

## SUMMARY

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

A. The first part deals with the preparation of the hydrocarbon, A, 28-nor lup-13(18)-ene from mercuric acetate oxidation product of 3 $\beta$ -acetoxy methyl betulinate.

B. The second part describes the elucidation of correct structure of the lactone B obtained by mercuric acetate oxidation of 3 $\beta$ -acetoxy betulinic acid and also studies on the novel E-homorearrangement product D obtained from the nor keto lactone C, and elucidation of its structure D.

C. The third part describes the preparation of the same hydrocarbon A, 28-nor-lup-13(18)-ene by lead tetraacetate oxidation of 3 $\beta$ -acetoxy betulanic acid.

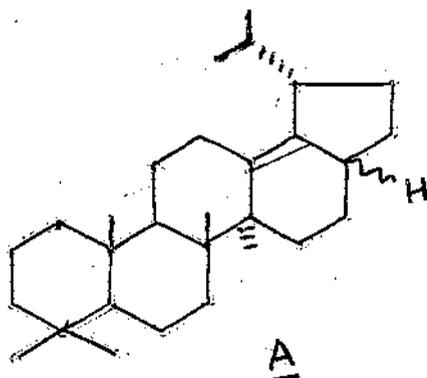
D. The fourth part deals with the chemical investigation on the neutral part of Macaranga denticulata, Muell Arg.

E. The last part (Part V) consists of investigations carried out on the benzene extract of the trunk bark of Bischofia javanica Blume.

A. Part I, Chapter II deals with the mercuric acetate oxidation of 3 $\beta$ -acetoxy methyl betulinate and conversion of the oxidation product by a series of reactions to the desired hydrocarbon A, 28-

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nor-lup-13(18)-ene. Mercuric acetate oxidation of 3 $\beta$ -acetoxy methyl

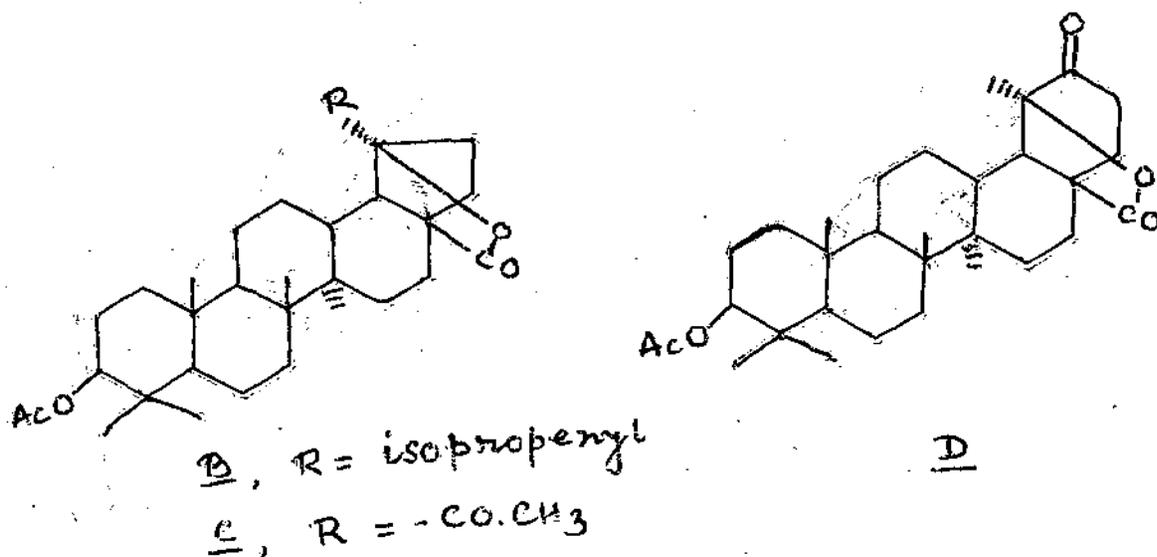


betulinate gave a non conjugated diene m.p. 218-19 $^{\circ}$ ,  $(\alpha)_{D} + 58^{\circ}$  which on hydrogenation afforded 3 $\beta$ -acetoxy lup-13(18)en-28-oate, m.p. 214-16 $^{\circ}$ ,  $(\alpha)_{D} + 20^{\circ}$ . The latter on hydrolysis furnished the corresponding hydroxy acid, m.p. 287-8 $^{\circ}$ ,  $(\alpha)_{D} + 10^{\circ}$  which on pyrolysis gave 28-nor-lup-17(18)-ene-3 $\beta$ -ol characterised as the 3-acetate, m.p. 210-12 $^{\circ}$ ,  $(\alpha)_{D} - 9^{\circ}$ . The nor-alcohol on CrO<sub>3</sub>-Py oxidation followed by Huang-Minlon reduction afforded the hydrocarbon 28-nor-lup-17(18)-ene which on isomerisation with 2N H<sub>2</sub>SO<sub>4</sub> furnished the desired hydrocarbon A, 28-nor-lup-13(18)-ene m.p. 193-4 $^{\circ}$ ,  $(\alpha)_{D} + 70^{\circ}$ .

