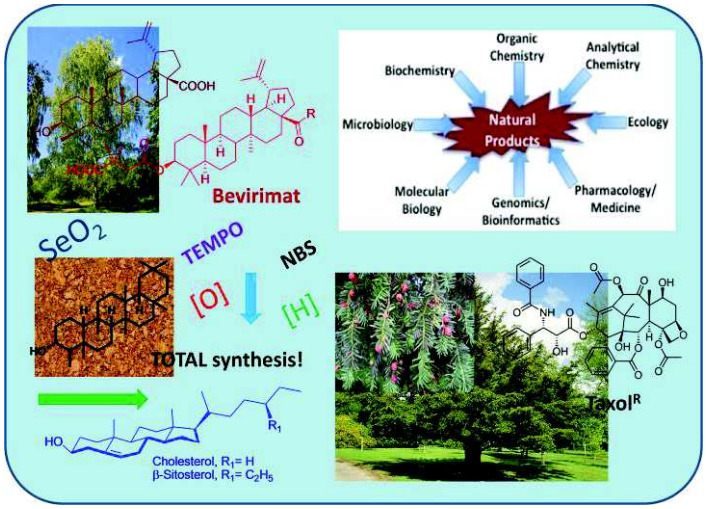
Abstract

The thesis entitled "Transformative reactions on carbocyclic compounds" comprises four chapters and a brief of their contents are as follows:

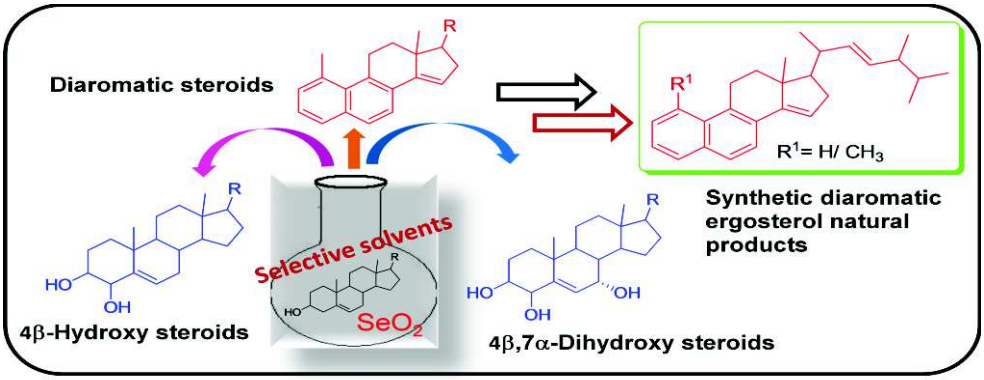
Chapter I: Carbocyclic compounds and their transformative reactions: A general perspective on natural products chemistry



Natural products include any substance produced by life. Now, due to the large extent of catenation capability of carbon, it can produce a large number of molecules made solely by them which in turn, implies that nature provides a huge number of carbocyclic compounds. And in virtue, nature itself is the richest source of a variety of carbocyclic compounds. Two or more carbocycles can be joined together in a number of different fashions to produce a number of different groups of carbocyclic compounds. And among the broad spectrum of all kinds of natural products, if we look for more abundant, easily available and highly useful carbocyclic natural products, we found mainly the steroids and terpenoids. Thus, having the opportunity of working in the field of natural products chemistry, the various known / new transformative reactions were carried out on some selective major steroids (cholesterol, β-sitosterol, ergosterol, diosgenin) and comparatively less-explored but highly potential pentacyclic triterpenoid- friedelin.

As a consequence, to have a general and very brief overview on the transformative reactions on these substrates, the present chapter demonstrates the important findings revealed so far.

