PHYTOCHEMISTRY OF *SAPINDUS MUKOROSSI* AND MEDICINAL PROPERTIES

D.K. Singh
Ex-Head, Department of Zoology, D.D.U. Gorakhpur University, Gorakhpur-273009, U.P., India

Devesh Pratap Singh
Assistant Professor, Pulmonary Medicine, All India Institute of Medical Sciences, Gorakhpur-273008, U.P., India

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Contents

Summary

Sapindus mukorossi Gaertn, distributed in tropical and sub-tropical region of Asian continent, is an important medicinal plant. The objective of the present chapter is to explore the knowledge of traditional practices as well as modern science on phytochemistry and medicinal properties of *S. mukorossi*. The major phytochemicals isolated and identified from the different parts of the *S. mukorossi* are triterpenoids, saponins of oleanane, dammaranes, tirucullanes. Phytochemicals such as flavonoids, carbohydrates, fatty acids, phenols and fixed oils are also found in fruit, seed and leaves of *S. mukorossi*. All these phytochemicals, found in different parts of *S. mukorossi*, are potential sources of different medicines. Its medicinal properties are based on traditional experiences passed from generation to generation. Scientists from various disciplines are now working on different aspects of medicinal properties of *S. mukorossi*. They have reported that crude as well as isolated phytochemicals possess pesticidal, herbicidal, piscicidal, anti-microbial, anti-cancer and free radical scavenging, skin wound healing, detergent, anti-gonorrheal, spermicidal, anti-platelet aggregation, anti-diabetic, anti-melanogenesis, neuritogenic, hepatoprotective, anti-inflammatory, anti-asthmatic, anti-protozonal, anti-lipid peroxidation activity. Recently, role of *S. mukorossi* on dental pulp measenchymal stem cells, as renewable bio-surfactants of

cotton fabrics and its role in nanoparticle synthesis of gold, silver and platinum are reported by different researchers.

1. Introduction

Sapindus mukorossi Gaertn, belongs to sapindaceae family, is a deciduous medicinal plant of China, Japan and India. Sapindaceae is valuable family consisting of 150 genera and 2000 species of plants (Evans, 2009). *Sapindus mukorossi* is cultivated and self grown in deep clay loamy soil with annual rainfall of 150-200 mm at an altitudes of 500 m in tropical and sub-tropical region (Jiang et al., 2013), mainly in Indo-Malaysian region of the world. Average height of *S. mukorossi* is about 12-15 m, but in some cases it may attain height up to 18 meters. (Chadha, 1972).

Genus *Sapindus* includes mainly three major species:

(1) American species:

- *Sapindus saponaria*,

(2) Two Asian species (Goyal et al., 2014).:

- *S. mukorossi*,
- *S. trifoliates*

(3) Other *Sapindus* species:

- *S. delayaye,*
- *S. detergens,*
- *S. emariginates,*
- *S. laurifolia,*
- *S. marginatus,*
- *S. vitiensis,*
- *S. tomentosus,*
- *S. oahuensis* and
- *S. rarak*

They are reported in different parts of the South East Asia, America, Samoa and Fiji (Adeyemi and Ogundipe, 2012, Singh and Sharma, 2019).

The color of *S. mukorossi* stem bark is greenish/pale-gray to brown. Leaves are paripinnate, with 5 to 15 cm long lanceolate leaflets. Flowers are bisexual, small and terminal, compound panicles. Flowering occurs in the month of May-June and fruits ripen during October-November on leafless tree. Fruits are globose fleshy. After ripening colour of fruit changes from yellow orange to dark brown. (Chadha 1972, Singh and Sharma, 2019).

