Introduction
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Steroids are compounds of natural origin and play an important role in biological systems. Cholesterol is a component of cell membranes in Eucaryotes, and serves as substrate for production of bile acids and steroid hormones. In cells, steroids are recognised by antibodies and enzymes. Synthetic receptors of steroids have been also reported. Some resorcinne are hosts have shown capability of complexation of bile acids derivatives, cholesterol and corticosteroids, while cellophans have been tested for recognition of androsterone and estrogens. Water-soluble cyclophane receptors are found effective for complexation of bile acid salts. Steroids themselves have been used as building blocks for designing and construction of molecular receptors which serve for recognition of guest molecules of diverse chemical nature. Some excellent review papers have been published. The first attempts to synthesize artificial receptors of steroid type have been reported by groups of Guthrie and Ueda and McKenna et al. The major types of cyclic host structures derived from steroids are cyclocholates made of up to four bile acid units, cholaphanes which incorporate two or more bile acid residues joined together by spacer groups of diverse chemical character, and steroid cyclophanes. Other bile acid-based artificial receptors are molecular clefts and molecular tweezers. Cholesterol is one of the main constituents of membrane lipids and has been considered to govern the membrane fluidity and permeability of solutes.

Cholest-5-en-3β-ol (cholesterol) is a biomolecule essential to animals for membrane integrity and biosynthesis of steroid hormones, bile salts, and Vitamin D. Structurally, cholesterol is a 17 carbon carbocyclic ring with an eight-member chain, branched at C25 and C20, attached at C17 to the carbocyclic ring, a methyl group at C10, a double bond at C5-C6, and one hydroxyl group attached at C3. The carbocyclic ring is a four ring structure that is a modified form of cyclopentenophenanthrene. The modified cyclophanenantrene ring and hydrocarbon chain produce cholesterol’s highly hydrophobic nature. The hydroxyl group at C3 is cholesterol’s lone source of hydrophilicy. The hydrophobic carbocyclic ring portion of cholesterol facilitates cholesterol’s ability to insert into the hydrophobic portion of the cell membrane and stabilize it, as well as serving as the main structure in the synthesis of steroid hormones, bile salts, and Vitamin D.

We report here on the synthesis of a new type of cholesterol derivatives, in chapter I, II, III and IV.
In chapter I, I have been interested in synthesis of cholesterol derivatives with the help of double Mannich reaction of ketone with methylamine was reported by Scheiber and Nemes. Although some double Mannich reactions have been reported in recent years. This novel method allows the synthesis of azacyclic ketone functionalized alkylidene cyclopentanes in good to excellent yields and selectivities. We moved on to examine more useful electrophile trapping reactions that would allow the creation of new carbon-carbon and carbon heteroatom bonds which are moderately more successful. I have synthesized azacyclic \([2,4-c,d]-N\)-methylpiperidinocholest-5-en-3-one 47, \([6,8-c,d]-N\)-methylpiperidinocholest-4-ene-7-one 49 and its analogue 51, 53 from easily accessible steroidal ketones 46, 48, 50 and 52 which is the mimic’s of sparteine sufficiently.

