S U M M A R Y

The work embodied in the present thesis has been presented into three parts.

PART I

OXIDATION OF TRITERPENOID (C-3) KETONES WITH SELENIUM DIOXIDE IN TERTIARY BUTANOL.

Part I has been divided into three chapters.

CHAPTER I

This chapter comprises a short review of selective oxidation with selenium dioxide.

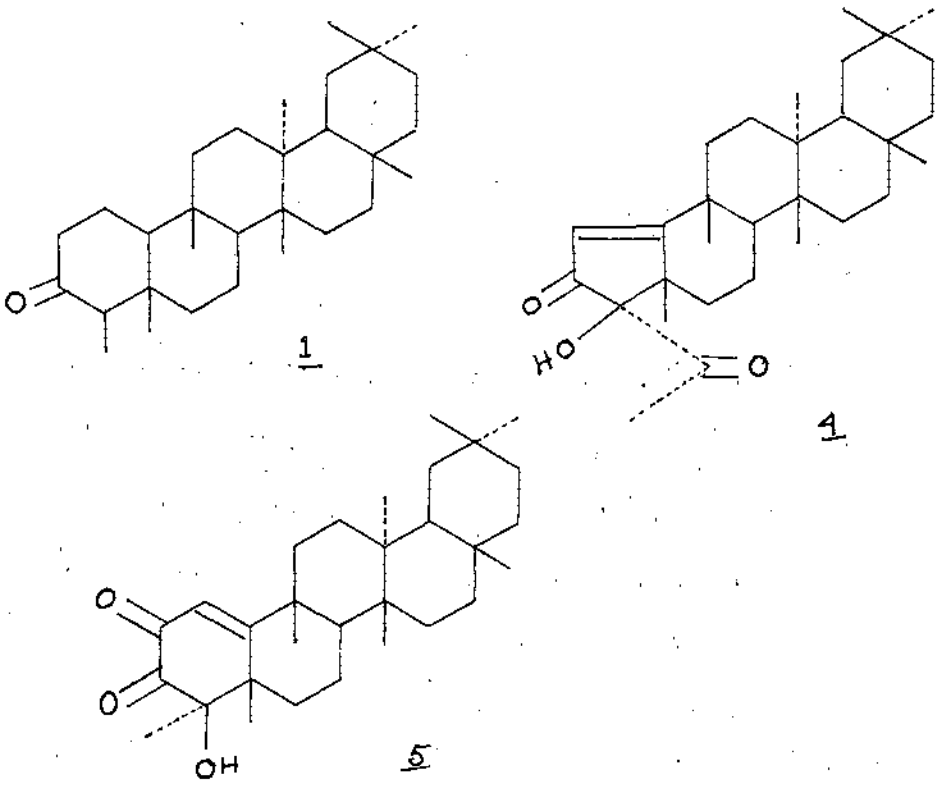
CHAPTER II

This chapter deals with the studies on oxidation of friedelin (1), methyl dihydrobetulonate (2) and taraxerone (3) with selenium dioxide in presence of tertiary butanol.

SECTION A

This section constitutes the studies on oxidation of friedelin 1. Friedelin 1 on prolonged heating with selenium dioxide in tertiary butanol furnishes two products, characterized as 3α-acetyl-4-nor-friedel-1(10)-en-3β-ol-2-one 4, $C_{30}H_{46}O_3$, m.p. 246-47°; mass : m/z 454 (M^+); IR : 3440 (-OH), 1705 (carbonyl), 1690 (carbonyl), 1592, 865 cm^{-1} (olefinic double bond) and friedel-1(10)-en-4β-ol-2, 3-dione 5, $C_{30}H_{46}O_3$, m.p. 272-73°; mass : m/z 454 (M^+); IR : 3440 (-OH),

1705 (carbonyl), 1680 (carbonyl), 1600, 840 cm^{-1} (olefinic double bond). The structure of 4 and 5 are based on spectral data (IR, UV, ^{1}H NMR, Mass and ^{13}C NMR).



