SYNOPSIS

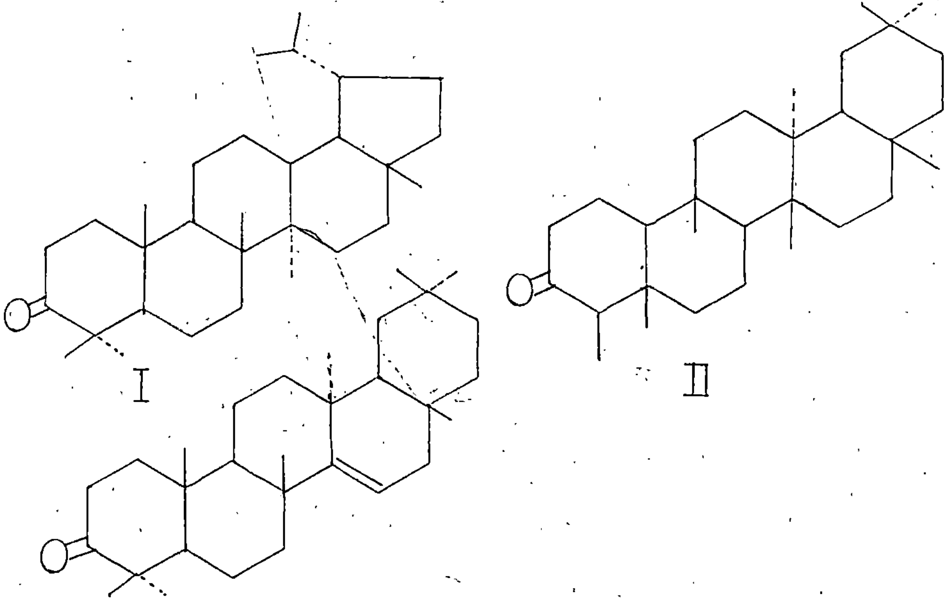
The work embodied in the present dissertation has been divided into two parts. Part I consists of oxidation of some triterpenoids, while isolation and identification of three plants of Flacourtiaceae family, namely, F. Jangomas, C. Kurzii and C. Graveolens have been incorporated in Part II. Part I has been divided into four chapters.

Chapter - I

In view of the fact that a substantial portion of Part I deals with oxidation of some triterpenoids by hydrogen peroxide in presence of selenium dioxide, it was felt pertinent to present a brief account of different oxidative transformation reactions with selenium dioxide, hydrogen peroxide and a combination of selenium dioxide and hydrogen peroxide. The review constitutes the subject matter of Chapter I of the thesis.

Chapter - II

This chapter deals with the oxidation of lupanone (I), friedelin (II) and taraxerone (III) by hydrogen peroxide in the presence of selenium dioxide.



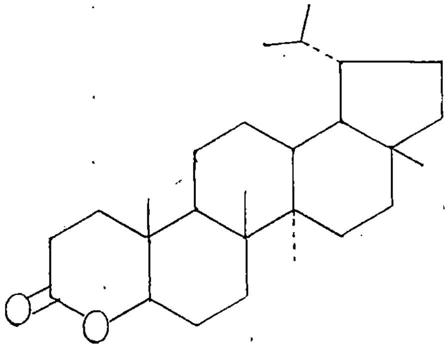
I

II

III

As the reaction results in bisdemethylation of ring A, some works on bisdemethylation has been reviewed in Section A.

Section B constitutes the results and discussion of the reaction of H_2O_2 with lupane in the presence of SeO_2 . It has been found that the reaction results in the conversion of ring A of the triterpenoid into δ-lactone (IV) by elimination of the gem dimethyl group. Other products formed as a result of the reaction include lup-1-ene-3-one (V), 2α-carboxy-A-nor-lupane (VI) and 2, 3-seco-lupane dicarboxylic acid (VII).