Tree **Leaves** **Tree with flowers**

Tree with green fruits **Tree with dry fruits** **Dry fruits**

Photo 1. Tree, flowers and fruits of *S.mukorossi*

2. History

Sapindus mukorossi is an ancient tree found in China and India. The book titled "Saint Heritage of India" points out that "Matsyendra Nath", who was the founder of "Hatha Yoga" was enlightened below a soapnut tree in 9th to 10th century. The "Historical Dictionary of Ancient India" mentioned that soapnuts were found in 6th century BC. Some notes on the history of soapnut, soap and washerman of India between 300 BC and 1900 AD indicate its use even at earlier than 6th century (theindianvegan.blogspot.com. The Earth of India, 2013).

3. Traditional Uses

From ancient times, botanicals are used as main medicinal sources to treat the various health problems. Medicine systems of Ayurveda, Unani and Chinese are rich sources of plant derived products. In developing countries, still today plant based medicines are frequently used in the treatment of various diseases. Eighty percent world population in the poor countries uses herbal medicine in primary health care (Vines, 2004). People, in different parts of the world, have trust on traditional plant based medicines, particularly in Africa, part of Asia and Central South America (Allkin, 2017). Continuous use of synthetic drugs and antibiotics in treatment of various health problems has created many health hazards in human population. Now, worldwide discussions have created awareness among the people, social workers, health experts and scientists, that herbal medicines are only remedy for safe and reliable treatment for various health problems.

It has been reported that approximately 3,90,800 species of plants are estimated on the earth (Chapman, 2009). Out of these 28,187 plant species are currently recorded as having medicinal value (Allkin, 2017). *Sapindus* is well known for its ethno-medicinal use. In traditional practice *S. mukurossi* is used as detergent and insecticide (Uphof, 1959). Fruits are used against head lice (Barwick, 2004, Goyal et al., 2014, Singh and Sharma, 2019) and number of common health problems, such as excessive salivation, pimples, epilepsy, chlorosis, migranes, eczema and psoriasis (Chopra et al., 1986, Kirtikar and Basu, 1991). Pericarp of *S. mukorossi* fruit in Japan is known as "enmei-h" means life prolonging pericarp, whereas in China it is called "Wu-humnan-zi", the "non illness fruit" (Goyal et al., 2014). The fruit and seeds are used as a cure for epilepsy in Northern India (http://www.worldagroforestry.org). Lather of the fruit is used in treatment of burns (Manandhar, 2002). The seeds of *S.mukorossi* are crushed and boiled to make a liquid. This liquid is added in certain Indian milk sweet "Rasogullas" (Facciola, 1998). Seeds are also used to bleach cardamom seeds to improve flavours and colour of spices (Facciola, 1998). Dental caries are treated with *S. mukorossi* seeds (www.worldagroforestry.org). In Vietnam, *S. mukorossi* wood is used for making furniture, sawing board, plywood etc. (Hoang et al., 2004).

The fruits of *S. mukorossi* are used in treatment of snake bite, scorpion stings and dandruff (Kunwar et al., 2009). The fruit is used as expectorant, demulcent, emetic, anthelmintic, purgative, and in treating epilepsy/cholera (Bajracharya, 1979, Baral and Kurmi, 2006). In Indian state Assam, fruit paste of *S. mukorossi* is used as febrifuge (Chadha, 1972). Leaves of the tree are used as animal fodder (Kiritker and Basu, 1991). Seeds of *Sapindus* are also made into rosaries (Chadha, 1972). Soapnuts are used as detergent for washing cloth. They are also used by Indian Jewelers for restoration of brightness in tarnished ornaments. In Kashmir soapnuts are the best soap for washing woolen shawls (Chadha, 1972).

