SUMMARY

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

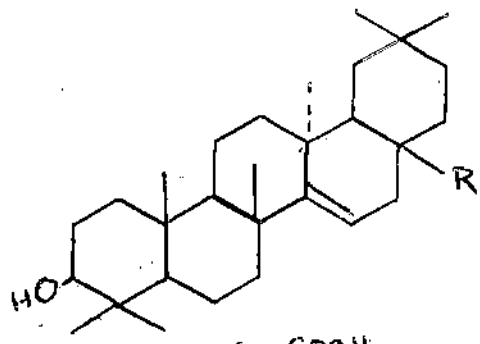
A. The first part (part I) consists of investigations carried out on the benzene extract of the trunk bark and stem of *Aleurites montana* (Euphorbiaceae).

B. The second part (part II) describes studies on autoxidation of β-amyrone and isomerisations taking place in ring A.

C. The third part (part III) describes the preparation of isomeric Δ^{12}-olenene-2,3,-diols by a new method.

D. The last part (part IV) deals with the investigations carried out on the benzene extract of the trunk bark and stem of *Sapium baccatum* Roxb.

A. Part I, chapter III deals with the acid fraction of *Aleurites montana* from which betulinic acid and a new triterpene acid $C_{30}H_{48}O_3$, m.p. 300-2° have been isolated. The name aleuritolic acid has been proposed for it by the author after the name of the species from which it has been isolated for the first time. The investigations on the elucidation of the structure of aleuritolic acid A have been discussed.



A, R = COOH
B, R = CH_2OH

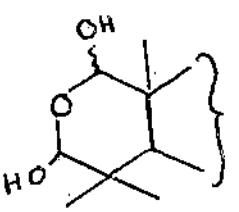
The presence of carboxyl group in A at a tertiary hindered position has been established as the corresponding methyl ester was resistant towards hydrolysis by alkali. The presence of one double bond was established by perbenzoic acid titration. That it is situated in a hindered position has been established by its inertness towards hydrogenation. The position of the double bond has been established from the mass fragmentation pattern of the methyl ester and the 3-keto methyl ester. Absolute configuration of the acid was established by conversion of the acid into a known triterpene myricadiol B.

Chapter V deals with work of the constituents of the neutral part of Aleurites montana. Isolation and identification of friedelin and β-sitosterol have been discussed.

B. Part II

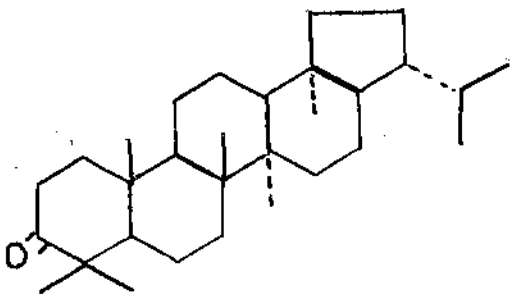
Chapter II comprises the work on the autoxidation of β-amyrone. β-amyrone in presence of potassium tertiary butoxide-tertiary butanol gave the corresponding diosphenol which on catalytic hydrogenation

yielded 2 keto -β-amyrin either by 1,2-addition of hydrogen followed by isomerisation or by 1,4-addition of hydrogen. Acetylation of the latter gave 2-keto-β-amyrin acetate consistent with NMR spectra. The diosphenol above on acetylation gave the diosphenol acetate which on hydrogenation as above yielded 2α-acetoxy-β-amyrone by 1,2-addition of hydrogen. To compare this compound with an authentic sample, 2α-acetoxy-β-amyrone was prepared by acetoxylation of β-amyrone using lead tetraacetate. NMR of these two compounds were not exactly identical and this has been discussed. Potassium-tertiary-butoxide treatment of 2-keto-β-amyrin in nitrogen atmosphere afforded an isomeric α-ketol which has been formulated as 2α-hydroxy-β-amyrone from its IR and NMR spectra. The latter however on treatment with acetic anhydride-pyridine gave the same 2-keto-β-amyrin acetate described earlier. 2α-acetoxy-β-amyrone isomerised to 2-keto-β-amyrin acetate after elution with benzene from a basic column of alumina. Acid hydrolysis of both 2-keto-3-acetoxy and 3-keto-2α-acetoxy compound in nitrogen atmosphere afforded a mixture of two isomeric ketols identified from R_f values (TLC) which on acetylation gave a single compound identical with 2-keto-β-amyrin acetate. The structure of the lactol C, $C_{29}H_{46}O_3$ isolated from the mother liquor after crystallisation of the diosphenol has been discussed.