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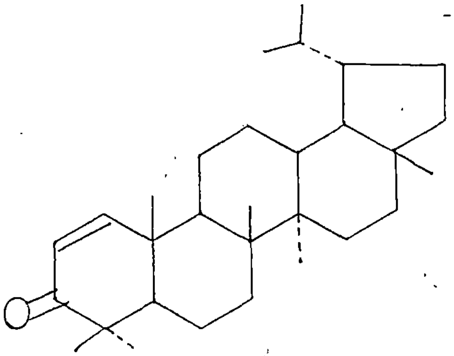

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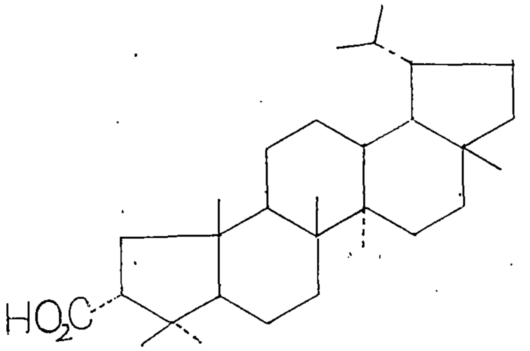

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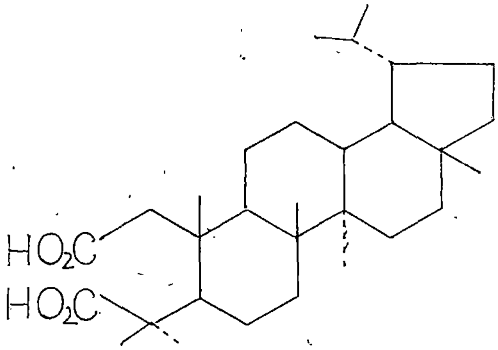
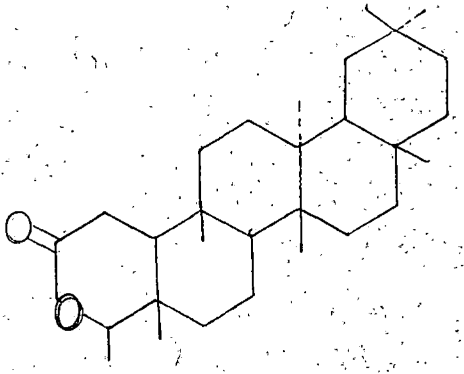
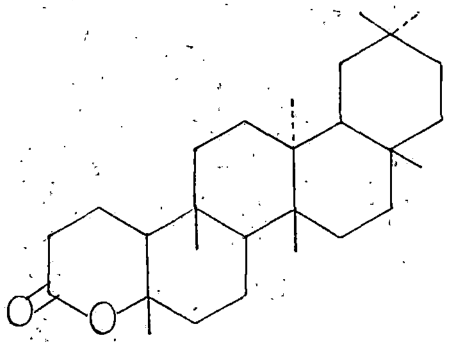


VII

The reaction of friedelin (II) with H_2O_2 in presence of SeO_2 in the same reaction medium has been reported in Section C of Chapter II. Friedelin also afforded a δ-lactone (VIII) but elimination of methyl group on C-4 position did not take place. The δ-lactone (VIII) is also different from the one (IX) reported earlier by oxidation of with peracetic acid. Other products isolated are 2,3-seco-friedelonic acid (X) and 2α-carboxy-A-nor-friedelin (XI).



VIII



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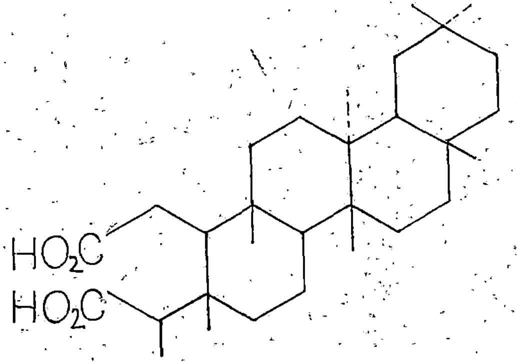
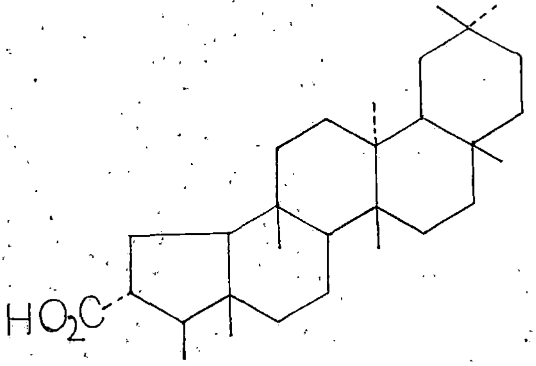
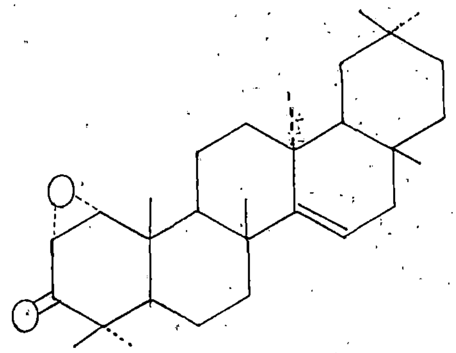