4. Phytochemistry

Plants of family sapindaceae contain saponins, cyanogenetic, glycosides and cyclitols. The seed fats contain a high proportion of about 65-70% oleic acid (Evans, 2009). More than 103 phytochemicals including flavonoids, triterpenoids, carbohydrates, fatty acids, phenols, fixed oil and saponins are identified in fruit, seed and leaves of *Sapindus mukorossi* (Evans, 2009, Sharma et al., 2011, Upadhyay and Singh, 2012, Goyal et al., 2014, George and Shanmugam, 2014, Yadav et al., 2018). *S. mukorossi* seed contains 23% oil with 92% triglycerides. The triglyceride fraction of oil contains 30% oleo-palmitoarachidin glyceride, 13.3% oleo-diarachidin glyceride and 56.7% di-olein type glyceride, dioleo-palmitin, dioleo-stearin and dioleo-arachidin (Dev and Guha, 1979, Suhagia et al., 2011, Singh and Sharma, 2019). Seed oil also contains non-glyceridic component cyanolipid (1-cyano-2-hydroxymethyl prop-1-ene-3-ol) (Sengupta and Basu, 2006). Leaf of *S. mukorossi* contains flavonoids like quercetin, apigenin, kaempferol and rutin (Zikova and Krivenchuk, 1970). Fruits of *S.mukorossi* contain sesquiterpenoidae glycosides and six different fatty esters of tetracyclic triterpenoids (Azhar et al., 1994). Different triterpene, saponins of oleanane, dammarane and tirucullane were reported in galls, fruits and roots of *S. mukorossi* (Suhagia et al., 2011).

The major phytochemicals found nearly in each part of *S. mukorossi* are saponins (10%: 11.5%) (Francis et al., 2002; Heng et al., 2014), which are mostly responsible for the various pharmacological activities (Upadhyay and Singh, 2012; Goyal et al., 2014). Though saponins are reported in different parts of *S. mukorossi* they are intense in the fruit. Saponins are high molecular weight secondary metabolite compounds with high polarity and divergent biological activities (Evans, 2009). Mostly they occur as complex mixtures with the components differing slightly in the sugars attached are in the structure of aglycone. They are hydrolyzed by acids to give an aglycone (sapogenin), sugars and uronic acid. On the basis of algycone (sapogenin) two kinds of saponins are identified i.e. the steroidal (teracyclic triterpenoids) and pentacyclic triterpenoid types (Figure 1). Both are common in their origin by mevalonic acid and isoprenoid unit.

