S U M M A R Y

The work embodied in the present thesis has been divided into three parts:

A. The first part (Part I) describes the formation of a δ-lactone by the action of hydrogen peroxide on olean-12, 15-dien-3, 11-diol obtained from Taraxeryl acetate.

B. The second part (Part II) consists of the partial synthesis of a natural product Aegiceradiol from Acetyl methyl aleuritolate.

C. The last part (Part III) deals with the isolation and characterisation of lupeol acetate, β-sitosterol, ursolic acid, α-amyrin acetate, β-amyrin acetate and stigmasterol from the bark and leaves of Finlaysonia obovata wall.

A. Part I

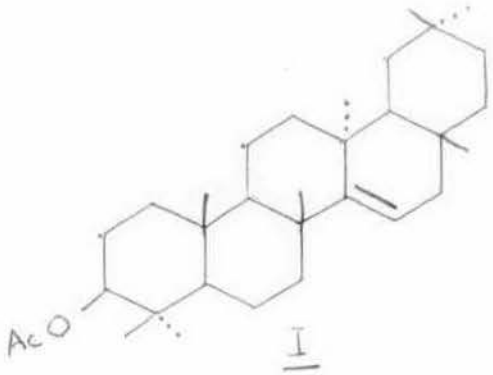
Chapter I describes the morphological features of the plants of Euphorbiaceae family and of Sapium baccatum Roxb.

Chapter II deals with the reinvestigation on the benzene extract of the bark of Sapium baccatum Roxb. The isolation of Taraxerone, 1-Hexacosanol, Taraxerol, β-sitosterol, Baccatin, Acetyl aleuritolic acid are described.

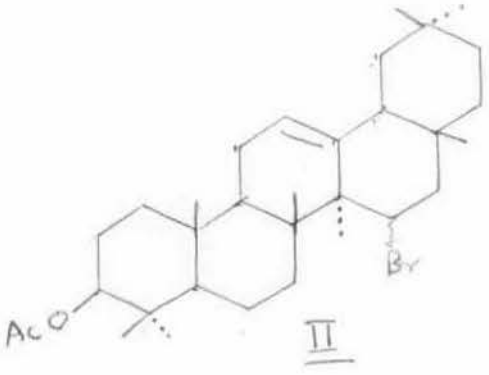
Chapter III gives a short review on the oxidative transformation reactions of the pentacyclic triterpenes.

Chapter IV deals with the studies of the reaction of hydrogen peroxide in presence of p-toluene sulphonic acid and tertiary butanol on the diol olean-12, 15-dien-3, 11-diol **VI** obtained from Taraxeryl acetate **I**.

Taraxeryl acetate **I** was treated with N-Bromo succinimide in presence of dimethyl sulfoxide in the dark when a solid of molecular formula $C_{32}H_{51}O_2Br$ **II** mp 180-82°, $(\alpha)_D$ 47.37° was obtained. The compound did not show any U.V. absorption in the region 220-300 nm. I.R. spectrum showed peaks at 1720 and 1250 cm^{-1} ($-OCOCH_3$). NMR spectrum showed a multiplet centered at 5.3 ppm (vinyl proton) and a multiplet at 4.30 ppm for one proton attached to a carbon containing bromine, peaks at 2.09 ppm ($-OCOCH_3$) and at 4.53 ppm for proton attached to the carbon bearing acetoxy group. The compound **II** on treatment with zinc dust and acetic acid yielded β-amyrin acetate. These facts and also the mass fragmentation pattern suggested that **II** was 15-Bromo β-amyrin acetate.

