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

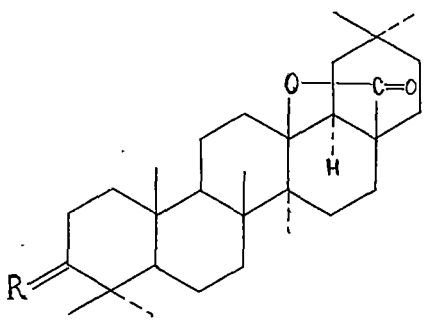
This chapter deals with the studies on the reduction of triterpenoid lactones (secondary & tertiary) with different sterical hindrances; 3-keto; isopropenyl double bond and sterically hindered esters.

S E C T I O N—A

(a) Studies on tertiary lactones:

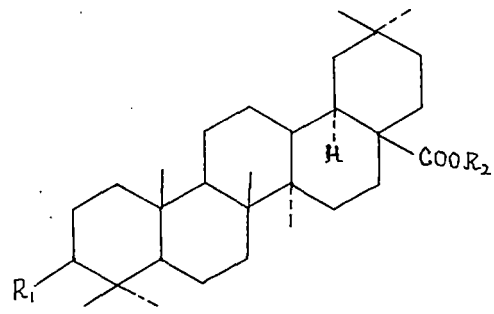
This section deals with the products obtained on reduction of 3-acetyl oleanan-18α-H-28→13β-olide 1 with Li-ethylenediamine. The products obtained after

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



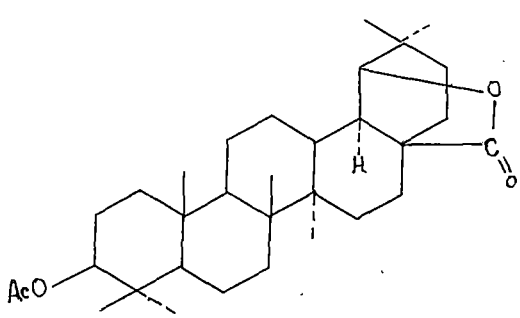
2a, R_1 = H ; R_2 = H
2b, R_1 = OH ; R_2 = H
2c, R_1 = OH ; R_2 = CH_3
2d, R_1 = OAc; R_2 = H

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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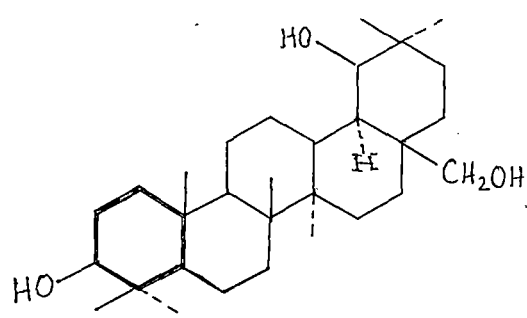

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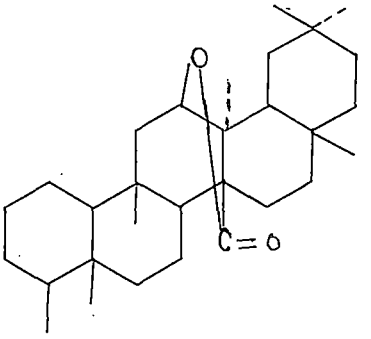
m.p. 290—92°, $[\alpha]_D$ +23°, m/e 442 ($M^+ - H_2O$), TNM test negative, was characterised as olean-18α-H-3β, 19β, 28-triol 4, by NMR and mass spectral analysis and preparation of its acetate derivative (triacetate), m.p. 211—12°.

(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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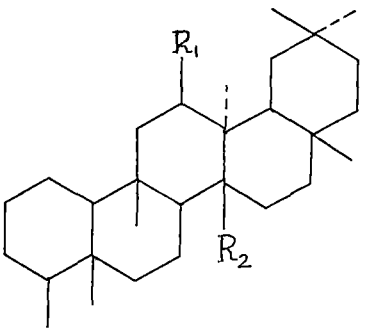
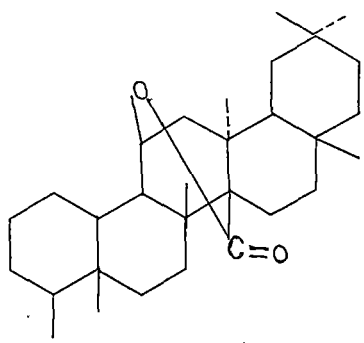


6a, R_1 = H; R_2 = COOH
6b, R_1 = H; R_2 = $COOCH_3$
6c, R_1 = OH; R_2 = CH_2OH

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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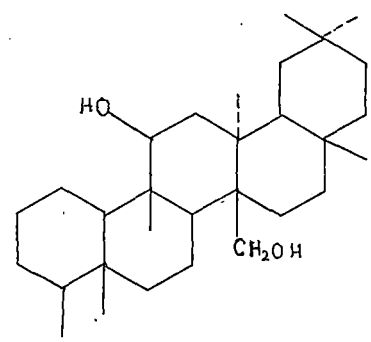