X

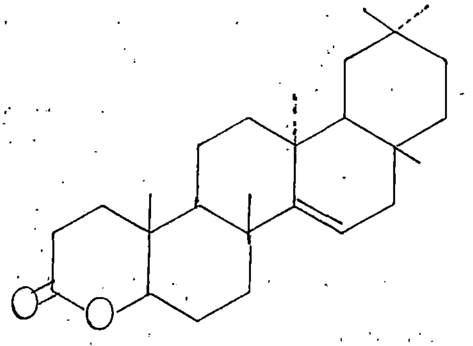


XI

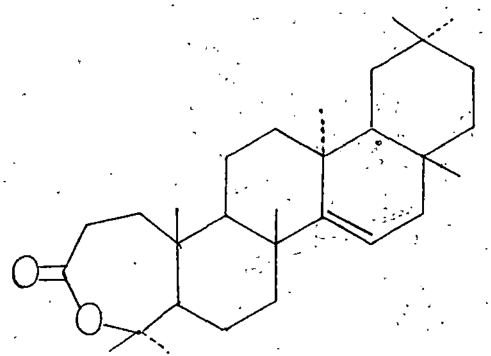
Section D contains the results of the reaction of hydrogen peroxide and selenium dioxide on Taraxerone (III). The products isolated are 1α, 2α-epoxy-3-one (XII); 4, 23, 24-tri-nor-taraxerene -3 → 5-olide, a δ-lactone (XIII) and taraxerene - ε -lactone (XIV) from neutral part and 2α-carboxy-A-nor-taraxerene (XV) together with taraxerene-2, 3-seco-dicarboxylic acid (XVI) from the acid part.



XII



XIII



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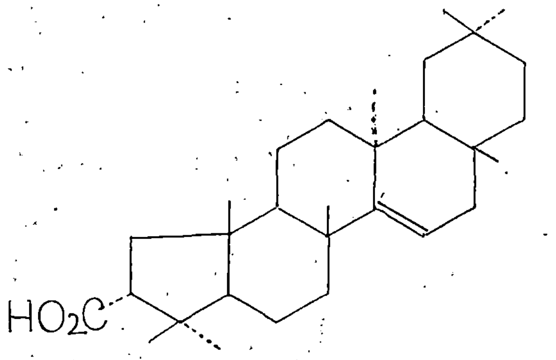

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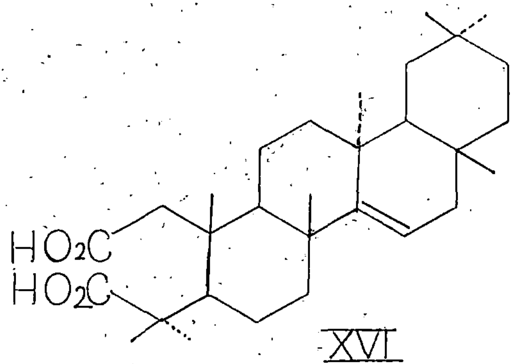


XVI

The possible mode of formation of α, β unsaturated ketone, dicarboxylic acids, A-nor-carboxylic acid and δ-lactones have been discussed in Section E.

The formation of α, β unsaturated ketone in the case of lupanone and 1α, 2α epoxide in the case of taraxerone, though in small quantities, indicate that dehydrogenation at positions α and β to the carbonyl group takes place. In the case of friedelin, however, dehydrogenation seems not to occur. The reason has been attributed to steric factor.

The formation of seco-dicarboxylic acids has been explained on the basis of intermediate stage of 2, 3 diketones, which in turn is further oxidised by H_2O_2 to carboxylic acids. The formation of A-nor-carboxylic acid, obtained in poor yield, has been explained on the basis of oxidation of 3-ketones by selenic acid followed by oxidation with hydrogen peroxide and subsequent rearrangement.