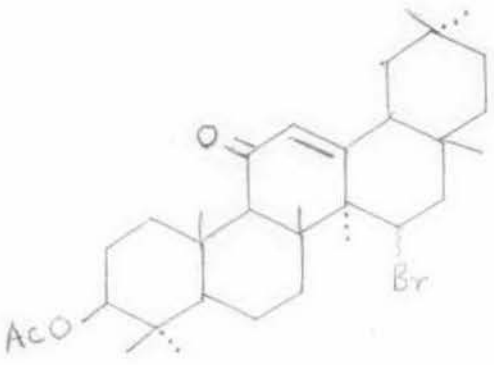


I



II

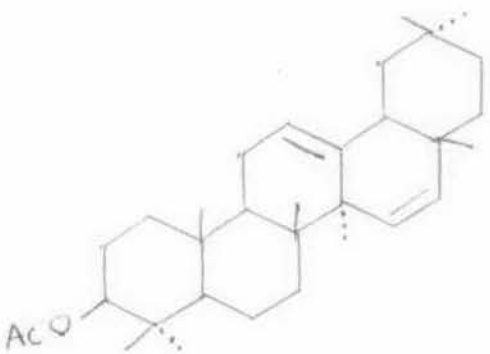
The bromo compound **II** on oxidation by means of sodium dichromate in acetic acid yielded the 11-keto compound, 15-Bromo β-amyrenonyl acetate **III** mp 240-241°. The compound showed U.V. absorption at λ_{max} 249 nm (ϵ 11000) showing the presence of α,β-unsaturated carbonyl group.



III

Dehydrobromination of this 15-Bromo β-amyrenonyl acetate **III** was tried with dimethyl aniline, s-collidine and also with potassium tertiary butoxide in dimethyl sulfoxide. All these attempts were found to yield a negative result.

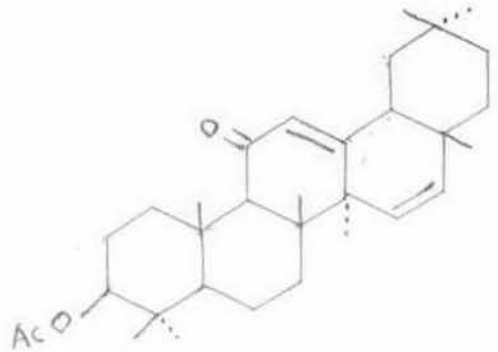
Attempt was therefore made to dehydrobrominate the bromo compound II by refluxing with dimethyl aniline when the dehydrobromo compound olean-12, 15-dien-3β-yl acetate IV was obtained. This corresponded to molecular formula $C_{32}H_{50}O_2$, had a mp 199-200°C, showed no U.V. absorption. NMR spectrum showed signals at 5.2 to 5.6 ppm for three vinyl protons. From these evidences, it was assigned structure IV.



IV

The compound IV was then oxidised by refluxing with sodium dichromate in acetic acid for a period of twenty four hours when the 11-keto compound 3β-acetoxy olean-12, 15-dien-11-one V mp 243-245°, $(\alpha)_D$ 28.57° was obtained.

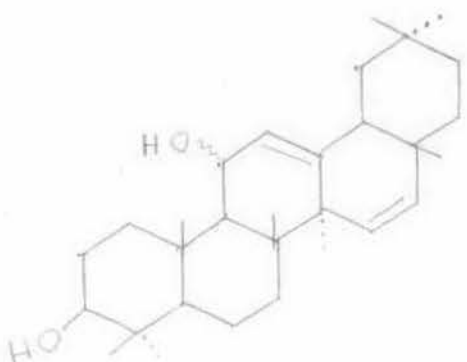
(v)



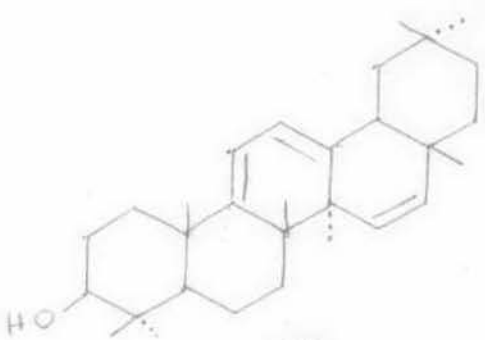
V

The proposed structure was in conformity with the observed spectral data. The compound showed U.V. absorption at λ_{max} 244 nm (ϵ 11376) indicating the presence of an α,β-unsaturated keto system at C-11. I.R. spectrum showed absorption at 1240 cm^{-1}, 1730 cm^{-1} showing the presence of acetoxy group, at 1660 cm^{-1} showing that the compound was a six membered ring α,β-unsaturated ketone. NMR spectrum showed signals at 0.8 to 1.5 ppm (methyl groups), 2.04 ppm ($-OCOCH_3$), 4.5 ppm ($-CH-OCOCH_3$), 5.5 to 5.7 ppm (three vinyl protons).