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4

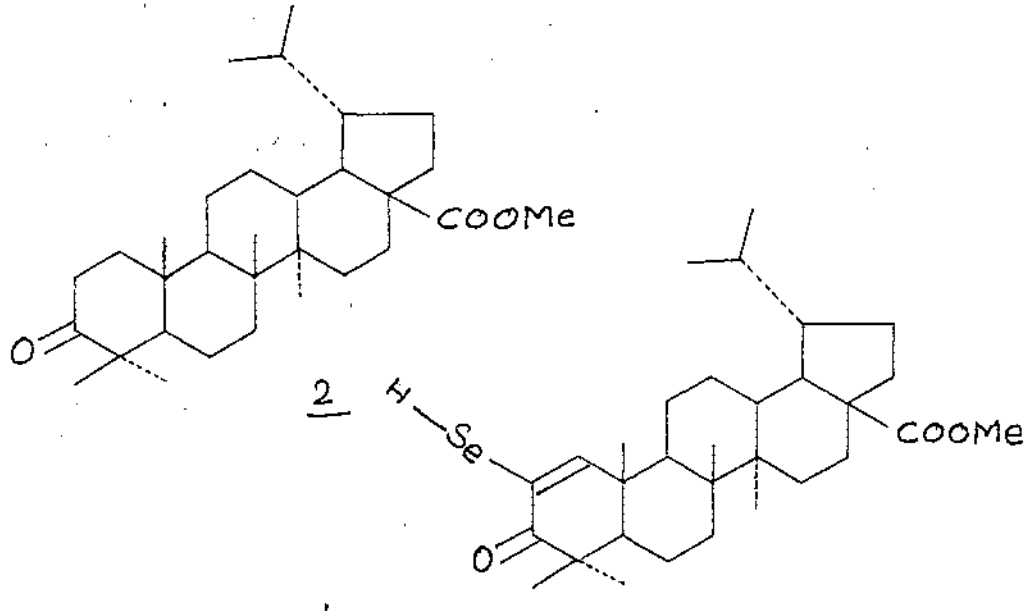
5

The mode of formation of two products 4 and 5 have been discussed.

SECTION B

This section describes the isolation and characterization of products obtained on oxidation of 4-gem dimethyl-3-keto triterpenoid, methyl dihydrobetulonate 2 with selenium dioxide in presence of tertiary butanol. The products isolated

are characterized as lup-28-carbomethoxy-1(2)-en-3-one-2-selenide 6, $C_{31}H_{48}O_3Se$, m.p. 265-66°; mass : m/z 468 (M^+-Se); IR : 1730 (carbomethoxy group), 1680 (carbonyl group), 1600, 830 cm^{-1} (olefinic double bond) and A-nor-lup-28-carbomethoxy-2-carb ⟶ 1-olide-3α -ol 7, $C_{31}H_{48}O_5$, m.p. 273-74°; mass : m/z 500 (M^+); IR : 3375 (-OH), 1810 (β-lactone), 1700 cm^{-1} (carbomethoxy group). The structures 6 and 7 have been established on the basis of spectral analysis (IR, UV, Mass, ^1H NMR and ^{13}C NMR).



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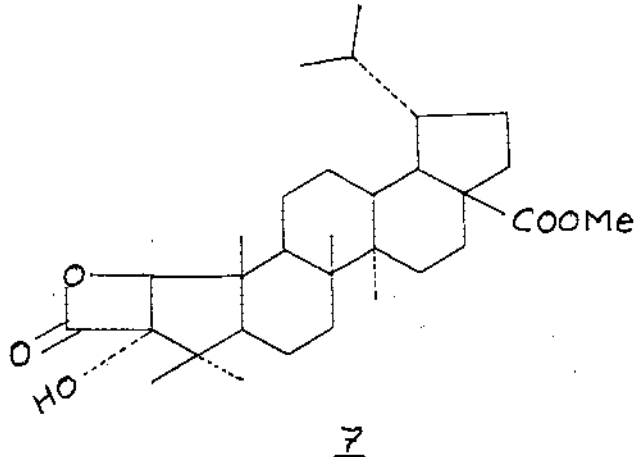

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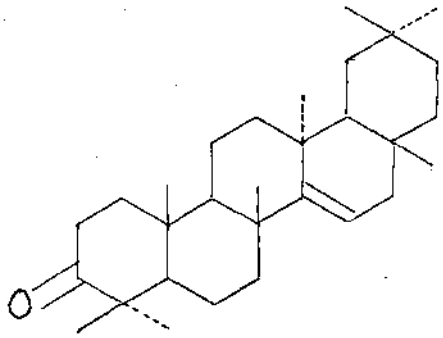
The possible mode of formation of 6 and 7 have also been discussed.