C

Section C contains a brief report of the work on the autoxidation of moretanone D which contains the same chair-chair conformation of A/B rings as in β-amyrone.



D

C. Part III

Chapter II described a new method developed by the author for the synthesis of isomeric Δ^{12}-oleanene-2,3-diols. Sodium borohydride reduction of the diosphenol obtained by autoxidation of β-amyrone gave 2α,3α-diol m.p. 240-42°, $(\alpha)_D$ + 101.88°, which on acetylation afforded the 2α,3α-diacetate m.p. 221-22°, $(\alpha)_D$ + 83.63°. 2 keto-β-amyrin and 2-hydroxy-β-amyrone also gave the same 2α,3α-diol on sodium borohydride reduction. 2α-acetoxy-β-amyrone (obtained by 1,2-addition of hydrogen during palladium-charcoal hydrogenation of diosphenol acetate) on LAH reduction gave a mixture of 2α,3α-diol and 2α,3β-diol m.p. 202-4°, separated by chromatography. However, sodium borohydride reduction of 2α-acetoxy-β-amyrone at P_H 8 gave 2α-acetoxy-β-amyrin m.p. 246-48° as the major product. The latter on acetylation afforded the 2α,3β-diacetate m.p. 216-18°. Hydrolysis of the latter with alkali gave the 2α,3β-diol m.p. 202-4°. Meerwein-Pondorff

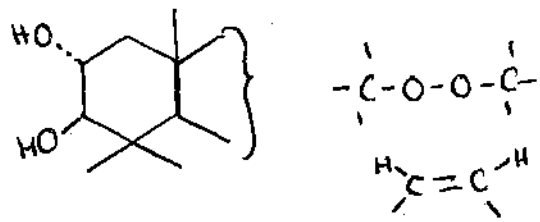
reduction of 2 keto-β-amyrin afforded a mixture of diols consisting of 6% of 2α,3β-diol and 92% of a new diol m.p. 278-80°. The new diol has been assigned 2β,3β-configuration as it was found to be identical with 2β, 3β-diol prepared by osmylation of β-amyrilene II and also from NMR spectra. The product in the osmylation reaction also gave 2α,3α-diol as a minor product (8%). Performic acid oxidation of β-amyrilene II by the method reported in literature afforded 2β,3α-diol m.p. 250-52°, $(\alpha)_D$ + 120°, acetate m.p. 161-3°. The structure of the diols were discussed on the basis of NMR spectra. Acetonide derivatives of the three out of the four isomeric diols have been prepared.

D. Part IV

Chapter I comprises of the work on the constituents of the neutral part of Sapium baccatum Roxb. Isolation and identification of taraxerone, 1-hexacosanol, taraxerol, β-sitosterol 3,3'-di-O-methyl ellagic acid have been discussed. Isolation of a new nor-triterpene $C_{29}H_{46}O_4$ and work on its partial structure have been discussed.

Section H comprises of the isolation of a new nor-triterpene alcohol $C_{29}H_{46}O_4$, m.p. 228-29°, $(\alpha)_D$ - 9.09°. Two of the oxygen functions have been found to be present as 2α,3β-hydroxy group by NMR spectra. Acetylation of this nor-triterpene gave a diacetate and from the IR it was evident that neither of the two remaining oxygen functions were present as hydroxyl or carboxyl group which was supported by chemical reaction. The presence of AB quartet (-CH=CH-) was indicated by the NMR spectra. The diacetate liberated two moles equiva-

lence of iodine for one mole of the compound in acetic acid solution. From this result the presence of peroxide linkage has been assumed. Hydrogenation of the diacetate of the new alcohol and subsequent acetylation gave interesting results from which it has been assumed that a unique type of rearrengement has taken place during this reaction. This has been discussed. Partial structure E has been postulated for the compound. Further work on this compound is in progress.



E