Chapter II: First report of solvent selective steroidal aromatization, efficient access to 4β,7α-dihydroxy steroids, and syntheses of natural diaromatic ergosterols



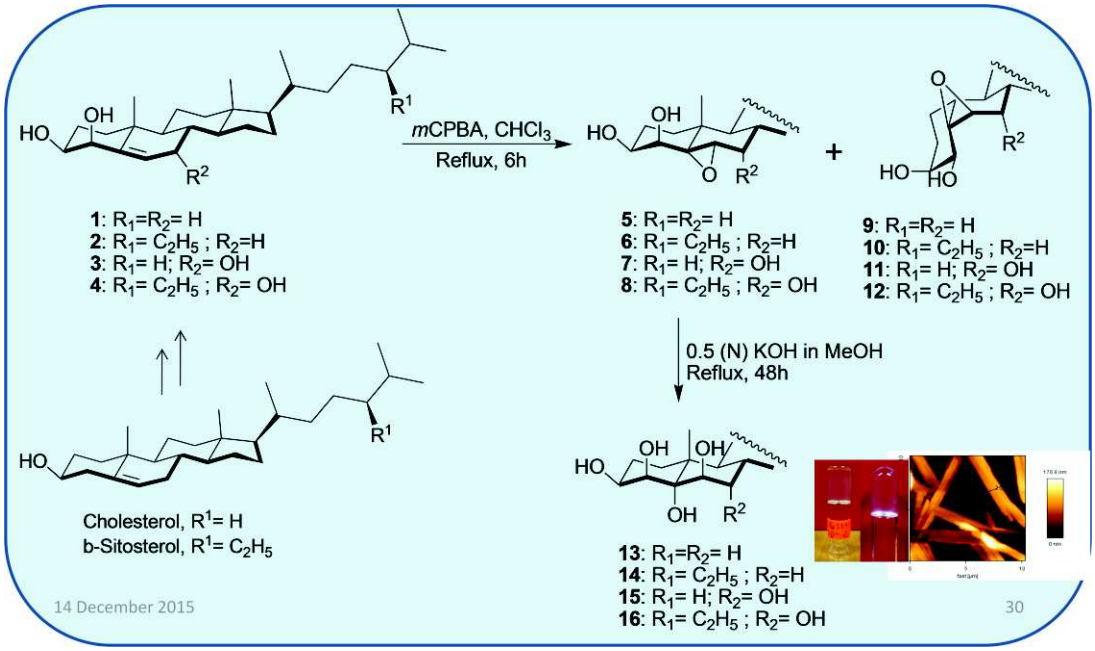
This chapter elaborates the syntheses of natural diaromatic ergosterol derivatives and other steroidal analogues in an unprecedented simple, one-pot and convenient synthetic route. In the process, the key factor- the selectivity of the solvents (having 1,4-ethereal oxygens) towards aromatization has been established. Of note, only ethereal solvents with two oxygens such as 1,4-dioxane, 1,3-dioxalane, 1,2-dimethoxy ethane and 1,2-diethoxy ethane were found able to result selective aromatization. Thorough solvent-dependant study of the model reaction reveals valuable product composition which may be exploited, specially, for the synthesis of biologically important steroid molecules. Efficient access to 4β,7α-dihydroxy cholesterol is also described. By using the established solvent-selective steroidal methodology, the yield of the natural product, diaromatic ergosterol was optimized at 12%. Analogous chemistry of β-sitosterol and diosgenin is also reported. Furthermore, single crystal X-ray crystallography has resolved the molecular structures, for the first time in their class, of similar diaromatic cholesterol derivative and triacetylated 4β,7α-dihydroxy cholesterol derivative.