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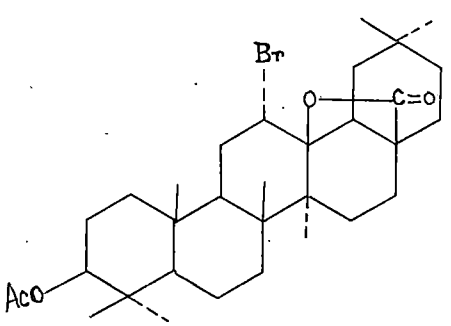
The neutral fraction on crystallisation furnished a solid (75%), m.p. > 350°, m/e 426 (M^+—H_2O), has been

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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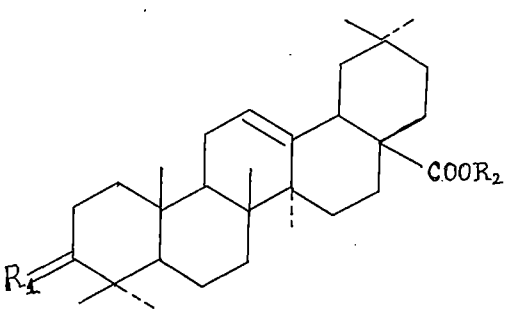
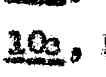
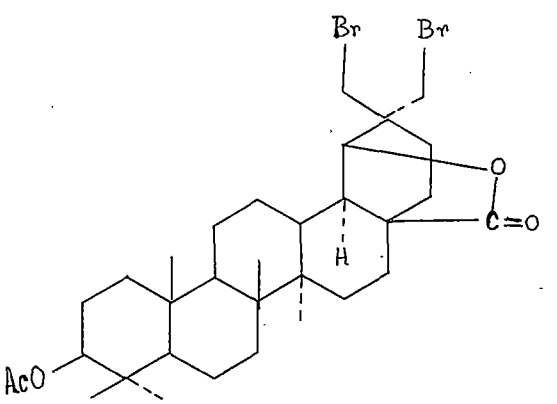


10a, $R_1 = H_2$; $R_2 = H$
10b, $R_1 = H_2$; $R_2 = CH_3$
10c, $R_1 =$  ; $R_2 = H$
10d, $R_1 =$  ; $R_2 = CH_3$
10e, $R_1 = O$; $R_2 = CH_3$

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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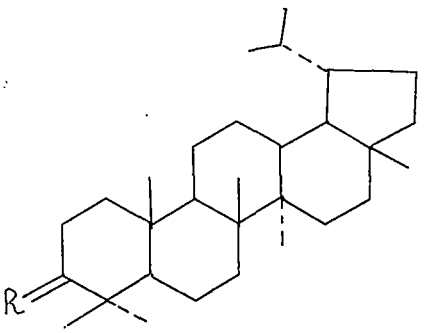
S E C T I O N—B

(a) Studies on 3-keto compounds:

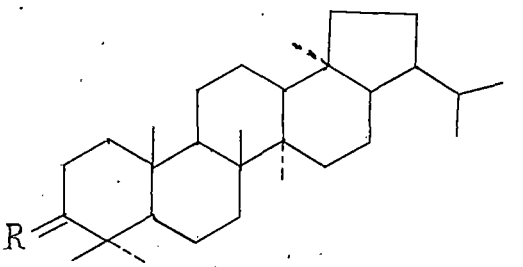
(i) Reaction of lupanone 12, with lithium-ethylenediamine furnished a single compound, m.p. 205°,

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



12, R = O

12a, R = OH / H



13, R = O

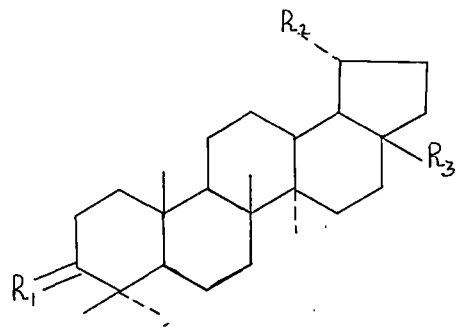
13a, R = OH / H

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

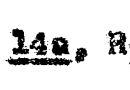
(b) Studies on hindered esters:

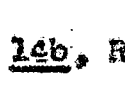
(i) Esters containing 3-keto and isopropenyl groups:

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

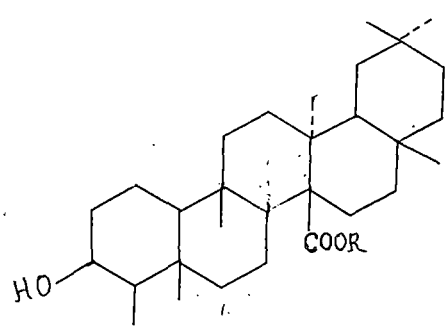
14b, R_1 = ; R_2 =  ; R_3 = COOH

(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

S E C T I O N—C

C o n c l u s i o n:

From the results obtained on reduction of lactones it may be concluded that the tertiary lactyl oxygen is cleaved at C—O bond to furnish the acids. These observations are in accordance with those that reported by Barton and his coworkers on the reduction of esters where the carbonyl group is attached to the tertiary carbon atom. It is noteworthy to mention here if the bromine is suitably attached to the carbons α to the lactyl oxygen then the acid produced generates a double bond at the carbon atom to which lactyl oxygen is attached, whereas the other tertiary lactones, furnished saturated acids.