The formation of δ-lactone in the case of lupanone and taraxerone proceeds via the formation of ϵ lactone, which undergoes hydrolysis and by Baeyer-Villiger oxidation results in the formation of δ-lactone. In the case of friedelin the reaction follows a different path. It is probable that selenium dioxide converts friedelin to 2, 3 diketone. One mole of H_2O_2 may attack the diosphenol to give the intermediate α-keto-ϵ-lactone, which then undergoes hydrolysis to furnish the α-keto acid. The acid on decarboxylation furnishes 3, 4-seco-C-3-nor-4-hydroxy friedelin-2-carboxylic acid, which undergoes lactonisation to form the δ-lactone.

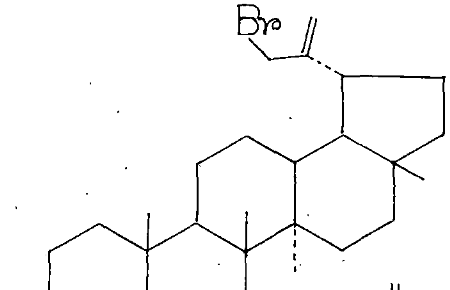
Section F describes the experimental details of the works contained in Chapter II.

Chapter-III

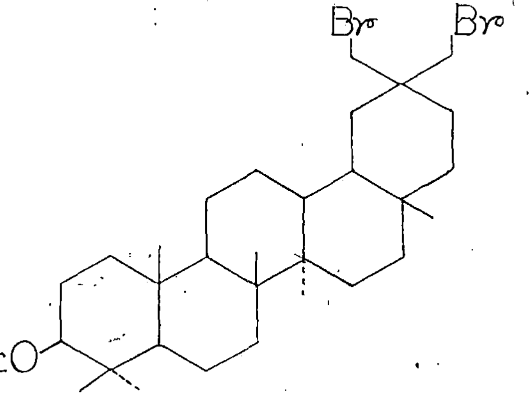
Chapter III contains the isolation and characterisation of the products formed as a result of reaction of N-bromosuccinimide with lupenyl acetate.

A short review of the reactions of N-bromosuccinimide with steroids and triterpenoids constitutes Section A of Chapter III. Particular emphasis has been given on bromination and dehydrobromination, oxidation of allylic methylene to carbonyl group and allylic hydroxylation.

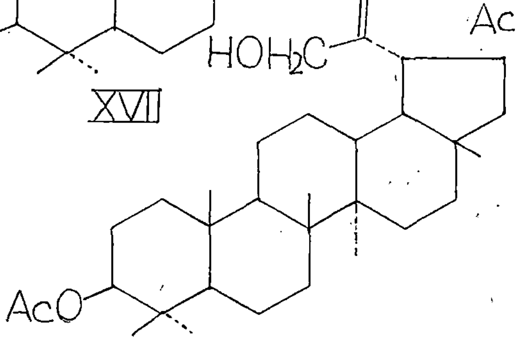
Section B contains results and discussion of the reaction of NBS with lupenyl acetate. Compounds (XVII), (XVIII) and (XIX) have been isolated and characterised.



XVII



XVIII



XIX

The formation of the dibromo compound has been proposed to take place following rearrangement of lupane system to oleanane system. It is suggested that 30-bromo-lup-20(29-en-3 -acetate has been attacked by the bromonium ion present in DMSO, the solvent that has been used in the reaction, on C 20-29 bond causing the formation of a carbonium ion, which probably compels carbon skeleton transformation from lupane to oleanane system.

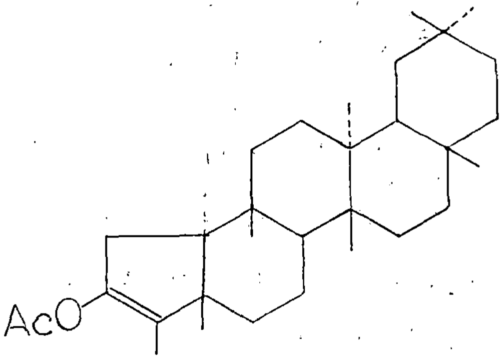
Section C contains the experimental details of Chapter III.

Chapter - IV

This chapter contains isolation and characterization of products formed following autoxidation of friedelin. A possible mode of formation has been suggested.

A short review of the works on autoxidation and isomerisation in ring A of some triterpenoids, namely, Euphol, Oleanolic acid, Lupeol, Lanostenyl acetate, -amyrone, Moretanone has been discussed in Section A.

