyl-(1 \rightarrow 2,6)- β -D-glucopyranoside [66]; 21 α -methoxy-3 β ,21(<i>R</i>),23(<i>R</i>)-epoxytirucalla-7,24-diene-3- <i>O</i> - α -L-dirhamnopyranosyl-(1 \rightarrow 2,6)- β -D-glucopyranoside [67]	27
	Roots	3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-arabinopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl (21,23 <i>R</i>)-epoxyl tirucalla-7,24-diene-(21 <i>S</i>)-ethoxyl-3 β -ol [68]; 3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-arabinopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl (21,23 <i>R</i>)-epoxyl tirucall-7, 24-diene-(21 <i>S</i>)-methoxyl-3 β -ol [69]	28
	Galls	21 α -methoxy-3 β ,21(<i>R</i>),23(<i>S</i>)-epoxytirucall-7,24-diene-3- <i>O</i> - β -D-glucopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [70]; 21 α -methoxy-3 β ,21(<i>R</i>),23(<i>S</i>)-epoxytirucall-7,24-diene-3- <i>O</i> - α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside [71]	29
S. delavayi	Pericarps	Oleanolic acid 3- <i>O</i> - α -L-arabinopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [72]; monodesmoside [73]; oleanolic acid 3- <i>O</i> - β -D-xylopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [74]; 3- <i>O</i> - β -D-xylopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside-3-acetyl [75]; 3- <i>O</i> - α -L-arabinopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl(1 \rightarrow 2)- β -D-arabinopyranosyl-3,5-acetyl [76];	30
	Pericarps	1- <i>O</i> - α -rhamnopyranosyl-(1 \rightarrow 2)-[α -rhamnopyranosyl-(1 \rightarrow 3)]- β -glucopyranoside-12-hydroxyfarnesol [77]; 1- <i>O</i> - α -rhamnopyranosyl-(1 \rightarrow 2)-[α -L-arabinopyranosyl-(1 \rightarrow 3)]- β -glucopyranoside-12-hydroxyfarnesol [78]; 1,12- <i>O</i> -bisglycoside- α -rhamnopyranosyl-(1 \rightarrow 3)-[α -rhamnopyranosyl-(1 \rightarrow 2)]- α -arabinopyranosyl-(1 \rightarrow 3)-[α -rhamnopyranosyl-(1 \rightarrow 2)] [79]; 1,12- <i>O</i> -bisglycoside- α -L-rhamnopyranosyl-(1 \rightarrow 3)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosyl-(1 \rightarrow 3)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosyl-(1 \rightarrow 3)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)] [80]; 1,12- <i>O</i> -bisglycoside- α -L-rhamnopyranosyl-(1 \rightarrow 3)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosyl-(1 \rightarrow 3)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)] [81];	31
S. saponaria	Fruit peel	3- β - <i>O</i> -[α -L-rhamnopyranosyl-(1 \rightarrow 3)]- β -D-glycopyranosyl]-hederagenin [82]	32
	Whole plant	3- <i>O</i> -{4-acetyl- β -D-xylopyranosyl-(1-3)- α -L-rhamnopyranosyl-(1-2)- α -L-arabnopyranosyl}-hederagenin [17]; 3- <i>O</i> -{ α -L-arabinopyranosyl-(1-3)- α -L-rhamnopyranosyl-(1-2)- α -L-arabnopyranosyl}-hederagenin [15]; 3- <i>O</i> -{ β -D-xylopyranosyl-(1-3)- α -L-rhamnopyranosyl-(1-2)- α -L-arabnopyranosyl}-hederagenin [6];	33
S. emarginatus	Pericarps	hederagenin 3- <i>O</i> - α -L-arabinopyranoside [83]; hederagenin3- <i>O</i> -(2- <i>O</i> -acetyl- β -D-xylopiranosyl)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [84]; 23- <i>O</i> -acetyl-hederagenin3- <i>O</i> -(4- <i>O</i> -acetyl- β -D-xylopyranosyl)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [85]; oleanoic acid 3- <i>O</i> -(4- <i>O</i> -acetyl- β -D-xylopyranosyl)-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside [86]	34
	Fruits	hederagenin-3- <i>O</i> - β -D-galactopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosyl [87]; hederagenin-3- <i>O</i> - β -D-galucuronopyranosyl-(1 \rightarrow 2)- β -D-galactopyranoside [88]	35
	Pericarps	3- <i>O</i> -{ β -D-xylopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl (1 \rightarrow 2)- α -L-arabinopyranosyl} hederagenin [6]; 3- <i>O</i> -{ α -L-arabinopyranosyl (1 \rightarrow 3)- α -L-rhamnopyranosyl(1 \rightarrow 2)- α -L-arabinopyranosyl}; [15]; β -sitosterol [89];	36
S. trifoliatus	Pericarps	1,12-bis- <i>O</i> - β -D-xylopyranosyl(1 \rightarrow 3)-[α -L-rhamnopyranosyl(1 \rightarrow 2)]- β -D-glucopyranoside [90]; 15-hydroxyfarnesol [95]; 15- <i>O</i> - β -xylopyranosyl(1 \rightarrow 3)-[α -rhamnopyranosyl(1 \rightarrow 2)]- β -glucopyranoside farnesol [92]; 15- <i>O</i> - β -xylopyranosyl(1 \rightarrow 3)-[α -rhamnopyranosyl(1 \rightarrow 2)]- β -glucopyranoside-15-hydroxyfarnesol [93]; Sesquiterpene oligoglycoside [94]	37