The reduction of secondary lactones 3 and 7 furnished comparatively larger amounts of diols (4 and 8) compared to the acids suggesting the facile cleavage of $-\overset{O}{\overset{\|}{C}}-O$ bond of lactone ring, showing that these lactones are comparatively less sterically hindered whereas the lactones 5 and 11 gave more of the acids and negligible amount of diols, suggesting that these secondary lactones are sterically much hindered thereby causing deoxygenation at carbon where lactyl oxygen is attached.

The 3-keto compounds on reduction gave the thermodynamically more stable alcohols with 100% purity. The hindered esters easily underwent reduction to give acids. The isopropenyl group has also been reduced to give the dihydro compound. A compound containing ester group, keto functional group, isopropenyl double bond can be reduced in a single step as exemplified in the case of methyl betulonate 14.

CHAPTER—III

Experimental portion has been discussed in this chapter.

PART—II

ACTION OF HYDROGEN PEROXIDE ON TRITERPENOID ALLYLIC ALCOHOLS

CHAPTER—I

This chapter gives a short review on the oxidative transformation on pentacyclic triterpenoids.

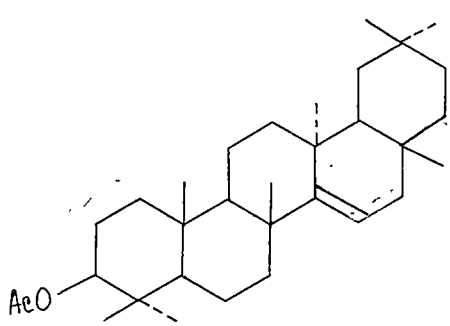
CHAPTER—II

This chapter deals with the action of hydrogen-peroxide in presence of p-toluene sulfonic acid on triterpenoid allylic alcohol in ring C and ring A.

S E C T I O N—A

This section deals with the action of hydrogen peroxide on olean-12, 15-dien-3,11 diol 21, which has been prepared from taraxeryl acetate 16.

Tarexeryl acetate 16 with NBS afforded a compound 17, $C_{32}H_{51}O_2Br$, (M^+ 546, Br 81), m.p. 180—82°, $[\alpha]_D$ +47.4°, characterised as 15-bromo- β -amyrin acetate 17. Treatment of 17 with sodium dichromate in acetic acid furnished 11-oxo-15-bromo- β -amyrenyl acetate 18, $C_{32}H_{49}O_3Br$, m.p. 240—41°, $[\alpha]_D$ +88°.



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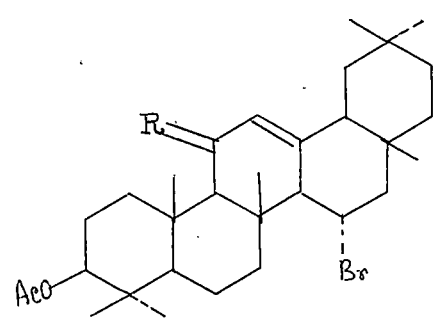
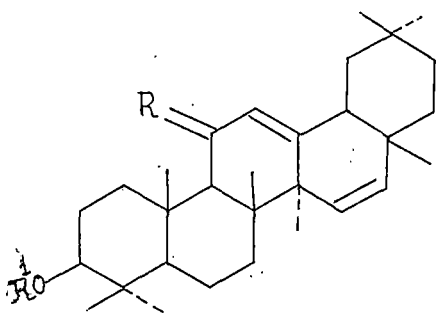


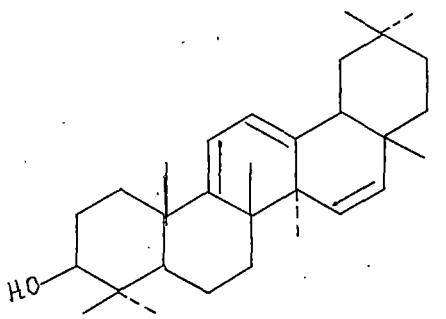
17, R = H, H

18, R = O

Attempts to dehydrobrominate 18 with dimethyl aniline/collidine gave the starting compound 18. A reverse route was followed to prepare the 11-oxo-12,15-diene by

dehydrobrominating 17, which furnished compound 19, $C_{32}H_{50}O_2$, m.p. 199—200°, $[\alpha]_D$ +42°. The diene 19 was oxidised to give the desired 11-oxo-12,15-diene 20, $C_{32}H_{43}O_3$, m.p. 243—45° $[\alpha]_D$ +28.6°, λ_{max} 244 nm.





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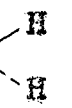
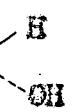
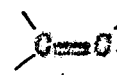
19, R =  ; R^1=Ac

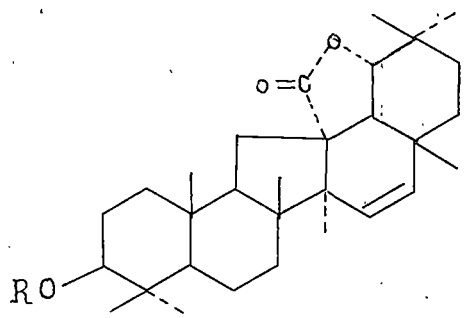
20, R = O ; R^1=Ac

21, R =  ; R^1=H

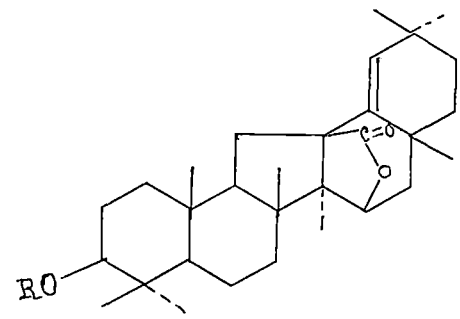
LAH reduction of the 11-oxo-diene 20, furnished a diene-diol 21, $C_{30}H_{48}O_2$, m.p. 198—200°, ν_{max} 3460 (—OH), 820 - () cm^{-1}; purification of the diol by chromatography yielded a homoannular diene 22, $C_{30}H_{46}O$, m.p. 189—90°.