SECTION C

This section contains isolation and characterization of products formed on oxidation of taraxerone 3 with selenium dioxide in presence of tertiary butanol. The products isolated are characterized as 1(2)-dehydro taraxerone 8, $C_{30}H_{46}O$, m.p. 248-49°; mass : m/z 422 (M^+); IR : 1660 (carbonyl group), 1600, 810 cm^{-1} (olefinic double bond); UV : λ_{max} at 228 nm (ϵ, 11,000); 1(2)-dehydro taraxer-3-one-2-selenide 9, $C_{30}H_{46}OSe$, m.p. 282-83°; mass : m/z 500 $(M-H)^+$, IR : 1660 (carbonyl), 1605, 822 cm^{-1} (olefinic double bond); UV : λ_{max} at 302 nm (ϵ, 8300); 2-nor-taraxer-1, 3-dione 10, $C_{29}H_{44}O_2, CH_3OH$, m.p. 260-61°; mass : m/z 424 (M^+); IR : 1740 (carbonyl), 1695 (carbonyl), 800 cm^{-1} (olefinic double bond); 1,2-dehydro taraxerone-2, 2'-seleno-taraxer-1', 3'-dione 11, $C_{60}H_{90}O_3Se$, m.p. 300-302°; mass : m/z 938 (M^+); IR : 1710 (carbonyl), 1695 (carbonyl), 1680 (carbonyl group), 820 cm^{-1} (olefinic double bond); 1β, 3α-dihydroxy-3-carboxy-A-nor-taraxerene 12, $C_{30}H_{48}O_4$, m.p. 275-76°; mass : m/z 472 (M^+); IR : 3300-2700 (broad, -OH), 1700 (-COOH), 820 cm^{-1} (olefinic double bond).

The structures of these compounds have been established on the basis of analytical data, spectral data (IR, UV,

^{1}H NMR, Mass and ^{13}C NMR) and by direct comparison with authentic specimens.



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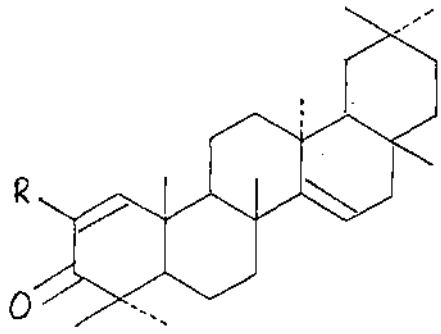
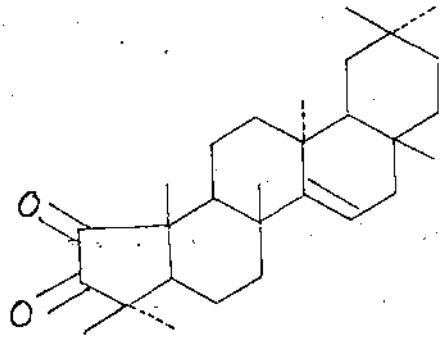


8, R = H

9, R = SeH



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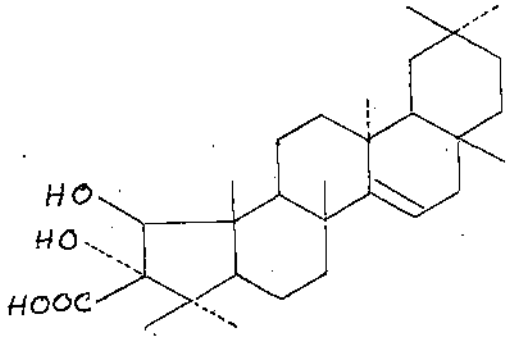

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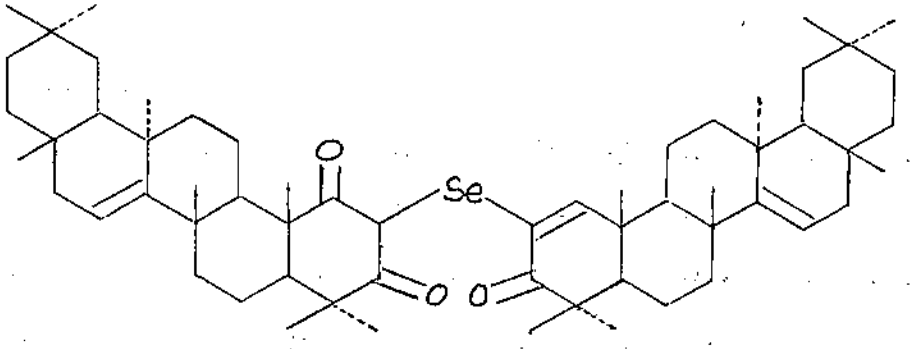

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The possible mode of formation of 1β , 3∝ -dihydroxy-3-carboxy-A-nor-taraxerene 12 and 2-nor-taraxer-1, 3-dione 10 have been discussed.

CHAPTER III

The experimental details of the works have been discussed in this chapter.

PART II

ALLYLIC OXIDATION OF TRITERPENOID C-12(13)-DOUBLE BOND WITH SELENIUM DIOXIDE AND HYDROGEN PEROXIDE : PREPARATION OF 11∝ , 12∝ -OXIRANE DERIVATIVES.

Part II has been divided into three chapters.

CHAPTER I

This chapter constitutes a short review on reaction of hydrogen peroxide in presence of selenium dioxide.

