S U M M A R Y

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

PART—I

STUDIES ON THE REDUCTION WITH LITHIUM-ETHYLENEDIAMINE ON TRITERPENOIDS

CHAPTER—I

It gives a short review of metal dissolving reactions in presence of base.

CHAPTER—II

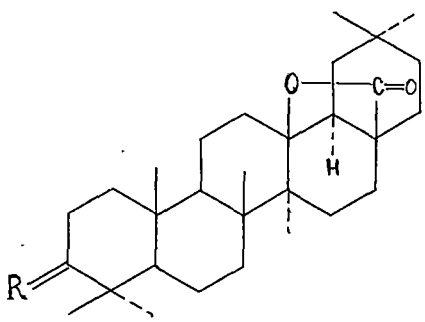
This chapter deals with the studies on the reduction of triterpenoid lactones (secondary & tertiary) with different sterical hindrances; 3-keto; isopropenyl double bond and sterically hindered esters.

S E C T I O N—A

(a) Studies on tertiary lactones:

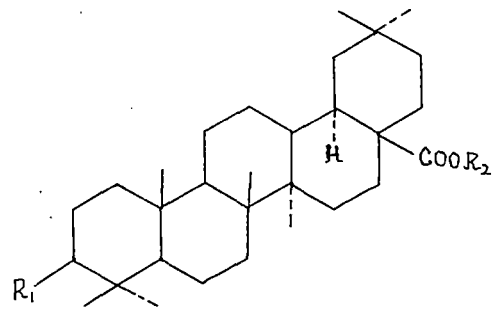
This section deals with the products obtained on reduction of 3-acetyl oleanan-18α-H-28→13β-olide 1 with Li-ethylenediamine. The products obtained after

refluxing for two hours under N_2 atmosphere have been separated by column chromatography. The first eluted, m.p. 270—71°, $C_{30}H_{50}O_2$, $[\alpha]_D$ +8.8°, has been characterised as oleanan-18-α-H-28-oic acid 2a, by means of PMR and mass spectral analysis. The second compound 2b, $C_{30}H_{50}O_3$, m.p. 295—96°, $[\alpha]_D$ +15°, (M^+ 458), methyl ester 2c, $C_{31}H_{52}O_3$, m.p. 198° (M^+ 472), acetyl acid 2d, $C_{32}H_{52}O_4$, m.p. 290°—91° (M^+ 500), was obtained.



1, R = OAc / H

1a, R = O



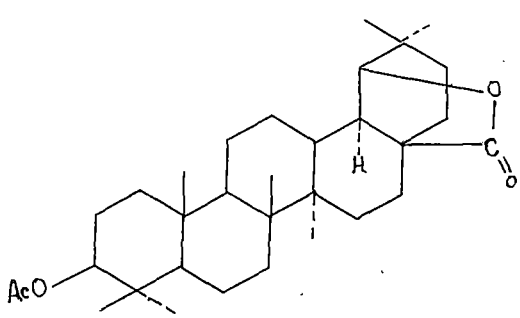
2a, R_1 = H ; R_2 = H
2b, R_1 = OH ; R_2 = H
2c, R_1 = OH ; R_2 = CH_3
2d, R_1 = OAc; R_2 = H

From the study of IR, NMR and mass spectral analysis, the second compound has been identified as 3-hydroxyoleanan-18α-H-28-oic acid 2b.

The reaction was repeated on 3-oxo-oleanan-18α-H-28$\rightarrow$13β-olide 1a. The product isolated contained only one compound which was obtained in 85% yield and had the m.p. 295—96°. It has been characterised as 3β-hydroxy-oleanan-18α-H-28-oic acid 2b by preparation of its methyl ester and the acetate derivatives.