The diol 21 was directly treated with hydrogen peroxide containing p-toluene sulfonic acid following the procedure adopted by Corey and his coworkers. The product furnished two compounds 23 and 25 of the same molecular formula $C_{30}H_{46}O_3$.

The compound 23, m.p. 240—41° on acetylation gave 24 and the structure of 24 was assigned as 3 β -acetate —C—12-nor-olean-13 en-13 α -carb—► 19 α -olide on the basis of ^{1}H, ^{13}C NMR and mass spectral analysis.

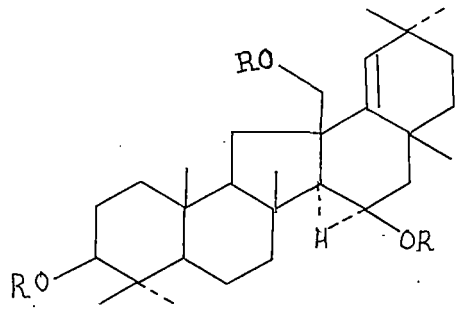


23, R = H
24, R = CH_3CO



25, R = H
26, R = CH_3CO

Another isomeric compound 25, m.p. 256—57°, obtained, was also acetylated and the acetylated product 26, $C_{32}H_{48}O_4$, m.p. 228—29° was assigned structure as 3β -acetate —C—12—nor—olean-18(19) en-13 β -carb—► 15 β -olide on the basis of ^{1}H NMR of the hydroxy lactone 25 and ^{1}H NMR and mass spectral analysis of 26. The structure of 25 was finally proved



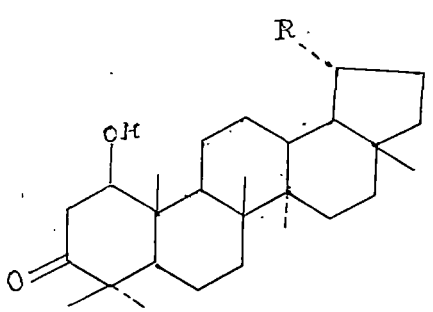
27, R = H
28, R = CH_3CO

by LAH reduction of the lactone that yielded a triol 27, $C_{30}H_{50}O_3$, m.p. 280—82°, acetylation of which gave a triacetate 28, $C_{30}H_{56}O_3$, m.p. 190—93°. The structure of the triacetate was proved by ^1H NMR, ^{13}C NMR and mass spectral analysis.

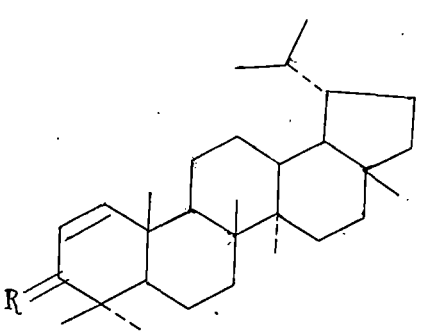
The mechanism of formation of two lactones has been also discussed.

S E C T I O N—B

The same reaction of H_2O_2 in presence of p-toluene-sulfonic acid on lup-1(2)-en-3 β -ol 31 has been carried out. Preparation of lup 1(2) en-3 β -ol has been discussed. Glochidonol 29 isolated from Glochidion accuminatum was hydrogenated using pt-catalyst to give the keto alcohol 29a. The compound 29a was dehydrated with acetic anhydride/pyridine to give



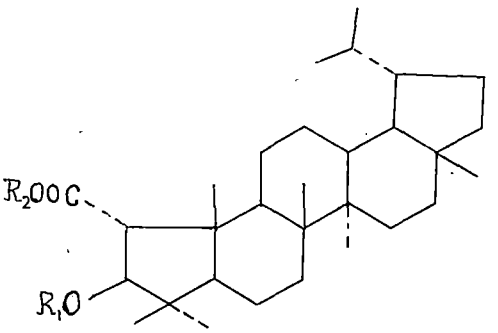
29, R = 
29a, R = 



30, R = O
31, R = 

lup-1(2)-en-3-one 30, m.p. 177—78°, $C_{30}H_{48}O$. LAH reduction of 30 gave the desired allylic alcohol, lup-1(2)-en-3β-ol 31, $C_{30}H_{50}O$, m.p. 214—15°.

The allylic alcohol was treated with hydrogen peroxide in presence of p-toluene sulfonic acid in t-butanol. After reaction and work up followed by chromatography furnished a compound 32 , $C_{30}H_{50}O_3$; IR showed acidic function at 1695 cm^{-1}. It was esterified and gave the methyl ester 32a, $C_{31}H_{50}O_3$, m.p. 265—66°. The structure of the ester was characterised by ^1H NMR and mass spectral analysis. The ester was acetylated to give 32b, $C_{33}H_{54}O_4$, m.p. 250—51°.