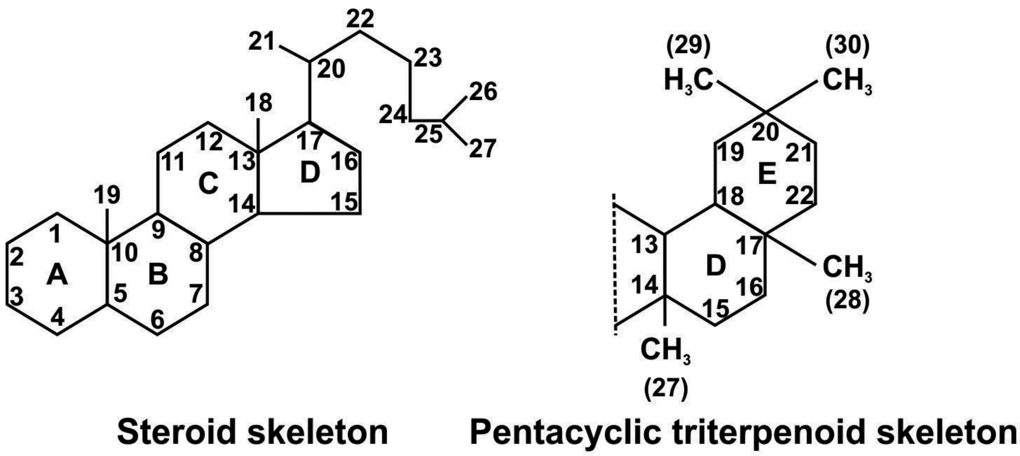

Figure 1. Types of saponins on the basis of attached aglycone

The steroidal saponins are less widely distributed in nature than penta-cyclic triterpenoid type. These saponins are common in many monocotyledonous plant families. The pentacyclic triterpenoid saponins are rare in monocotyledonous and found abundantly in dicontyledonous plant families. Sapinidaceae family is one of them (Evans, 2009). Saxena et al., (2004) has identified six different types of saponins from the fruits of *Sapindus mukorossi*, with the help of liquid chromotography (LC) and mass spectroscopy (MS). They reported Sapindoside A., Sapindoside B, Sapindoside C, Sapindoside D, Mukorozisaponin E, and Mukorozisaponin Y. Saponins are structurally related compounds of triterpenoid aglycone (sapogenin), attached with one or more oligosaccharide moieties by glycosidic linkage. Sapogenin may contain one or more unsaturated C-C bonds. The oligosaccharide chain is usually linked at the C_3 position (monodesmosidic). Additional sugar moieties may attached at the $C_{2,6}$ or $C_{2,8}$ position (bidesmosidic) (Francis et al., 2002). Complexity of the saponin structure is due to variability of the aglycone structure, nature and attachment position of side chain on the aglycone. However, classification of saponins is difficult, a state of the art on classification based on the biosynthesis of the saponin carbon skeleton in plants was extensively discussed by Vincken et al., (2007) and Evans (2009) (Figure 2).