CHAPTER II

This chapter deals with the studies on the action of selenium dioxide in presence of hydrogen perioxide on triterpenoids of oleanane and Ursane Skeletons.

i) β-amyrin acetate 13 on prolonged heating with hydrogen peroxide and selenium dioxide in tertiary butanol furnishes two compounds which are characterized as 11α, 12α-epoxy-taraxer-14-en-3β-yl acetate 14, $C_{32}H_{50}O_3$, m.p. 307-308°; mass : m/z 482 (M^+); IR : 1735, 1260 (-OAc), 880 (epoxide ring), 820 cm^{-1} ($>C = C<_H$) and 11α, 12α-epoxy-taraxer-14-en-3β-ol 15, $C_{30}H_{48}O_2$, m.p. 285-86°; mass : m/z 440 (M^+); IR : 3500 (-OH), 880 (epoxide ring), 820 cm^{-1} ($>C = C<_H$).

ii) Oxidation of α-amyrin acetate 16 with selenium dioxide and hydrogen peroxide affords two compounds which are identified as 11α, 12α-epoxy-urs-14-en-3β-yl acetate 17, $C_{32}H_{50}O_3$, m.p. 213-14°; mass : m/z 482 (M^+); IR : 1735, 1260 (-OAc), 880 (epoxide ring), 820 cm^{-1} ($>C = C<_H$) and 11α, 12α-epoxy-urs-14-en-3β-ol 18, $C_{30}H_{48}O_2$, m.p. 245-46°; mass : m/z 440 (M^+); IR : 3450 (-OH), 880 (epoxide ring), 820 cm^{-1} ($>C = C<_H$).

iii) Both acetyl oleanolic acid 19 and methyl acetyl oleanolate 20 on oxidation with selenium dioxide and hydrogen peroxide furnish two identical products 11α, 12α-epoxy-oleanan-28 ⟶ 13-olide-3β-yl acetate 21, $C_{32}H_{48}O_5$,

m.p. 293-94°; mass : m/z 512 (M^+); IR : 1765 (γ-lactone), 1720, 1240 (-OAc), 880 cm^{-1} (epoxide ring) and 11α, 12α-epoxy-oleanan-28⟶13-olide-3β-ol 22, $C_{30}H_{46}O_4$, m.p. 269-70°; mass : m/z 470 (M^+); IR : 3530 (-OH), 1770 (γ-lactone), 880 cm^{-1} (epoxide ring).

iv) Reaction of methyl acetyl ursolate 23 with selenium dioxide and hydrogen peroxide affords two compounds which are identified as 11α, 12α-epoxy-urs-28⟶13-olide-3β-yl acetate 24, $C_{32}H_{48}O_5$, m.p. 281-82°; mass : m/z 512 (M^+); IR : 1775 (γ-lactone), 1740, 1250 (-OAc), 885 cm^{-1} (epoxide ring) and 11α, 12α-epoxy-urs-28⟶13-olide-3β-ol 25, $C_{30}H_{46}O_4$, m.p. 295-96°; IR : 3300 (-OH), 1775 (γ-lactone), 885 cm^{-1} (epoxide ring).

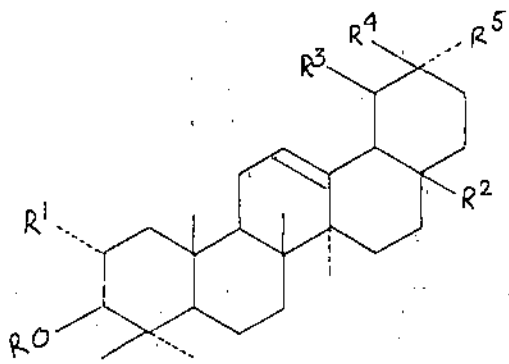
v) Oxidation of erythrodiol 26 with selenium dioxide and hydrogen peroxide furnishes 11α, 12α-epoxy-oleanan-28⟶13-olide-3β-ol 22, $C_{30}H_{46}O_4$, m.p. 266-67° ; IR: 3530 (-OH), 1770 (γ-lactone), 880 cm^{-1} (epoxide ring).

vi) Uvaol 27 on oxidation with selenium dioxide and hydrogen peroxide gives compound 11α, 12α-epoxy-urs-28⟶13-olide-3β-ol 25, $C_{30}H_{46}O_4$, m.p. 292-93°; IR : 3300 (-OH), 1775 (γ-lactone), 885 cm^{-1} (epoxide ring).

vii) Olean-12-en-2α, 3β, 28-yl triacetate 28 on prolonged heating with hydrogen peroxide and selenium dioxide furnishes two compounds which are characterized as 11α, 12α-epoxy-taraxer-14-en-3β-ol-2α, 28-yl diacetate 29, $C_{34}H_{52}O_6$,

m.p. 295-96°; mass : m/z 556 (M^+); IR : 3400 (-OH), 1750, 1720, 1280, 1240 (-OAc), 880 (epoxide ring), 820 cm^{-1} ($>C=C<_H$) and 11α, 12α-epoxy-taraxer-14-en-2α, 3β-diol-28-yl acetate **30**, $C_{32}H_{50}O_5$, m.p. 266-67°; mass : m/z 514 (M^+); IR : 3200-3600 (broad, -OH), 1720, 1250 (-OAc), 880 (epoxide ring), 820 cm^{-1} ($>C=C<_H$).