32, R_1 = H ; R_2 = H
32a, R_1 = H ; R_2 = CH_3
32b, R_1 = $COCH_3$; R_2 = CH_3

The mechanism of ring A contraction has also been discussed.

Chapter III describes the experimental portion.

PART—III

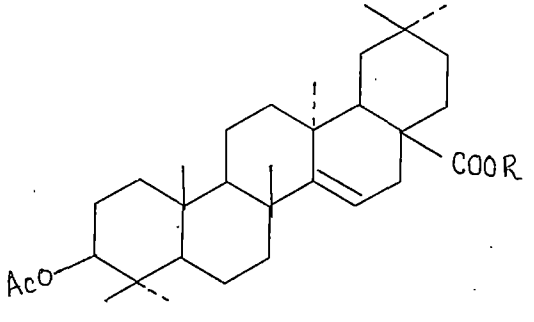
ACTION OF N-BROMOSUCCINIMIDE ON TRITERPENE ACIDS AND ESTERS

CHAPTER—I gives a short review on NBS reaction on triterpenoids.

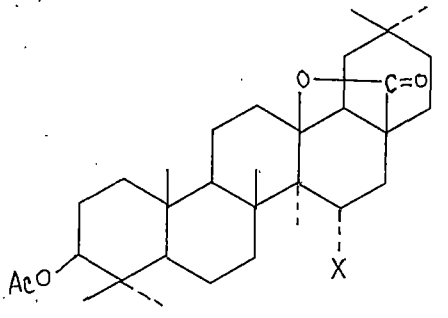
CHAPTER—II

(i) Treatment of NBS on acetyl methyl aleuritolate 33a:

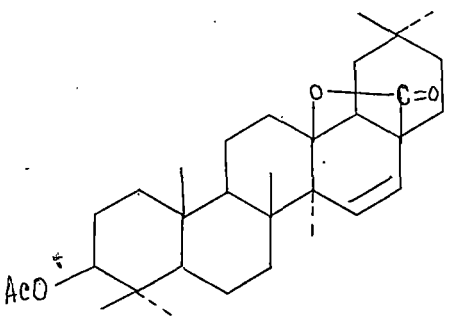
Acetyl methyl aleuritolate 33a was treated with NBS in DMSO in dark for 12 hours, followed by chromatography and crystallisation furnished a solid, analysed for $C_{32}H_{49}O_4Br$, m.p. 280—82°, $[\alpha]_D$ +19.51°, was found to be a γ -lactone from IR spectrum (ν_{max} 1780 cm^{-1}). It's structure as 34 was proved by PMR spectrum. Beilstein test was positive.



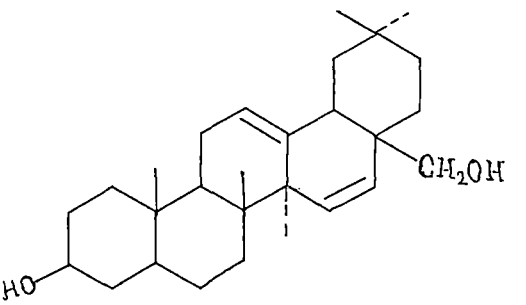
33a, R = CH_3
33b, R = H



34, X = Br
35, X = H



35



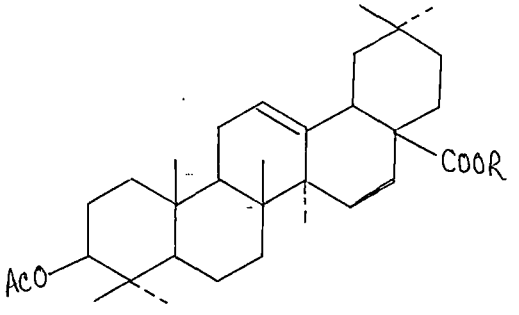
37

Repeatation of the reaction with acetyl aleuritolic acid 33b, furnished the same bromolactone 34 while compared with an authentic specimen. The structure of the bromolactone has been established as 34, on the fact that the compound on dehydrobromination with dimethylaniline afforded 15,16-dehydrolactone 35, $C_{32}H_{48}O_4$, m.p. 308—10°, which on catalytic hydrogenation afforded 3 β -acetyl-oleanan-28⟶13 olide 36, $C_{32}H_{50}O_4$, m.p. 293—94°, identical with authentic specimen (mmp and CO—IR). The compound 35 on LAH reduction furnished aegeceradiol 37, $C_{30}H_{48}O_2$, m.p. 235—36°, identical with an authentic sample (mmp and CO—IR comparison).

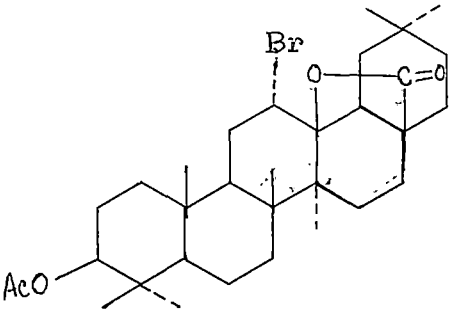
(ii) Treatment of NBS on acetyl methyl oleanolate 38a:

Acetyl methyl oleanolate 38a when treated with NBS following the same procedure afforded a compound 39, $C_{32}H_{49}O_4Br$, m.p. 215—16°, IR showed that it contains a γ -lactone; Beilstein

test for halogen was positive, was identified as 3 β -acetyl-12 α -bromo-oleanan-28$\rightarrow$13-olide 32, when compared with an authentic specimen.