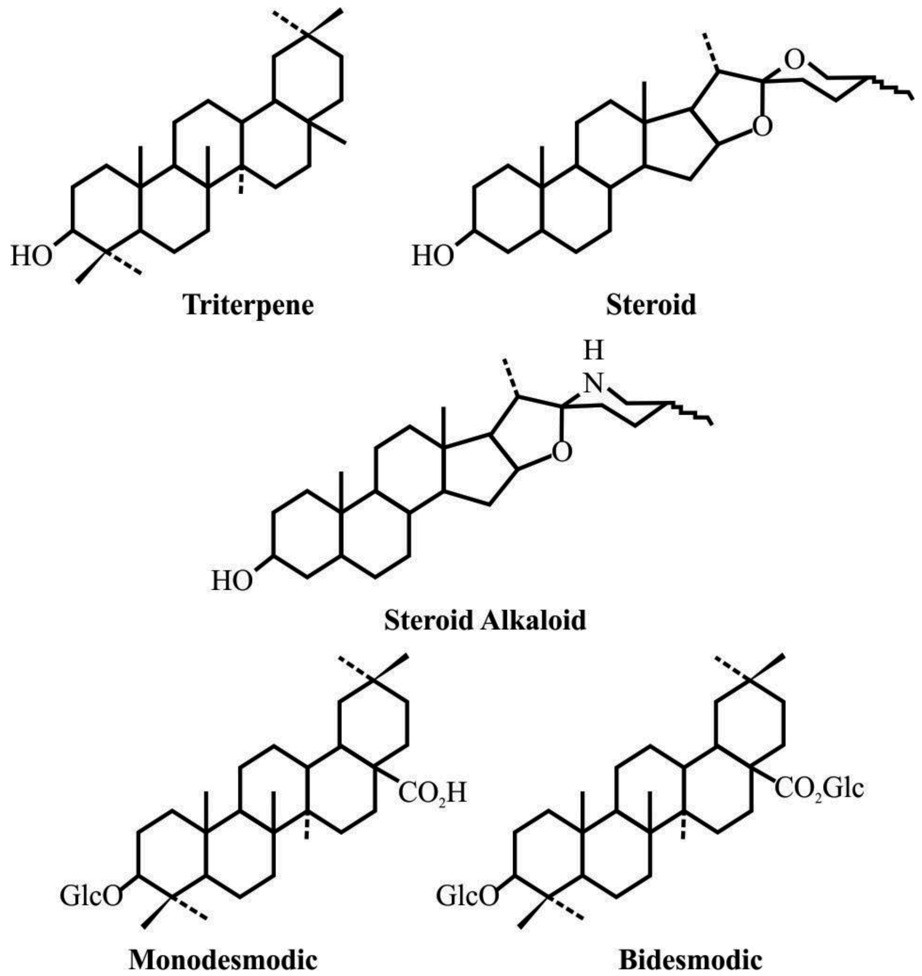

Figure 2. Different classes of saponin

Different types of triterpene, saponins of oleanane, dammarane and tirucullane types are isolated from the galls, fruits and roots of *S.mukorossi* (Suhagia et al., 2011, Upadhyay and Singh, 2012; Goyal et al., 2014). Oleanane type triterpenoid saponins named Sapindoside A and B (Figures 36 and 37) were reported from the fruits of S*apindus mukorossi* (Chirva et al., 1970a). Sapindoside C (Figure 38) (Chirva et al., 1970b), Sapindoside D (Figure 39) (Chirva et al, 1970c), which is a hexaoside of hederagenin, and Sapindoside E (Figure 40) (Chirva et al., 1970d), a nonaoside of hederagenin, was isolated and identified from the methanolic extract of the fruits of *Sapindus mukorossi*.

Dammarane-type saponins, named sapinmusaponins A and B (Figures 13 and 14), C-E (Figures 17, 18 and 19) with three known phenylpropanoid glycosides, were isolated from the galls of *Sapindus mukorossi* (Yao et al., 2005). Tirucallane: type saponins, sapinmusaponnis F-J (Figures 20-24), were isolated from the galls of *Sapindus mukorossi* as reported by Huang et al., (2006). The structures of all these saponins were elucidated on the basis of spectroscopic analysis including ID and 2D NMR techniques.

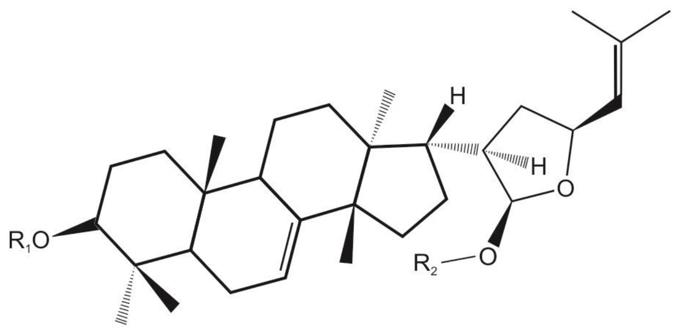

FIGURE: STRUCTURE OF SAPIMUKOSIDES A-J

Figure	R_1	R_2
3	3-Ara Glc 2-Rha	H
4	Glc_6-Rha	H
5	3-Ara Glc 2-Rha	Et
6	3-Ara Glc 2-Rha	Me
7	3-Ara Glc 2-Rha_3-Ara	Et
8	3-Ara Glc 2-Rha_3-Xyl	Et
9	3-Ara Glc 2-Rha_3-Xyl	Me
10	3-Ara Glc 2-Rha_3-Ara	Et
11	3-Rha Glc 2-Rha_3-Ara	Me
12	Glc_6-Rha E	

Abbreviations
Glc: β-D-Glucopyranosyl
Rha: α-L-Hamnopyranosyl
Ara: α-L-Rabinopyranosyl
Xyl: β-D-Xylopyranosyl

Figures 3 to 12. Structure of different saponins isolated from the *S. mukorossi*

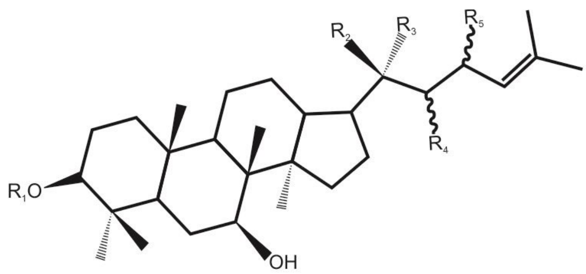

FIGURE: STRUCTURE OF SAPIMUSAPONINS A-B AND O-P

Figure	R_1	R_2	R_3	R_4	R_5
13	Glc_2-Rha	H	OH	OH	H
14	Glc_2-Rha	H	OH	OH	OH
15	Glc_2-Rha	OH	CH_3	H	H
16	Glc_2-Rha	CH_3	OH	H	H