The structures of these reaction products have been established on the basis of analytical data, spectral data (^1H NMR, Mass, ^{13}C NMR and IR) and by direct comparison with authentic specimens.



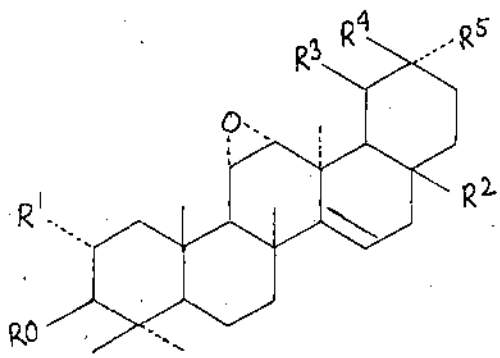
13, R=Ac, $R^1=R^3=H$, $R^2=R^4=R^5=Me$

16, R=Ac, $R^1=R^4=H$, $R^2=R^3=R^5=Me$

19, R=Ac, $R^1=R^3=H$, $R^2=COOH$, $R^4=R^5=Me$

20, R=Ac, $R^1=R^3=H$, $R^2=COOMe$, $R^4=R^5=Me$

26, $R=R^1=R^3=H$, $R^2=CH_2OH$, $R^4=R^5=Me$



14, R=Ac, $R^1=R^3=H$, $R^2=R^4=R^5=Me$

15, $R=R^1=R^3=H$, $R^2=R^4=R^5=Me$

17, R=Ac, $R^1=R^4=H$, $R^2=R^3=R^5=Me$

18, $R=R^1=R^4=H$, $R^2=R^3=R^5=Me$

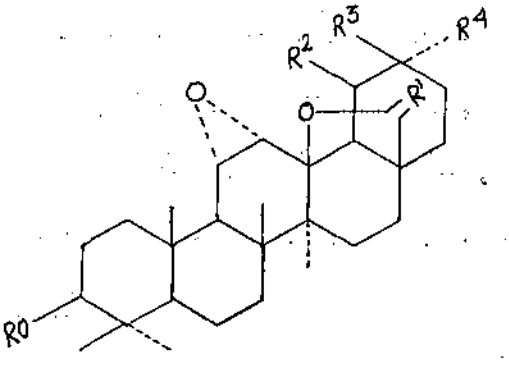
23, R=Ac, R^1=R^4=H, R^2=COOMe, R^3=R^5=Me

27, R=R^1=R^4=H, R^2=CH_2OH, R^3=R^5=Me

28, R=Ac, R^1=OAc, R^2=CH_2OAc, R^3=H, R^4=R^5=Me

29, R=R^3=H, R^1=OAc, R^2=CH_2OAc, R^4=R^5=Me

30, R=R^3=H, R^1=OH, R^2=CH_2OAc, R^4=R^5=Me



21, R=Ac, R^1=O, R^2=H, R^3=R^4=Me

22, R=R^2=H, R^1=O, R^3=R^4=Me

24, R=Ac, R^1=O, R^3=H, R^2=R^4=Me

25, R=R^3=H, R^1=O, R^2=R^4=Me

The mode of formation of products 14, 15, 17, 18, 29, 30, 21, 22, 24, 25 have been discussed.

CHAPTER III

This chapter describes the experimental details of the works.

PART III

STUDIES ON THE REDUCTIVE ACTION OF LITHIUM-ETHYLENEDIAMINE ON TRITERPENOIDS.

Part III has been divided into three chapters.

CHAPTER I

This chapter constitutes a short review of the reactions of dissolving alkali metals in presence of bases.

CHAPTER II

This chapter deals with the studies on the action of lithium-ethylenediamine on triterpenoids containing (a) isopropenyl group, (b) carbonyl group at C-3 position with or without isopropenyl group, (c) aldehyde group at C-17 position with or without isopropenyl group, (d) sterically hindered ester with or without isopropenyl group, (e) on steroid and triterpenoid α,β-unsaturated ketones and (f) on triterpenoid conjugated dienes. The case study of acid isomerization of 18(19) double bond in lupane skeleton is also described in this chapter.