38a, R = CH_3
38b, R = H

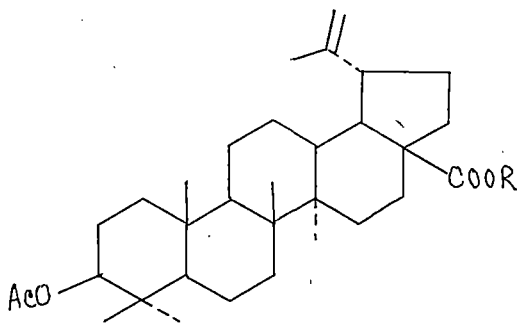


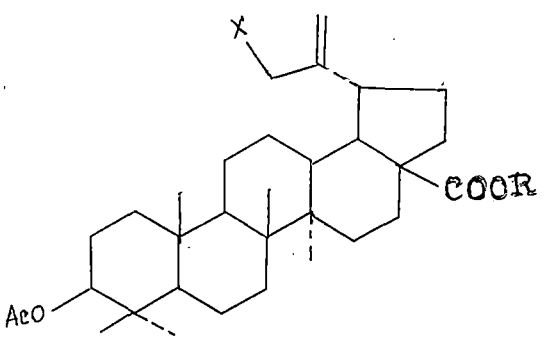
39

Acetyl oleanolic acid 38b furnished the same bromo lactone when treated with NBS/DMSO (compared with authentic specimen)

(iii) Treatment of NBS on methyl-3β-acetyl-betulenate 40a:

Methyl-3 β -acetyl-betulenate 40a on similar reaction with NBS in DMSO afforded three different bromo compounds, separated by column chromatography. The less polar one, 41a, $C_{33}H_{51}O_4Br$, m.p. 235--36°, $[\alpha]_D$ +42.55°, was identified as methyl-30-bromo-3 β -acetyl betulenate on the basis of IR,



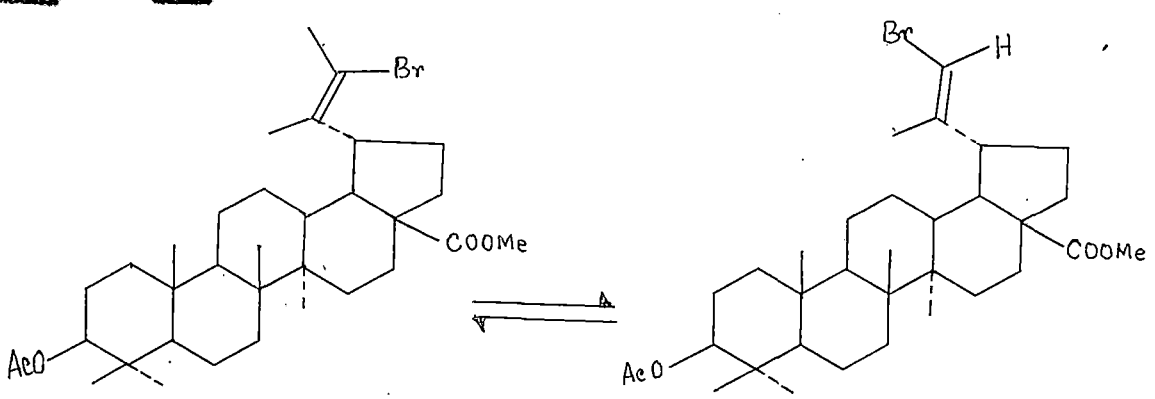


40a, R = CH_3
40b, R = H

41a, R = CH_3 ; X = Br
41b, R = H ; X = Br

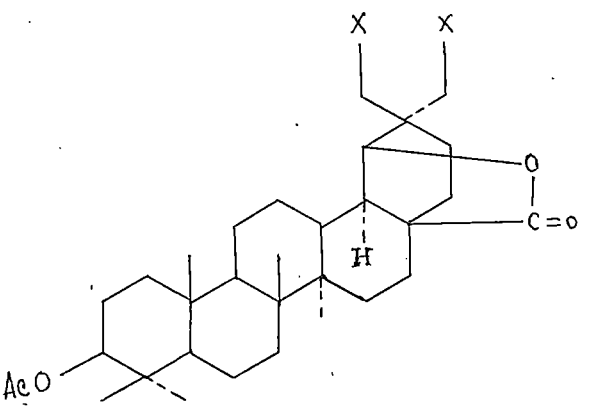
PMR spectra and further proved by debrominating 41b, with Zn/AcOH to give methyl-3β-acetyl betulenate 40a.

In the same polarity another bromo compound, $C_{31}H_{51}O_4Br$, m.p. 228--30°, $[\alpha]_D$+50° was obtained. PMR spectrum gave two singlets at 1.7 and 1.8 ppm for three protons suggested the presence of methyl group on a double bond. The structure was assigned as a mixture of cis-trans isomers 42a and 42b on the basis of total PMR spectra.