Chapter III: Polyhydroxy and epoxy-polyhydroxy steroids: design, synthesis and study of their preliminary gelation behaviour

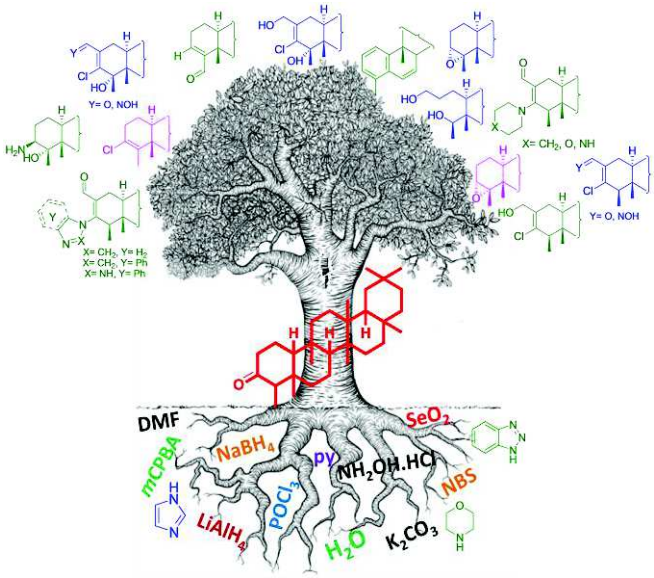
The present work associated with this chapter demonstrates basically two aspects of some new polyhydroxy steroids - designed synthesis and their preliminary gelation behavior.

Altogether sixteen polyhydroxy steroids (PHS, 12 new) of cholesteryl and β-sitosteryl series were synthesized and characterized. Among them eight (all new) are, in precise, epoxy-polyhydroxy steroids (5,6-epoxy-3β,4α-dihydroxy- and 5,6-epoxy-3β,4α,7α-trihydroxy-), of which the α-diastereomers were utilized further to synthesize novel new tetraols (3β,4β,5α,6β-tetrahydroxy-) and pentaols (3β,4β,5α,6β,7α-pentahydroxy steroids). Thus, epoxidation followed by alkaline-opening of the oxirane-ring of appropriate steroidal 5-ene-3β,4β-diols and -5-ene-3β,4β,7α-triols, to furnish novel steroidal tetrols and pentols respectively consequences, in practical, a three-step synthetic route for the transformation of 3β,4β,5α,6β-tetrahydroxy- and 3β,4β,5α,6β,7α-pentahydroxy steroids starting directly from their corresponding basic steroids, cholesterol and β-sitosterol.

As a new class of polyhydroxy steroids, preliminary gelation behavior of the molecules was evaluated. At 1% or below CGC (critical gelation concentration), five PHS derivatives were found to be gelators of some selective organic solvents. Some selective organogels were characterized through T_{gel} (gel melting temperature) and related physical parameters (ΔH etc.), rheological data, and by morphology analysis (electron microscopes).



Chapter IV: Syntheses of new friedelane triterpenoids: A-ring modifications including 2-*homo*derivatives



Syntheses of a number of A-ring modified friedelane triterpenoids have been accomplished. These also include the 2-*homo* derivatives for which, as the key step, the transformation of friedelin with Vilsmeyer-Haack reagent was used. 3-Chloro-2-formylfriedel-2-ene, the main product isolated from the reaction was transformed suitably into various derivatives and hence, following two or three simple steps starting from friedelin, it rendered possible to produce a library of C2,C3-, C3,C4-, and C2,C3,C4- functionalized friedelane triterpenoids. Besides, some useful methodologies were thus established during the various transformative attempts. These include a two-step aromatization of friedelin by *N*-bromosuccinimide, a one-pot dechlorination with simultaneous C-23 activation, and selective 4α-hydroxylation with simultaneous oxidation of allylic alcohol by selenium dioxide. Again, syntheses of some friedelane derivatives, *viz.*, 3β-amino-4α-hydroxy-, 2-carboxamide, 2,3-*seco*diol, 4α-hydroxy-3-chloro-2-formylfriedel-2-ene and 3-chloro-4α-hydroxy-2-hydroxymethylfriedel-2-ene, in a few steps, were found very much effective to enrich the A-ring modifications of friedelane triterpenoids. On the other hand, heterocycle-linked (to C3 of friedelanes) 2-*homo*friedelane derivatives were achieved. We believe to use these friedelane triterpenoids for future biological applications as well as to explore more interesting and usefull multifunctionalized derivatives of the particular class of pentacyclic triterpenoids.