

## Natural distribution of saponin

Saponins are widely distributed in nature, being present in more than 1730 plant species belonging to 104 families, 627 of these species were found to contain triterpenoid saponins and 127 to contain steroidal saponins (Tschesche and Wulff 1973) i.e. triterpenoidal saponins are most abundant in plant kingdom. The pentacyclic triterpenoid saponins of rare occurrence in monocotyledones. They are more frequent in dicotyledones, being abundant in *Caryophyllaceae*, *Sapindaceae*, *Polygalaceae* and *Sapotaceae* and of common occurrence in *Phytolaccaceae*, *Chenopodiaceae*, *Ranunculaceae*, *Berberidaceae*, *Papaveraceae*, *Linaceae*, *Zygophyllaceae*, *Rutaceae*, *Myrtaceae*, *Cucurbitaceae*, *Araliaceae*, *Umbelliferae*, *Primulaceae*, *Oleaceae*, *Lobeliaceae*, *Campanulaceae*, *Rubiaceae* and *Compositae*.

Triterpenoid saponins are also present in *Amarantaceae*, *Papaveraceae*, *Violaceae*, *Magnoliaceae*, *Eberaceae*, *Verbenaceae*, and *Campanulaceae* (Paris 1963) It's not easy, however, to determine whether or not the individual glycosides are specific to certain species, or common to a large number.

Among the best known compounds of the triterpenoid class are aescine (glycoside of aecigenin) which has only been isolated from *Aesculus hippocastanum*, on the other hand the saponins of

*Agrostemma githago*, which are derived from gypsogenin, are similar to those in other *Caryophyllaceae*. Aralin (glucoside of aralidin) has only been isolated from *Aralia japonica*, whereas cyclamin (*Cyclamin europaeum*) is probably present in other *Primulaceae*, although its structure is not completely known. It is the same with gypsophilo saponin (*Gypsophila*), which appears to be present in a number of *Caryophyllaceae*. The glycosides of hederagenin (hederins) were first isolated from *Heder helix*, but have also been detected in other genera of *Araliaceae* and *Sapindaceae*.

Kensil *et al* (1991) purified saponins from one of the species of the Rosaceae, the chilean soap-tree (*Quillaja saponaria*) Molina bark by silica gel and reverse phase chromatography.

The most specific compound, perhaps, of the steroidal saponins (Paris 1963) is digitonin, which is only found in *Digitalis*.

The steroidal saponins of the Liliaceae have, however, been most examined, because of their potential interest as precursors for cortisone synthesis. Numerous saponins were isolated from *Chlorogalum*, *Dioscorea*, *Yucca*, *Trillium*, *Agave*, *Hechtia*, *Manfreda* and so on. Often, one species was found to contain several saponins, and some saponins were found in neighbouring species and genera, so that there appears to be no close connection between the presence of these compounds and botanical classification.

Other families have been extensively *examined* (*Amaryllidaceae*, *Dioscoreaceae*). It was found that although more than half of the species examined contained haemolytic substances, only a quarter of these contained steroidal saponins. In the different genera, the proportion with saponins varied widely, being 47% in *Yucca*, 24% in *Agave* and only 10% in *Dioscorea*. Of fourteen sapogenins isolated, Six (diosgenin, gitogenin, hecogenin, sarsasapogenin, smilagenin and yammogenin) were found to be relatively specific; hecogenin in *Agave*, diosgenin in *Dioscorea*, and sarsasapogenin in *Yucca*. More interestingly a relationship was found between the configuration of the steroid ring and certain groups of plants. For example, some species of *Agave* yielded *trans* derivatives (tigogenin, hecogenin, gitogenin), while others gave *cis* compounds (smilagenin). The same happens in *Yucca* and *Dioscorea*. This considerable investigation indicates the need to undertake systematic research to obtain results of real value in chemical plant taxonomy (Paris 1963).

As previously shown, saponins occur primarily in the plant kingdom, but this fact is not exclusive as they could be also produced by some marine animals, such as seaslug, and starfish (Shibata, 1977). Saponin of lanosterol type is a small and less important group of animal origin (Kamel 1995).

## Biosynthesis of saponin

The isoprene rule for the biogenesis of terpenes stated that terpenes are multiples of  $C_5$  units linked together head to tail. It soon appeared that neither steroids, nor several other related compounds obeyed the rule, and the skeleton could not be dissected into isoprene units.

The key acyclic precursor of the aglycon part of saponin (sapogenin) is considered to be squalene which is synthesized from acetate via mevalonic acid pathway (Bonner, 1965). The enzyme squalene-oxidocyclase I mediates an attack by a hydroxyl cation at C-3 followed by a concerted non stop cyclization of squalene into 5- or 6- membered rings (Nicholas 1967). This cyclization proceeds in various ways (genetically controlled) to give rise to various triterpenes or sterols which are lanosterol. Lanosterol ( $C_{30}$ ) is converted to cholesterol. Heftmann, (1965) demonstrated the metabolic conversion of cholesterol to diosgenin (sapogenin). Kryptogenin is intermediate in this conversion. (Fig. 1).

The results of Henry *et al.*, (1992) strongly suggested that two of the 2,3 - oxidosqualene- cyclases namely 2,3- oxidosqualene- amyrine cyclase, and 2, 3 - oxidosqualene-cycloartenol cyclase, are regulating steps in the isoprenoid pathway orienting the biosynthetic flux towards either tetracyclic or pentacyclic triterpenes.