42a 42b

The third compound 43 (10%) was a dibromo lactone, $C_{32}H_{48}O_4Br_2$, m.p. 303—4°, $[\alpha]_D$ +47°, CD(n-hexane) 218 nm (ϵ = -0.99). The structure of the compound was assigned as 3 β -acetyl, 29,30, dibromo-18 αH-oleanan-28⟶ 19 β -olide 43a on the basis of PMR, ^{13}C NMR and mass spectral analysis. It resisted dehydrobromination with dimethylaniline but on debromination with Raney Nickel—hydrogen gave 43b, $C_{32}H_{50}O_4$, m.p. > 360°, $[\alpha]_D$ +59°, identical with 3 β -acetyl-oleanan-28⟶ 19 β -olide (compared with authentic specimen).



43a, X = Br
43b, X = H

3 β -acetyl betulenic acid 40b also furnished the same bromo lactone 43a on treatment with NBS in DMSO and 3 β -acetyl-30-bromobetulenic acid 41b, which was converted to the methyl ester 41a. These two compounds were identified as 43a and 41a when compared with authentic specimen.

Chapter-III describes the experimental portion.

PART—IV

CHEMICAL INVESTIGATION OF THE ROOT OF LEUCAS ASPERA SPRENG

Chapter—I gives the introduction and Chapter—II gives the morphological features of Lebiatae family and Leucas Aspera spreng

Chapter—III : Section A and B(i), deals with the extraction of the powdered root of Leucas Aspera with the ethyl alcohol, hydrolysis of the alcohol extract with 7% H_2SO_4 and extraction of the neutral fraction with ether. Column chromatography of the residue from the neutral part furnished two compounds. The first compound, m.p. 154—56°, $[\alpha]_D$ -50°, molecular formula $C_{28}H_{43}O$, was identified as stigmasterol by preparation of its acetate, $C_{31}H_{50}O_2$, m.p. 137—39°, $[\alpha]_D$ -34° (M^+ 454) and compared with authentic specimen.

Section B(ii) deals with the purification and characterisation of a new dihydroxy lactone-leucolactone, $C_{30}H_{48}O_4$. The second component eluted by benzene:ether = 4:1, on crystallisation and purification from chloroform-methanol mixture furnished crystalline solid, analysed for $C_{30}H_{48}O_4$ (M^+472), m.p. 310°. IR spectrum showed two hydroxyl groups and a γ-lactone ring at ν_{max} 3607, 3450 and 1750 cm^{-1} respectively. The compound has been designated as leucolactone 44.

Section B(iii) deals with the preparation of acetyl derivative 45, which has been analysed for $C_{34}H_{52}O_6$ (M^+ 556), m.p. 284—85°. It showed two acetate groups at ν_{max} 1740, 1729, 1235 and 1218 cm^{-1} and γ-lactone at 1768 cm^{-1}.

Section B(iv) deals with the preparation of diketo derivative 46 by oxidation with CrO_3—Py. The diketo leucolactone so formed, was analysed for $C_{30}H_{44}O_4$ (M^+ 468), m.p. 323—24°. IR spectrum showed a broad carbonyl absorption at 1705—1715 cm^{-1} and γ-lactone ring at 1760 cm^{-1}.

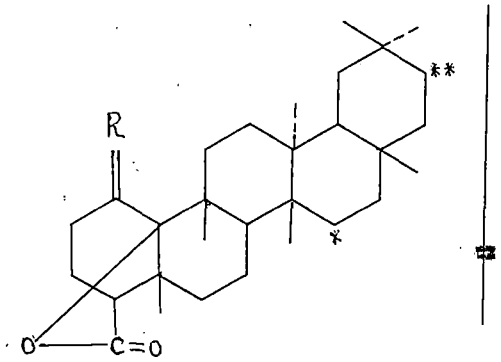
Section C(i) gives the PMR spectral data of leucolactone 44. The peaks were observed at 0.85 (1,t CH_3), 0.92 (3t-CH_3), 0.95 (1t, CH_3), 1.18 (1t CH_3), 1.28 (1t CH_3), 2.6 (1H, m), 3.18 ($W_{\frac{1}{2}}$ = 8Hz), 3.85 ($W_{\frac{1}{2}}$ =11Hz).

Section C(ii) deals with the NMR spectral analysis of the leucolactone acetate. Tertiary methyl signals at 0.85, 0.92, 1.18, 1.28 ppm showed the presence of seven methyl groups; the acetoxy methyl protons at 2.05 and 2.14 ppm. A proton α to the carbonyl group of the lactone ring showed up at 2.8 ppm had double doublets with J value of 8Hz indicating the equatorial orientations of α-proton and axial nature of the lactone carbonyl. The triplet centred at 4.45 ppm with

J value 18Hz was due to the methine proton, geminal to one of the acetate groups, which must be axially oriented. A doublet appeared at 4.9 ppm with coupling constant 8Hz indicated that the second acetoxy group is attached to a carbon containing a proton which is equatorially oriented having either only one or two neighbouring protons, the dihydral angle of one of which would be around 90°, thereby causing minimum coupling with the acetoxy methine proton. ^{13}C NMR showed the presence of 34 carbon atoms, the lactone carbonyl appeared at 176.9 ppm and the carbon containing the lactyl oxygen appeared at 90.2 ppm as singlet showing that the lactone ring is terminated at the tertiary carbon atom. Off resonance CW decoupled experiments showed the presence of 9—CH_3, 10—CH_2, 5—CH, 10—C— carbon atoms in leucolactone acetate.