B. Part II, Chapter I deals with the assignment of the correct structure of the lactone B obtained by mercuric acetate oxidation of 3 $\beta$ -acetoxy betulinic acid. Physical (spectroscopic) studies particularly circular dichroism Cotton effect considerations coupled with various chemical degradations involving lead tetra-acetate cleavage of the tetra-ol derived from the lithium aluminium hydride

(iii)

reduction of the nor-keto lactone C, established unequivocally the correct structure of the lactone as depicted in B. Treatment of the nor-keto lactone C by K-tertiary butoxide gave the E-homo rearrangement product for which the structure D has been proposed. This structure D is in accord with the physical evidences obtained for the compound. This rearrangement is only explicable if the original lactone has got the structure B. The mechanism for this reaction has been discussed.

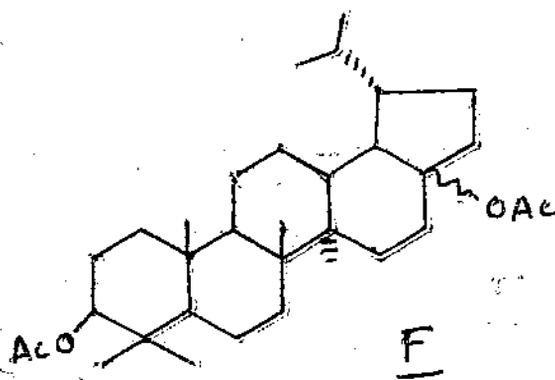
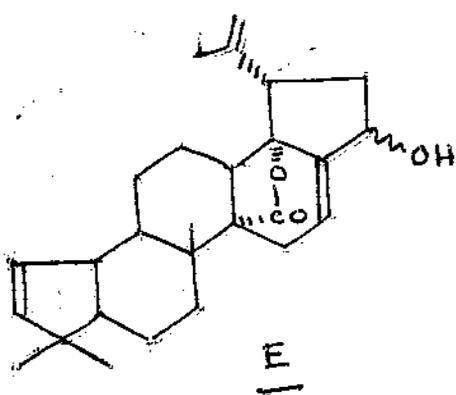


C. Part III, Chapter III deals with the lead tetra acetate oxidation of 3 $\beta$ -acetoxy betulanic acid whereby a mixture of hydrocarbons and a diacetate were isolated. The hydrocarbon mixture was converted by a series of reactions to the same hydrocarbon A, 28-nor-lup-13(18)-ene.

(iv)

Lead tetraacetate oxidation of 3 $\beta$ -acetoxy betulamic acid furnished a hydrocarbon mixture m.p. 170-6 $^{\circ}$ ,  $(\alpha)_D + 28.27^{\circ}$  and a diacetate m.p. 207-9 $^{\circ}$ ,  $(\alpha)_D + 23.01^{\circ}$ . The hydrocarbon mixture on hydrolysis followed by CrO<sub>3</sub>-Py oxidation gave a ketone m.p. 145-50 $^{\circ}$ ,  $(\alpha)_D + 48.19^{\circ}$  which on Huang Minlon reduction, gave a hydrocarbon mixture m.p. 156-8 $^{\circ}$ ,  $(\alpha)_D - 7.00^{\circ}$ . The latter was isomerised in 2N H<sub>2</sub>SO<sub>4</sub> to the same hydrocarbon A, 28-nor-lup-13(18)-ene. Their identity was confirmed by m.m.p. and by comparison of IR, NMR and mass spectra. This observation unequivocally established the stereochemistry of C-19 isopropenyl substituent in Hg(OAc)<sub>2</sub> oxidation products as  $\alpha$  i.e. trans with respect to the C-17 $\beta$ -substituent as is present in the original compounds. In view of the above results emmolactone can now be fully represented by structure E.

The diacetate, m.p. 207-9 $^{\circ}$ ,  $(\alpha)_D + 23.01^{\circ}$  was shown by spectral and chemical evidences to possess the structure F.



D. Part IV, Chapter III comprises of the work on the constituents of the neutral part of Macaranga denticulata. Isolation and identification of taraxerone, a new triterpene alcohol - 3-epi-taraxerol, and  $\beta$ -sitosterol have been discussed.

Section C, deals with the isolation and identification of taraxerone.

Section D, deals with the elucidation of the structure of 3-epi-taraxerol. The configuration of the hydroxyl group at C-3 position was indicated by NMR.  $\text{CrO}_3$ -Py oxidation gave taraxerone. Its structure and stereochemistry was confirmed by partial synthesis from taraxerone by Paton's method as well as by  $\text{Na}$ -isoamyl alcohol reduction.

Section E, deals with the isolation and identification of  $\beta$ -sitosterol.

E. Part V. Chapter II deals with the investigations on the benzene extract of Bischofia javanica, Blume. Betulinic acid has been isolated and identified from acid fraction and epifriedelanol acetate, friedelin and  $\beta$ -sitosterol have been isolated and identified from the neutral fraction.