SECTION A

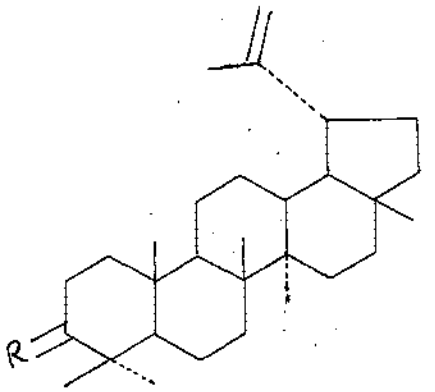
a) Studies on triterpenoids containing isopropenyl group

(i) Reaction of lupeol 31a, with lithium-ethylenediamine furnishes lupanol 32a, $C_{30}H_{52}O$, m.p. 204-05°; IR : 3330 cm^{-1} (-OH), confirmed by preparing acetyl derivative and by comparison with authentic specimen.

(ii) Reduction of moretenol 33b with lithium-ethylenediamine affords moretanol 34b, $C_{30}H_{52}O$, m.p. 222-23°; IR : 3320-3400 cm^{-1} (-OH), confirmed by direct comparison with authentic specimen.

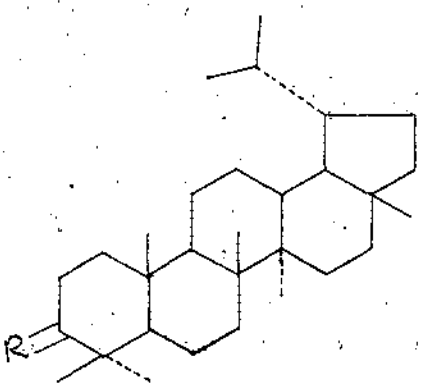
(iii) Moretene 33a on reduction with lithium-ethylenediamine gives moretane 34a, $C_{30}H_{52}$, m.p. 176-7° and 194-95° (double melting); IR : no absorption in the region 870 to 900 cm^{-1}, confirmed by comparison with authentic specimen.

(iv) Reaction of betulinic acid 35 with lithium-ethylenediamine furnishes dihydro betulinic acid 36, $C_{30}H_{50}O_3$, m.p. 322-23°, IR : 3440 cm^{-1} (-OH), 1690 cm^{-1} (-COOH), confirmed by preparing ester derivative and by direct comparison with authentic specimen.

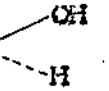


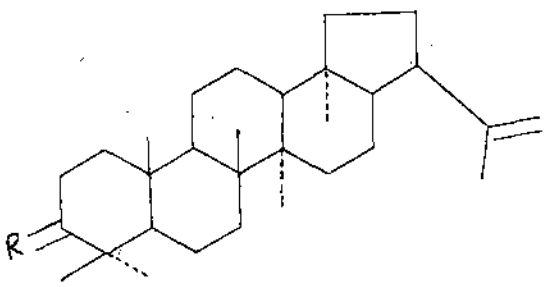
31, R=O

31a, R= 



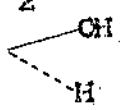
32, R=O

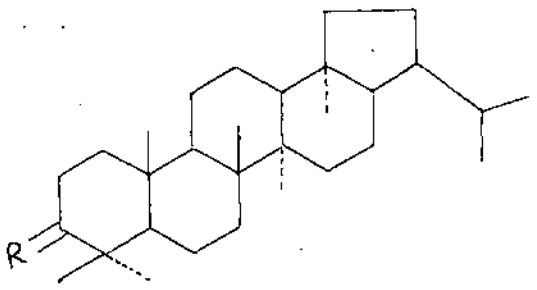
32a, R = 



33, R=O

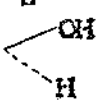
33a, $R=H_2$

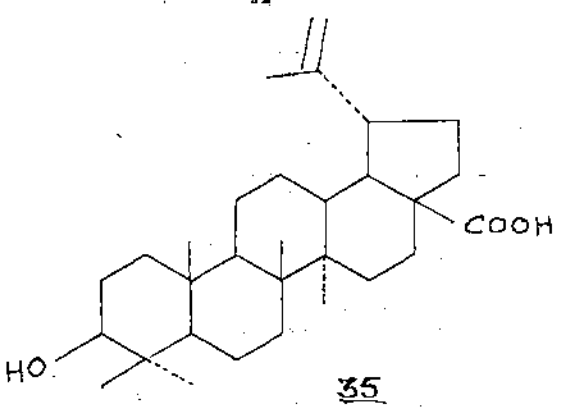
33b, R= 



34, R=O

34a, $R=H_2$

34b, R= 



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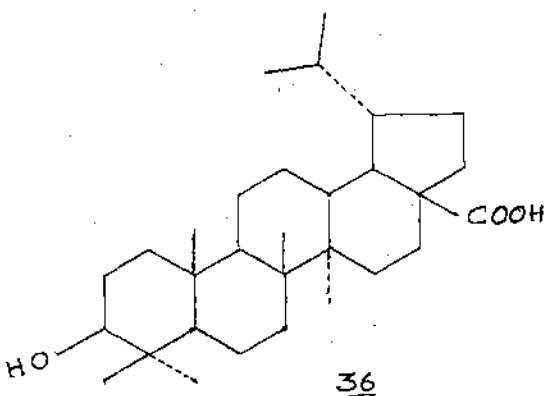

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b) Studies on 3-keto triterpenoids with or without isopropenyl group.