Section B consists of results and discussion of the autoxidation of friedelin. The compounds identified are (XX), (XXI) and (XXII).



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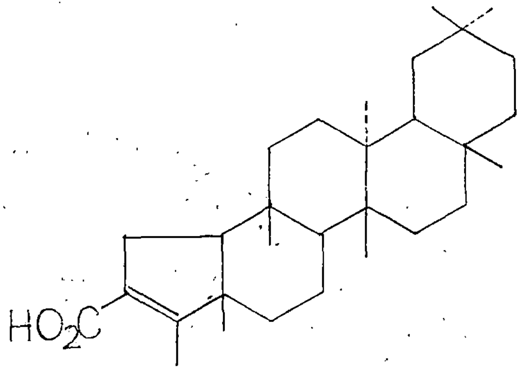
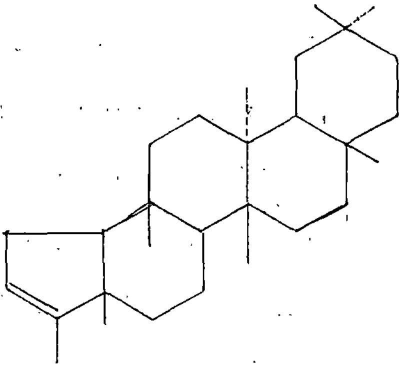


XXI



XXII

The formation of 3-nor-Δ2(4)-friedelin-2-acetate (XX) has been proposed to proceed through the formation of α-hydroperoxy ketone, which cleaved subsequently to seco-2-aldehyde-3-carboxylic acid. This undergoes further oxidation to form 2,3 seco-dicarboxylic acid, which upon cyclization forms the anhydride. The anhydride under basic medium rearranges to form β-keto acid. This undergoes decarboxylation followed by acetylation to afford compound XX.

Friedelin undergoes enolisation to give friedel-3(4)-en-3-ol, which may undergo oxygenation to form 3, 4-seco-4-keto-friedelin-3-carboxylic acid. This in turn cyclizes to give 3-nor-$\Delta^{2(4)}$-friedelin-2-carboxylic acid (XXI). This α,β unsaturated carboxylic acid undergoes easy decarboxylation in pyridine to yield the unsaturated hydrocarbon, the nor friedelin (XXII).

Section C describes the experimental details of Chapter IV.

Part II has been divided into four chapters.

Chapter - I

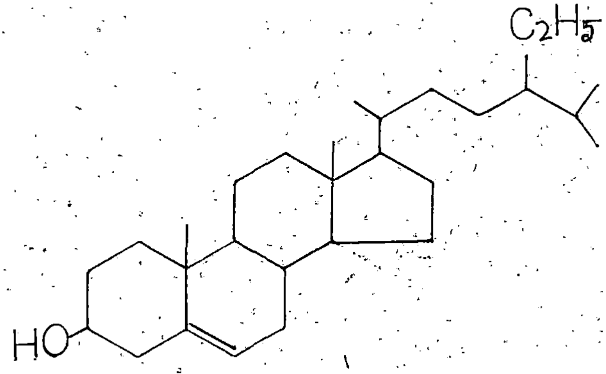
This chapter contains the morphological features of the plants of Flacourtiaceae family in Section A, while some previous works on the plants of the same family have been reported in Section B.

Chapter - II

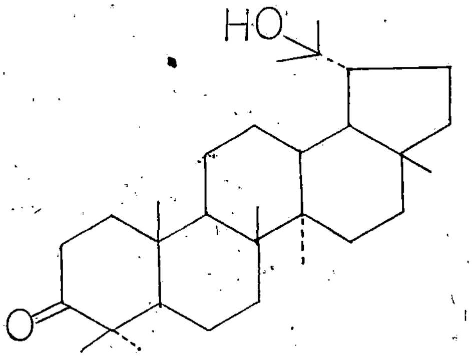
Chapter II comprises of the works done on the constituents of neutral and acid parts of benzene extract of Flacourtiaceae Jangomas.

In Section A extraction of trunk, bark and Stem of F. Jangomas by benzene as well as separation of neutral and acid parts of the extract has been described.