(b) Studies on secondary lactones:

The third compound that was studied is 3-acetyl-oleanan-18α-H-28$\rightarrow$19β-olide 3. The products obtained after reduction were separated into acid and neutral parts. The acid part on chromatographic separation yielded the first compound, m.p. 269—70°, $[\alpha]_D$ +8.8°, that was characterised as oleanan-18α-H-28-oic acid 2a (by mmp and GC—IR comparison). The next polar compound from the acid part had m.p. 295—96°, $[\alpha]_D$ +14.5°. The compound was characterised as 3-hydroxy-oleanan-18α-H-28-oic acid 2b, by preparation of its methyl ester and the acetate derivatives. The neutral part afforded a compound (yield 15%) that had the



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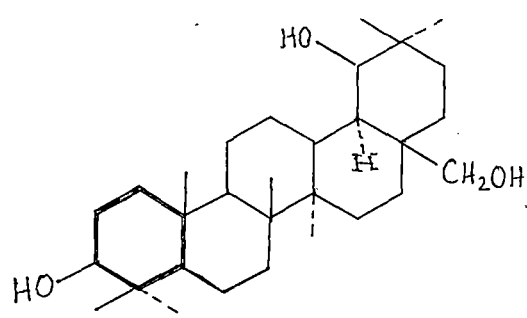

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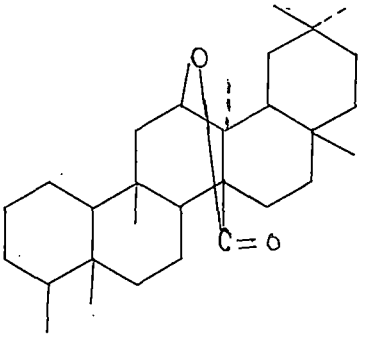
m.p. 290—92°, $[\alpha]_D$ +23°, m/e 442 ($M^+ - H_2O$), TNM test negative, was characterised as olean-18α-H-3β, 19β, 28-triol 4, by NMR and mass spectral analysis and preparation of its acetate derivative (triacetate), m.p. 211—12°.

(c) Studies on sterically hindered secondary lactones:

(i) 3-deoxy-adolactone—friedelan-26→12β-olide 5, on reduction with lithium-ethylenediamine afforded two different compounds. The acidic component, m.p. 290—91°, $[\alpha]_D$ +28.57° (M^+ 442), methyl ester of the compound had the m.p. 180°, $[\alpha]_D$ +30.3° (M^+ 456), has been characterised as methyl-3-deoxy-trichadenate 6b, by study of mass and NMR spectral analysis.



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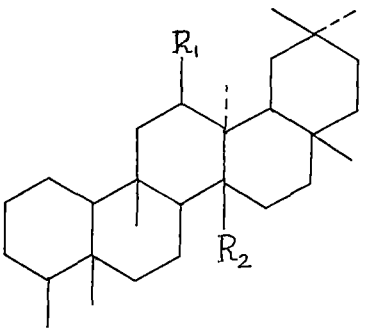
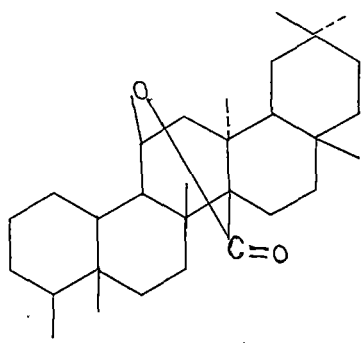


6a, R_1 = H; R_2 = COOH
6b, R_1 = H; R_2 = $COOCH_3$
6c, R_1 = OH; R_2 = CH_2OH

The neutral part of the above reaction product afforded a compound, $C_{30}H_{50}O_2$, m.p. 240—41°, m/e 426 (M^+—H_2O), PMR signals at 0.724 (d, J = 6Hz), 0.797, 0.899, 0.967, 0.983, 1.002, 1.244 ppm for seven methyl groups, 4.0 (2H, AB, q), 3.88 (1H, m) ppm, has been characterised as friedelan-12 β ,26-diol 6a.

(ii) Reduction of friedelan-3→ 11 β -olide 7, with lithium-ethylenediamine on reflux for two hours afforded one acidic component and one neutral component. The acid component on crystallisation furnished a compound, $C_{30}H_{50}O_2$, m.p. 293—94°, the methyl ester had the m.p.180°, has been characterised as 3-deoxy-trichadenic acid 6a.