Figures 13 to 16. Structure of different saponins isolated from the *S. mukorossi*

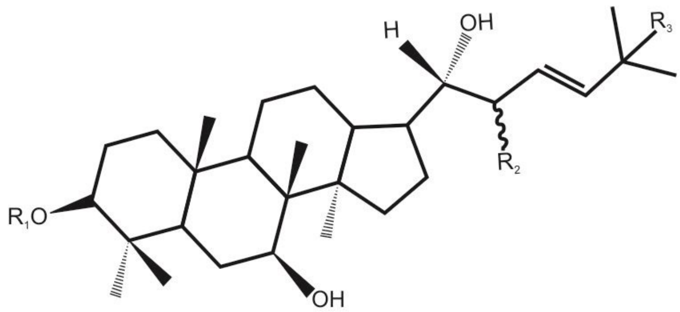

FIGURE: STRUCTURE OF SAPIMUSAPONINS C-E

Figure	R_1	R_2	R_3
17	Glc_2-Rha	OH	OH
18	Glc_2-Rha	OH	OCH_3
19	Glc_2-Rha	H	OCH_3

Figures 17 to 19. Structure of different saponins isolated from the *S. mukorossi*

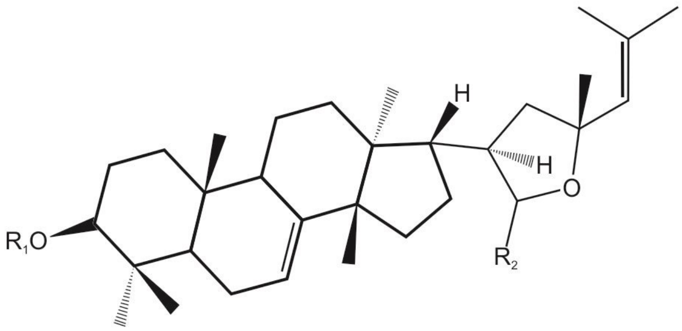

FIGURE: STRUCTURE OF SAPIMUSAPONINS F-J, Q-R

Figure	R$_1$	R$_2$
20	Glc$_6$-Rha	β-OCH$_3$
21	Glc$_6$-Rha	α-OCH$_3$
	3-Ara	
22	Glc$_2$-Rha	α-OCH$_3$
	2-Rha	
23	Glc	β-OCH$_3$
	6-Rha	
	2-Rha	
24	Glc	α-OCH$_3$
	6-Rha	
25	Glc$_2$-Glc	α-OCH$_3$
	2-Glc	
26	Glc	α-OCH$_3$
	6-Rha	

Figures 20 to 26. Structure of different saponins isolated from the *S. mukorossi*