The α,β -unsaturated ketone V was then reduced by means of lithium aluminium hydride when the diol $C_{30}H_{50}O_2$ VI mp 198-200° was obtained. Attempts towards the purification of this diol resulted in the formation of the homoannular diene VII as was evidenced from the U.V. spectral data λ_{max} 276 mm



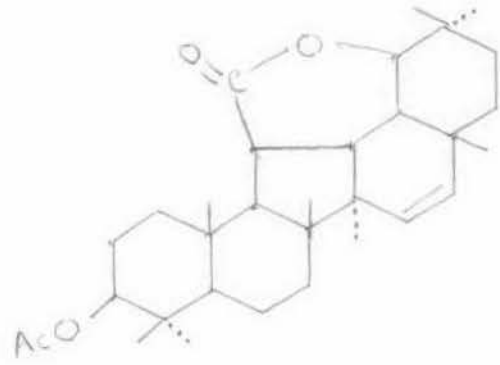
VI



VII

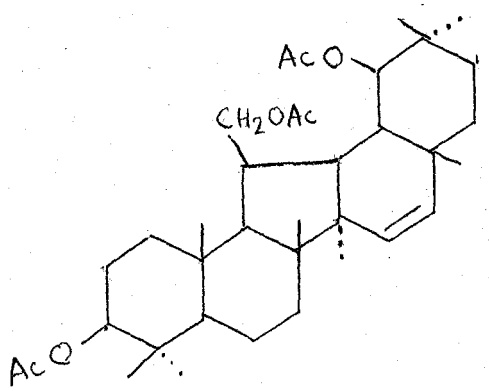
(ϵ 5260). Therefore the crude diol was directly treated with hydrogen peroxide, p-toluene sulphonic acid and tertiary butyl

alcohol for a period of twenty four hours as described by Corey et al. After usual work up, the product $C_{30}H_{46}O_3$ mp 240-241° was obtained. I.R. spectrum of this compound showed absorptions at 3520 cm^{-1} (-OH group), 975 cm^{-1} (-CH = CH-). An absorption at 1775 cm^{-1} indicated that the compound was a lactone. The compound was then acetylated at room temperature using acetic anhydride and pyridine. The structure of the acetate $C_{32}H_{48}O_4$ mp 215-216° was confirmed as



from consideration of its NMR and I.R. spectral data.

The acetate was subjected to LAH reduction when the lactone ring was cleaved producing the triol $C_{30}H_{52}O_3$ mp 280-282°. This was also acetylated at room temperature when a triacetate $C_{36}H_{58}O_6$ mp 185-190° was obtained. Study of the NMR spectrum showed that the triacetate had the structure.



The formation of this triacetate from the lactone confirmed the structure of the lactone.

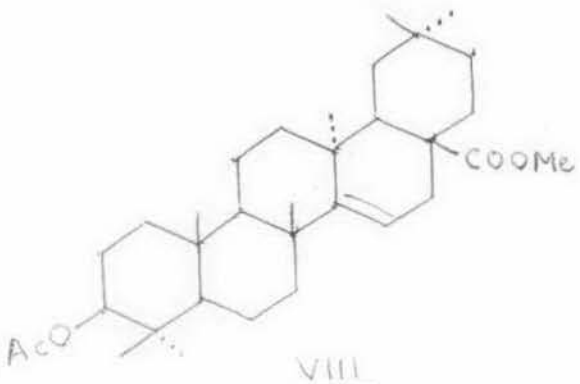
Chapter V describes the experimental section.

B. Part II

Chapter I describes the first isolation of Aegiceradiol and partial synthesis of Aegiceradiol from genin-A. It also discusses the partial synthesis of Aegiceradiol from acetyl methyl aleuritolate VIII.

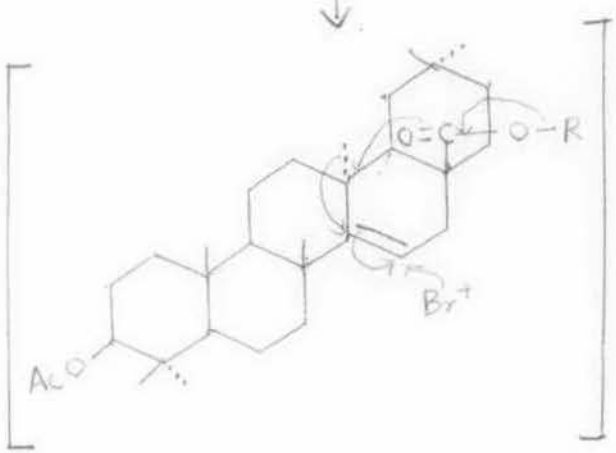
Acetyl methyl aleuritolate VIII on treatment with N-Bromo succinimide in presence of dimethyl sulfoxide in the dark afforded a solid $C_{33}H_{51}O_4Br$ IX mp 280-282°. The NMR and I.R. spectra showed that it was a lactone. A similar experiment was also carried out with Acetyl aleuritolic acid to prove whether lactonisation proceeded via ester hydrolysis i.e. acid formation. The product was the identical lactone IX. To ascertain whether ester hydrolysis occurs during the reaction, a similar reaction using acetyl methyl dihydro betulinate was also carried out employing NBS-DMSO when the ester was found to be unhydrolysed. Therefore the following mechanism was proposed for the lactone formation:

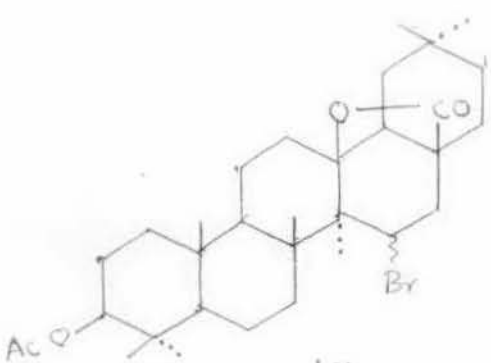
(x)



VIII

NBS/DMSO

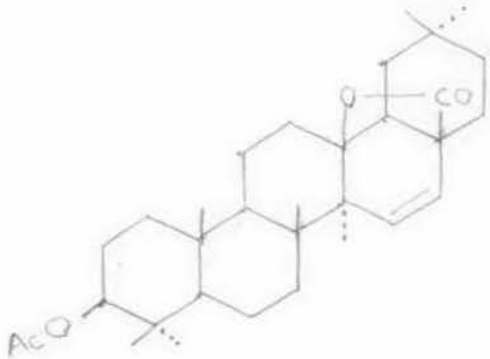




IX

The bromo compound IX was dehydrobrominated by refluxing with distilled dimethyl aniline when the compound X $C_{33}H_{50}O_4$ mp 308-310° was obtained.

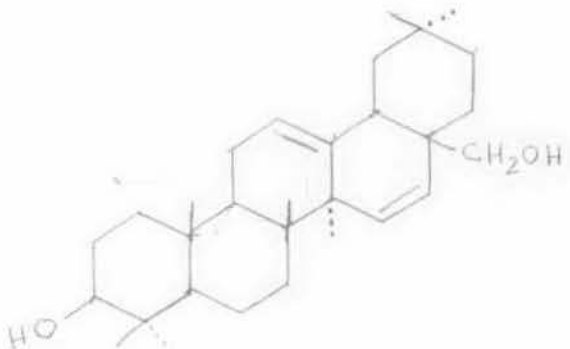
The 15, 16-dehydrooleanolic lactone acetate was hydrogenated when oleanolic lactone acetate mp 293-295°, identical with an authentic sample, was obtained. The formation of this oleanolic lactone acetate from the compound X correctly established the structure of X.



X

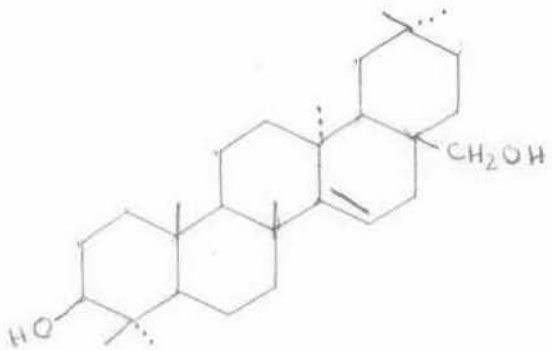
The compound X was then subjected to LAH reduction when the lactone ring was cleaved producing $-CH_2OH$ group at C-17 position and an -OH group at C-13 position. The acetoxy group at C-3 was also reduced to -OH group. The -OH group at

C-13 readily underwent dehydration producing 12,13-double bond, i,e rearranged to the β-amyrin skeleton very easily and the product obtained was identical with the authentic sample of Aegiceradiol XI.