(i) Reaction of lupanone 32 with lithium-ethylenediamine affords lupanol 32a, $C_{30}H_{52}O$, m.p. 204-05°; IR : 3330 cm^{-1} (-OH).

(ii) Reduction of moretanone 34 with lithium-ethylene-diamine furnishes moretanol 34b, $C_{30}H_{52}O$, m.p. 224°; IR : 3320-3400 cm^{-1} (-OH).

(iii) β-amyrone 37, on reduction with lithium-ethylenediamine gives β-amyrin 37a, $C_{30}H_{50}O$, m.p. 196-97°; IR : 3250-3435 cm^{-1} (-OH).

(iv) Reaction of taraxerone 38 with lithium-ethylenediamine affords taraxerol 38a, $C_{30}H_{50}O$, m.p. 280-82°; IR : 3300-3400 cm^{-1} (-OH).

(v) Reduction of glutenone 39 with lithium-ethylenediamine furnishes 3α-glutenol 39a, $C_{30}H_{50}O$, m.p. 201-02°; IR : 3300-3400 cm^{-1} (-OH).

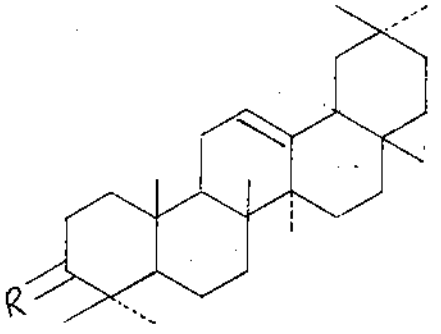
(vi) Germanicone 40 on reduction with lithium-ethylenediamine gives germanicol 40a, $C_{30}H_{50}O$, m.p. 177-79°; IR : 3300-3400 cm^{-1} (-OH).

(vii) Reaction of friedelin 41 with lithium-ethylenediamine furnishes friedelinol 41a, $C_{30}H_{52}O$, m.p. 299-302°; IR : 3450 cm^{-1} (-OH).

(viii) Reduction of lupenone 31 with lithium-ethylenediamine affords lupanol 32a, $C_{30}H_{52}O$, m.p. 204-05°; IR : 3330 cm^{-1} (-OH).

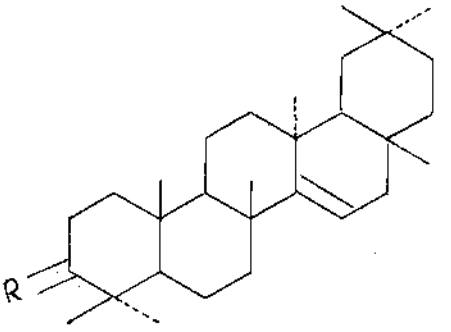
(ix) Moretenone 33 with lithium-ethylenediamine furnishes moretanol 34b, $C_{30}H_{52}O$, m.p. 222-23°; IR : 3320-3400 cm^{-1} (-OH), confirmed by direct comparison with authentic specimen.

All these alcohols have been confirmed by preparing acetyl derivative and by direct comparison with authentic specimens.