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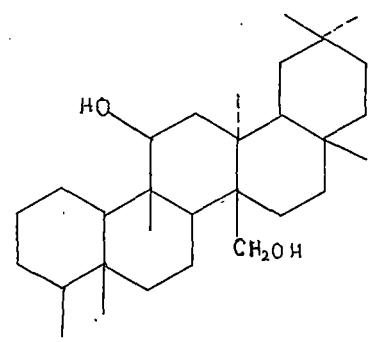

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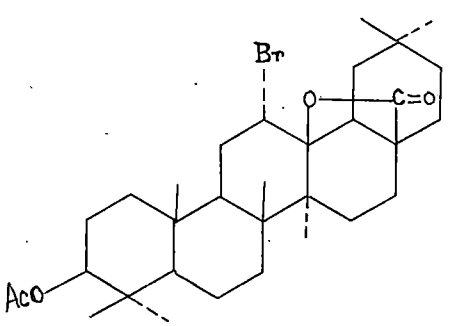
The neutral fraction on crystallisation furnished a solid (75%), m.p. > 350°, m/e 426 (M^+—H_2O), has been

characterised as friedelan-11 β , 28 diol 8 from mass and NMR spectral analysis.

(d) Studies on triterpenoid bromolactones:

In order to examine the effect of bromine on the nature and yield of the products formed on lithium-ethylenediamine reduction the following compounds have been selected and studied for the purpose:

(1) Reaction on 3-acetyl-12 α -bromo-oleanan-28⟶13 β -olide 9, with lithium-ethylenediamine furnished the acidic components. The first one, m.p. 265—66°, was characterised as 3-deoxy-oleanolic acid 10a, by preparing its methyl ester 10b, m.p. 169°, TNM test positive.



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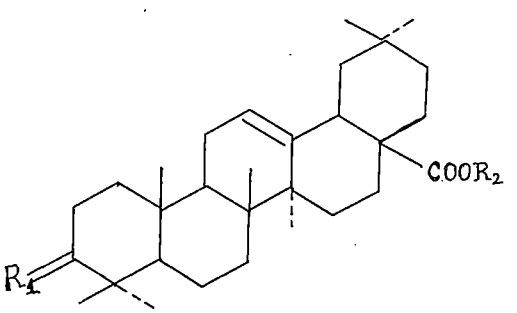
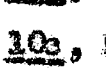
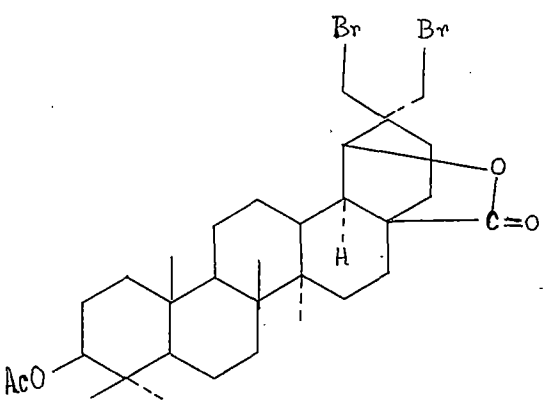


10a, $R_1 = H_2$; $R_2 = H$
10b, $R_1 = H_2$; $R_2 = CH_3$
10c, $R_1 =$  ; $R_2 = H$
10d, $R_1 =$  ; $R_2 = CH_3$
10e, $R_1 = O$; $R_2 = CH_3$

The second compound isolated was analysed for $C_{30}H_{48}O_3$, m.p. 303—4°, was characterised as oleanolic acid 10c, by preparing its methyl ester 10d, m.p. 198—99°, (M^+470). FNM test was found to be positive.

(ii) Reaction on 3-acetyl-29,30-dibromo-oleanan-18α-H-28→19β-olide 11, with lithium-ethylenediamine furnished two acidic compounds. The first one, m.p. 270—71°, has been identified as oleanan-18α-H-28-oic acid 2a and the second one was identified as 3-hydroxy-olean-18α-H-28-oic acid 2b, (by mmp and CO—IR comparison with authentic samples).