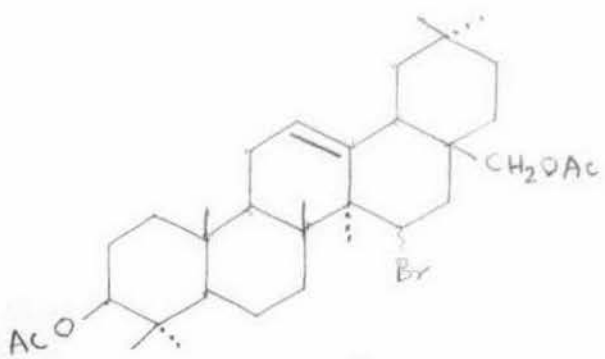
XI

In another route, acetyl methyl alcuritolate VIII was first reduced by LAH when Myricadiol $C_{30}H_{50}O_2$ mp 265-267° XII was obtained.



XII

This on acetylation with acetic anhydride and pyridine afforded the diacetate $C_{34}H_{54}O_4$ mp 256-258°. This on treatment with NBS-DMSO in the dark produced 15-Bromo erythrodiol diacetate XIII.



XIII

which when refluxed with dimethyl aniline got dehydrobrominated producing aegiceradiol diacetate $C_{34}H_{52}O_4$. The diacetate on hydrolysis with 10% methanolic caustic soda produced aegiceradiol XI, identical with an authentic sample.

Chapter II describes the experimental part.

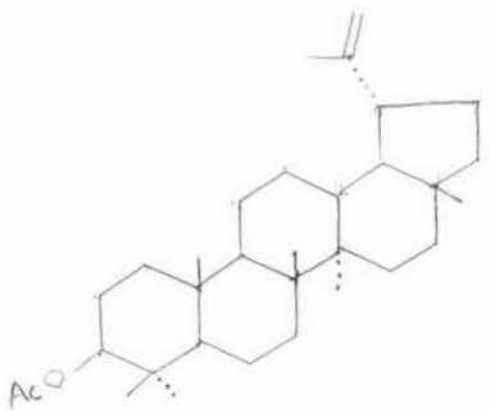
C. Part III

Chapter I describes the morphological features of plants of Asclepiadeae family and that of Finlaysonia obovata wall.

Chapter II deals with the investigation on the neutral part and acid part of the bark of Finlaysonia obovata wall.

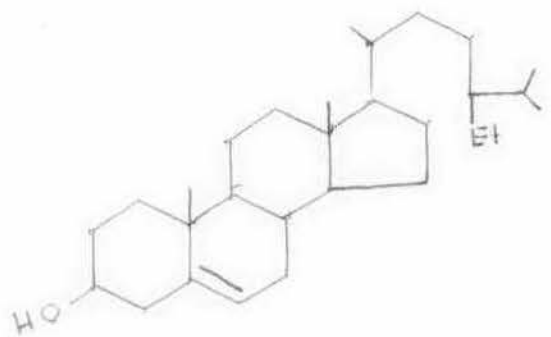
Section A describes the extraction of the plant material with petroleum ether and benzene in soxhlet apparatus.

Section B deals with the chromatography of the petroleum ether extract and isolation of lupeol acetate XIV.



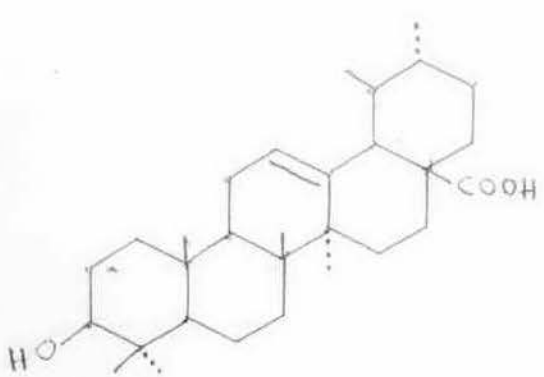
XIV

Section C describes the isolation of β-sitosterol XV from the neutral part of the benzene extract.



XV

Section D shows the presence of Ursolic acid XVI in the acid part of the benzene extract.



XVI

Chapter III describes the experimental section.

Chapter IV deals with investigation on the leaves of Finlaysonia obovata wall.

Section A describes the extraction of the leaves by means of petroleum ether, benzene and alcohol.

Section B shows the presence of α-amyrin acetate and β-amyrin acetate in the petroleum ether extract.

Section C describes the isolation of β-sitosterol and Ursolic acid from the benzene extract.

Section D shows the presence of stigmasterol in the alcohol extract.

Chapter V - Experimental portion has been described in this chapter.