Section C(iii) contains discussion on NMR spectral analysis of diketoleucolactone. XL—300 NMR showed the presence of 7-tertiary methyls at 0.82, 0.93, 1.02, 1.06, 1.10, 1.18 and 1.30 ppm. The multiplets between 2—3 ppm showed the presence of 5-protons α- to the carbonyl groups indicating that the two ketonic groups contain four α-protons, the lactone carbonyl having one α-proton. The doublets centred at 2.18 and 2.78 ppm are coupled with gem coupling separated by 0.6 ppm probably due to anisotropic effect of the adjacent

carbonyl. These two protons have no other neighbouring proton. The proton that appeared at 2.78 ppm showed a very low coupling ($J = 0.5$ Hz) with the methyl at 1.18 ppm suggesting that this proton being situated very close to a tertiary methyl group at 1.1 ppm. The absence of a singlet for a proton eliminates the position 18 for the oxygen function. The multiplet of the eight lines between 2.4 to 2.5 ppm showed that the CH_2 group next to the second carbonyl have two protons as CH_2 neighbour. This tied down one of the oxygen functions at C—1 positions, the α-protons of which have two neighbouring protons situated at C—3 position. The methyl peak that appeared at 1.18 ppm has been assigned to the C—28 methyl of friedelane skeleton by comparison with previously known friedelaneskeleton. Since it couples with one of the α-protons of the oxo group the second oxygen function is probably situated at C—15 or C—21 positions. Thus from the above spectral data the following probable structure is suggested.



= Either * or **
may contain second R group.

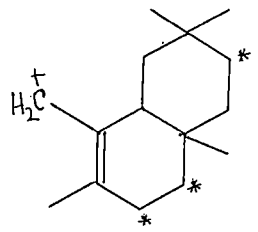
44, R = H, OH

45, R = H, OCOCH$_3$

46, R = O

S E C T I O N—D

Mass spectral analysis of leucolactone, leucolactone acetate, and diketo leucolactone suggested the formation of fragments a, b, c and d, typical of friedelane skeleton. The existance of fragment c and d excluded the possibility of existance of second oxygen function at 11, 12, 15, 16 position.



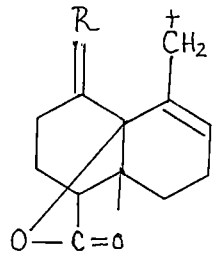
a

* Any one of the positions containing group R,

when R = OH, a = m/e 220

R = CH_3COO, a = m/e 262

R = O , a = m/e 218

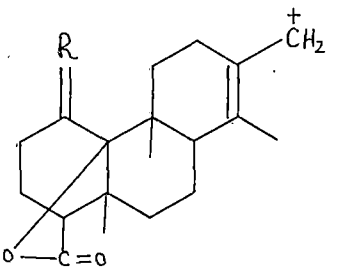


b

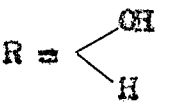
when R =  , b = m/e 221

R =  , b = m/e 263

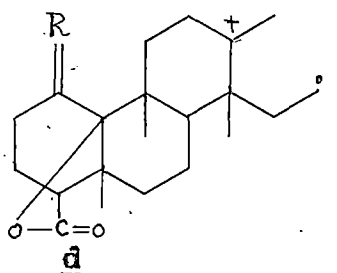
R = O , b = m/e 219



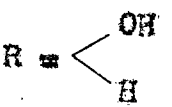
c

R =  , c = m/e 303

R = O , c = m/e 301

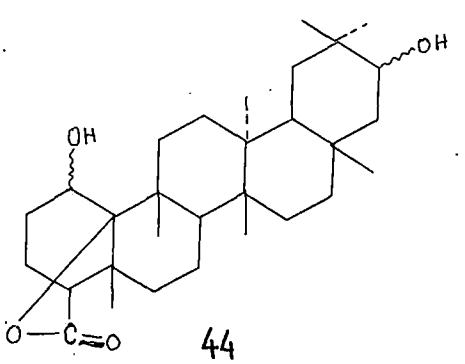


d

R =  , d = m/e 332

R = O , d = m/e 330

Thus from the mass spectra it is concluded the second oxygen is situated at C—21 position. Hence the probable structure of leucoleotone may be written as 44 without the stearochemistry of the two hydroxyl groups.



44

Further work to establish the stearochemistry of the two hydroxyl groups and some chemical transformation is in progress.

Chapter—IV describes the experimental portion.

LIST OF PUBLICATIONS

1. ACTION OF HYDROGEN PEROXIDE ON OLEAN-12,15-DIEN, 3,11-DIOL : PREPARATION OF C-NOR-TRITERPENE LACTONES.

   B.P.Pradhan, M.M.Mukherjee, D.K.Chakraberti and J.N.Shoolery, Tetrahedron, 39, 2819 (1983).

2. ACTION OF N-BROMOSUCCINIMIDE ON TRITERPENE ACIDS AND ESTERS IN DIMETHYL SULFOXIDE.

   B.P.Pradhan, M.M.Mukherjee, D.K.Chakraberti and J.N.Shoolery, Indian Journal of Chemistry, 22B, 12 (1983).

3. NOVEL METHOD FOR THE LACTONE RING OPENING.

   Bhim. P. Pradhan, Abul Hassan, Dilip K. Chakraberti and Sikha Dutta (Communicated).