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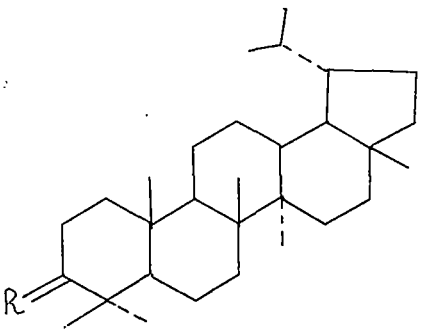
S E C T I O N—B

(a) Studies on 3-keto compounds:

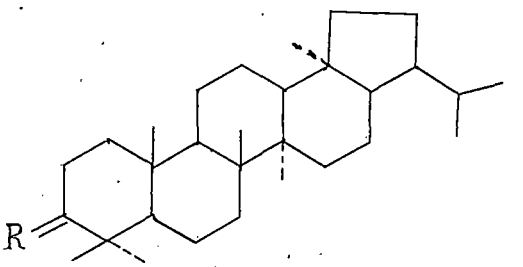
(i) Reaction of lupanone 12, with lithium-ethylenediamine furnished a single compound, m.p. 205°,

$[\alpha]_D$ -17.8°, that was identified as lupanol 12a.



12, R = O

12a, R = OH / H



13, R = O

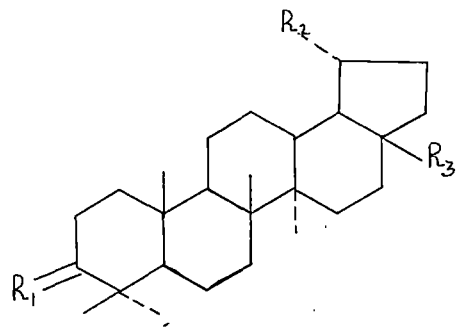
13a, R = OH / H

(ii) Reaction on moretanone 13 with lithium-ethylenediamine furnished a single compound, m.p. 223—24°, that was identified as moretanol 13a.

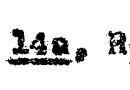
(b) Studies on hindered esters:

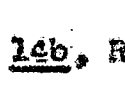
(i) Esters containing 3-keto and isopropenyl groups:

Reduction of methyl betulonate 14 with lithium-ethylenediamine furnished dihydrobetulinic acid 14a (yield 80%), m.p. 323—24°, $[\alpha]_D$ +26.0° (M^+ 458), confirmed by preparing acetyl derivative 14b, m.p. 310—11°, $[\alpha]_D$ -11.5° (M^+ 500) and comparison with authentic sample.



14, R_1 = O; R_2 = ⟨ ; R_3 = $COOCH_3$

14a, R_1 = ; R_2 =  ; R_3 = COOH

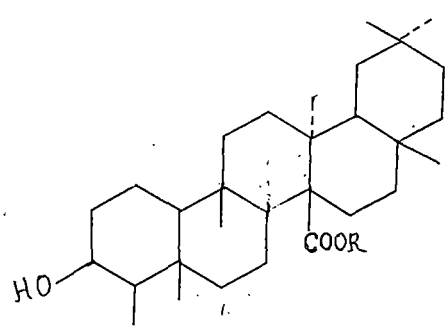
14b, R_1 = ; R_2 =  ; R_3 = COOH

(ii) Ester containing 3-keto, 12-13 double bond:

Reaction of methyl oleanonate 10a with lithium-ethylenediamine furnished a single compound, m.p. 301—302°. It was identified as oleanolic acid 10c (by map and IR comparison with authentic specimen).

(iii) Sterically hindered ester:

Reaction of methyl trichadenate A 15, with lithium-ethylenediamine furnished a single compound, m.p. 330—32°, $[\alpha]_D$ +35°, identified as trichadenic acid A 15a (by comparison with authentic sample).



15, R = CH_3

15a, R = H