In chapter II encouraged our interest in synthesizing several new compounds featuring various heterocyclic rings, attached to 4-thiazolidinone moieties. As a part of our aim to search for biologically active heterocycles containing sulfur and nitrogen, we have undertaken the synthesis of some steroidal 1,3,4-thiazolidinones, eg. cholest-5-en-(3\(R\))-spiro-3,3'-aminoethyl-1',3',4'-thiazolidinone 92, cholest-5-en-(3\(R\))-spiro-3,3'-[2"-(2"-phenyl-1"''',3'''',4''''-thiazolidinon-3''''-yl)ethyl]-1',3',4'-thiazolidinone 94, 5\(\alpha\)-cholestan-(6\(R\))-spiro-6,3'-aminoethyl-1',3',4'-thiazolidinone 97, 5\(\alpha\)-cholestan-(6\(R\))-spiro-6,3'-[2"-(2"'-phenyl-1''',3''',4'''-thiazolidinon-3''''-yl)]ethyl-1',3',4'-thiazolidinone 99, 3\(\beta\)-chloro-5\(\alpha\)-cholestan-(6\(R\))-spiro-6,3'-aminoethyl-1',3',4'-thiazolidinone 102, 3\(\beta\)-chloro-5\(\alpha\)-cholestan-(6\(R\))-spiro-6,3'-[2"-(2"'-phenyl-1''',3''',4'''-thiazolidinon-3''''-yl)]ethyl-1',3',4'-thiazolidinone 104, 3\(\beta\)-acetoxy-5\(\alpha\)-cholestan-(6\(R\))-spiro-6,3'-aminoethyl-1',3',4'-thiazolidinone 107, 3\(\beta\)-acetoxy-5\(\alpha\)-cholestan-(6\(R\))-spiro-6,3'-[2"-(2"'-phenyl-1''',3''',4'''-thiazolidinon-3''''-yl)]ethyl-1',3',4'-thiazolidinone 109.

In addition, of chapter III 1,3,4-oxadiazole constitute an important family of heterocyclic compounds. Since many of them display a remarkable biological activity.

Thus, inspired by these results obtained by earlier workers, we have made an attempt to synthesize steroidal pyrazoles and oxadiazoles from steroidal hydrazides belonging to cholestane series. Here, we have synthesized 3\(\beta\)-[(3'-methyl-5'-oxa-2'-pyrazolin-1'-yl)carbonylmethoxy]cholest-5-ene 111, from cholest-5-en-3\(\beta\)-O-acetyl hydrazide 110 using methyl acetoacetate. The treatment of compound 110 with benzoic acid or 4-chloro benzoic acid in presence of phosphorous oxychloride affords 3\(\beta\)-[5'-phenyl-1',3',4'-oxadiazol-2'-yl]methoxycholest-5-ene 112 and 3\(\beta\)-[5'-(4'-
chlorophenyl)-1',3',4'-oxadiazol-2'-yl]methoxycholest-5-ene 113. During the reaction, the acid was first converted to acid chloride, which subsequently reacted with compound 110 to give the corresponding acyl hydrazinocarbonyl compound, which underwent cyclodehydration to yield final products 112, 113. The compounds of 3\(\beta\)-[5'-{(4"-ethylphenyl)-1',3',4'-oxadiazole-2'-yl}methoxycholest-5-ene 114 and 3\(\beta\)-[5'-phenyl-1',3',4'-oxadiazole-2'-yl]methoxycholest-5-ene 112 are synthesized via cyclodehydration of diacylhydrazine. The cyclodehydration reaction condition was promoted by heat and anhydrous reagent POCl₃. The compound 110 was obtained from easily accessible ethyl-5-cholesten-3\(\beta\)-O-acetate 109. Compound 109 was obtained by treating cholest-5-en-3\(\beta\)-ol (cholesterol) 108 with ethyl chloroacetate. The structures of new compounds were established on the basis of analytical and spectral studies.

It might be expected that polymers of steroidal ketones (or ketone derivatives) would readily be formed in reaction media of high acidity or basicity. There seems, however, to be only two instances of an aldol type of product having been isolated in sufficient quantity and purity to have merited reporting in the literature.

Here in chapter IV, I am presenting new dimeric steroids namely that cholest-5-en-3\(\beta\)-pro-[6'a,5'-oxa]-5'a-cholest-3'-one 68, cholest-5-en-7\(\beta\)-pro-[4'a,5'-oxa]-5'a-cholest-7'-one 70 and 3\(\beta\)-substitutedcholest-5-en-7\(\beta\)-pro-[4'a,5'-oxa]-3'\(\beta\)-substituted-5'a-cholest-7'-ones 72 and 74 which were prepared from cholest-5-en-3-one 67, cholest-5-en-7-one 69 and 3\(\beta\)-substituted-cholest-5-en-7-ones 71 and 73 respectively by amine catalysed dimerization using reducing agent DMAP and xylene.