The isolation and characterization of compounds present in neutral and acid parts have been discussed in Section B. The neutral part has been found to contain 1-hexacosanol (XXIII), β-sitosterol (XXIV), 20-hydroxy lupanone (XXV) and 20-hydroxy lupanol (XXVI). The acid part contains ursolic acid (XXVII). Physical data and



XXIV



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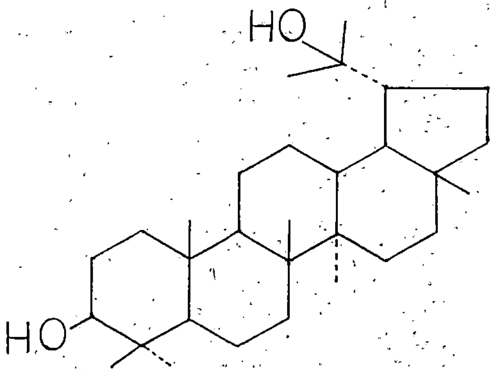
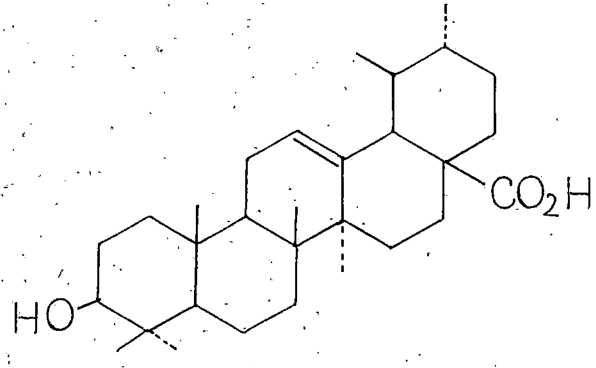


XXVI



XXVII

chemical reactions in support of the characterization of the compounds have been reported.

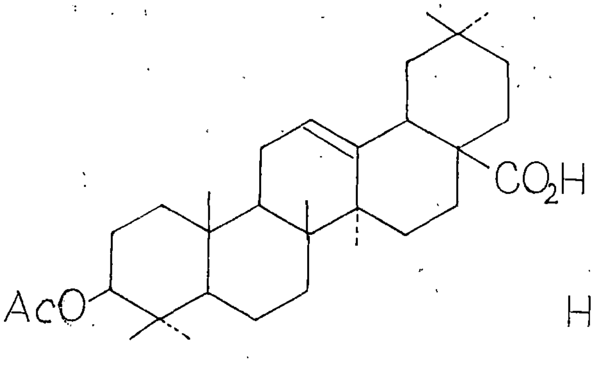
Section C describes the experimental details of the works reported in Chapter II.

Chapter - III

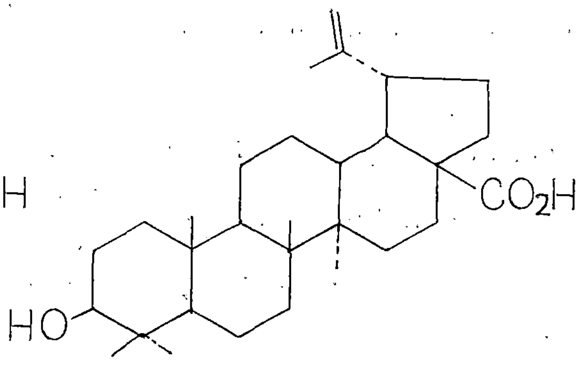
In Chapter III investigations on the neutral and acid parts of the benzene extract of bark and stem of caseria kurzii clark have been reported.

Section A describes the extraction of the plant material with benzene and separation of benzene extract into neutral and acid parts.

Section B deals with the isolation and identification of the compounds. 1-hexacosanol (XXIII) and β-sitosterol (XXIV) have been isolated from the neutral part while acetyl oleanolic acid (XXVIII) and betulinic acid (XXIX) have been found to be present in the acid part.



XXVIII



XXIX

The experimental details of the works presented in Chapter III has been described in Section C.

Chapter - IV

Chapter IV consists of investigations on the neutral and acid parts of the benzene extract of bark and stem of Caseria Graveolens Dalz.

Section A describes the extraction of the plant material with benzene and separation of benzene extract into acid and neutral parts.

Section B deals with isolation and identification of the constituents. The neutral part has been found to contain 1-hexacosanol (XXIII) and β-sitosterol (XXIV) and the acid part contains betulinic acid (XXIX).

Section C describes the experimental details of the works presented in Chapter IV.