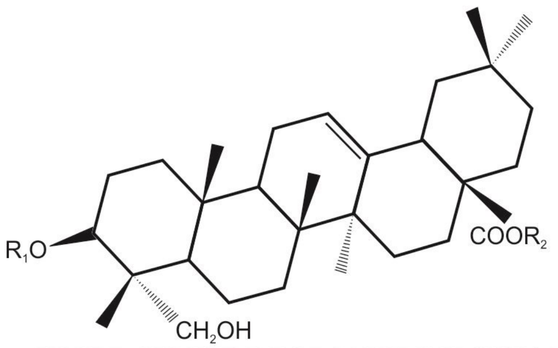

FIGURE: STRUCTURE OF SAPIMUSAPONINS K-N, SAPINDOSIDE A-E, MUKOROZI SAPONIN E1, G, Y2, Y2 & X

Figure	R$_1$	R$_2$
27	Ara$_2$-Rha$_3$-Ara$_3$-OAC	H
28	Ara$_2$-Rha$_3$-Rha$_4$-OAC	H
	2-OAC	
29	Ara$_2$-Rha$_3$-Xyl	H
	3-OAC	
	2-OAC	
30	Ara$_2$-Rha$_3$-Xyl	H
	4-OAC	
	3-OAC	
31	Ara$_2$-Rha$_3$-Xy	H
	4-OAC	
32	Ara$_2$-Rha$_3$-XYL$_4$-OAC	H
33	Ara$_2$-Rha$_3$-Xyl	Glc$_2$-Glc
34	Ara$_2$-Rha$_3$-Xyl	Glc$_2$-Glc
35	Ara$_2$-Rha$_3$-Xyl	Glc$_2$-Glc
36	Ara$_2$-Rha	H
37	Ara$_2$-Rha$_3$-Xyl	H
38	Ara$_2$-Rha$_3$-XYL$_4$-Glc	H
	6-Rha	
39	Ara$_2$-Rha$_3$-XYL$_4$-Glc	H
	2-Glc	
		6-Rha
40	Ara$_2$-Rha$_3$-Xyl	Ara$_2$-Rha$_3$-XYL$_4$-Glc
		2-Glc

Figures 27 to 40. Structure of different saponins isolated from the *S. mukorossi*

Triterpene saponins of oleanane type like, Sapinmusaponin K-N (Figures 27-30), Mukorozisaponin G and E1 (Figures 31-32), Sapindoside A and B along with dammarane types like Sapinmusaponin O and P (Figures 15 and 16) were isolated from fruits and the galls of *Sapindus mukorossi* as per Huang et al., (2008). Nakayama *et al.*, (1986), isolated Mukorozisaponin Y1 (Figure 33), Y2 (Figure 34), X (Figure 35) from the pericarp of *Sapindus mukorossi*.

Fractionation of an ethanolic extract of the galls of *Sapindus mukorossi* has resulted in the isolation of two tirucallane type triterpenoid saponins, sapinmusaponin Q and R (Figures 25-26), along with three known oleanane type triterpenoid saponins: sapindoside A, sapindoside B, and hederagenin-3-O-[β-D-xylopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)+-α-L arabinopyranoside (Huang et al, 2007). The roots of *Sapindus mukorossi* contain tirucallane-type triterpenoid saponins like Sapimukoside A and B (Teng et al., 2003), Sapimukoside C and D (Ni et al., 2004). Further, investigation of the roots of *Sapindus mukorossi* by Ni et al., (2006) reported the presence of Sapimukosides E-J (Ni et al., 2004). The structures of Sapimukosides A-J are shown in Figures 3-12, respectively. Chemical details of different saponins from *Sapindus mukorossi* are given in Table 1.

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Biographical Sketeches

Prof. D.K. Singh is Ex-Head, Department of Zoology at D.D.U. Gorakhpur University, Gorakhpur, U.P., India, and has been actively engaged in the study of molluscan physiology, biochemistry and snail control for four decades. He has successfully isolated and identified pure molluscicidal compounds from more than three dozen medicinal plants and observed their mode of action on snails at the cellular level. He is an internationally recognized expert in the field of formulation and use of synthetic and bio-pesticides for integrated vector management. Prof. Singh serves as a referee for the Third World Academy Award sponsored by TWA, Italy. He has published 213 research papers (18 review articles) in over 108 reputed international journals as well as three reference books and three book chapters. He is a fellow of the Zoological Society of India and Academy of Environmental Biology, a life member of various national and international academic societies and editor and reviewer of various international journals.

Dr. Devesh Pratap Singh, M.D., Department of Pulmonary Medicine, All India Institute of Medical Sciences, Gorakhpur, U.P., India. He has published 9 national and international research papers.