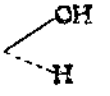


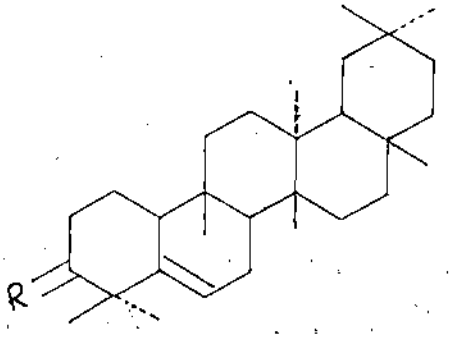
37, R=O

37a, R= 



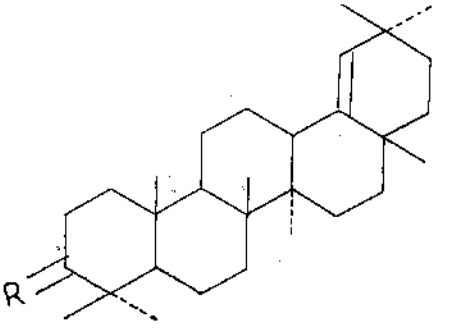
38, R=O

38a, R= 

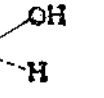


39, R=O

39a, R= 



40, R=O

40a, R= 

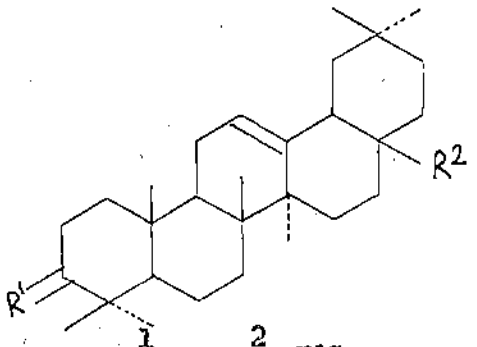
41, R=O

41a, R= 

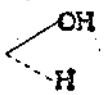
c) Studies on triterpenoids containing 17-aldehyde group with or without isopropenyl group.

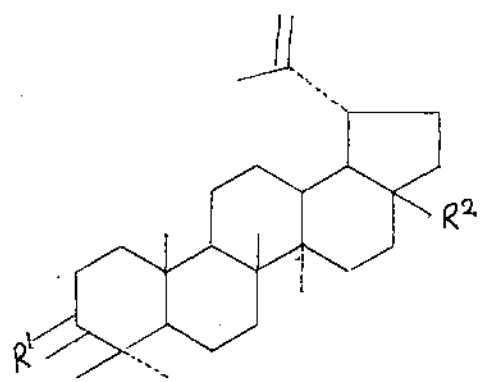
i) Reduction of oleanonic aldehyde 42 with lithium-ethylenediamine furnishes a single compound erythrodiol 42a, $C_{30}H_{50}O_2$, m.p. 230-31°; IR : 3300-3400 cm^{-1} (-OH), confirmed by preparing acetyl derivative and by direct comparison with authentic specimen.

ii) Reaction of betulonic aldehyde 43 with lithium-ethylenediamine affords a single compound dihydrobetulin 44, $C_{30}H_{52}O_2$, m.p. 277-78°; IR : 3400-3500 cm^{-1} (-OH), confirmed by preparing acetyl derivative and by direct comparison with authentic specimen.

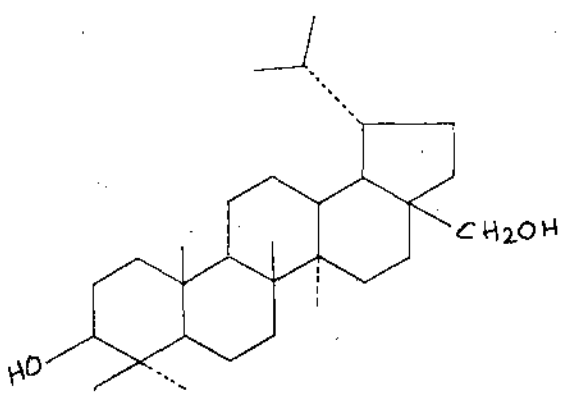


42, R^1=O, R^2=CHO

42a, R^1=  , R^2=CH_2OH



43, R^1=O, R^2=CHO



44

d) Studies on triterpenoid hindered esters with or without isopropenyl group.

i) Reduction of methyl betulonate 45 with lithium-ethylenediamine affords dihydrobetulinic acid 36, m.p. 322-23°.

ii) Reaction of methyl betulinate 45a with lithium-ethylenediamine furnishes dihydrobetulinic acid 36, m.p. 322-23°.

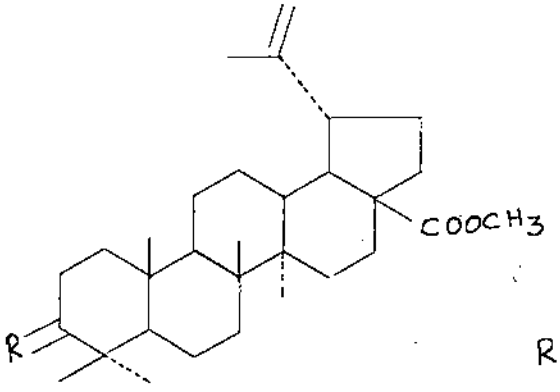
iii) Methyl oleanonate 46 on reduction with lithium-ethylenediamine gives oleanolic acid 46a, $C_{30}H_{48}O_3$, m.p. 302-4°; IR : 3450 (-OH), 1690 cm^{-1} (-COOH).

iv) Reduction of methyl trichadinate 47 with lithium-ethylenediamine affords trichadenic acid A 47a, $C_{30}H_{50}O_3$, m.p. 289-90°; IR : 3440 (-OH), 1690 cm^{-1} (-COOH).

v) Reaction of methyl ursonate 48 with lithium-ethylenediamine furnishes ursolic acid 48a, $C_{30}H_{48}O_3$, m.p 284-85°; IR : 3400 (-OH), 1690 cm^{-1} (-COOH).

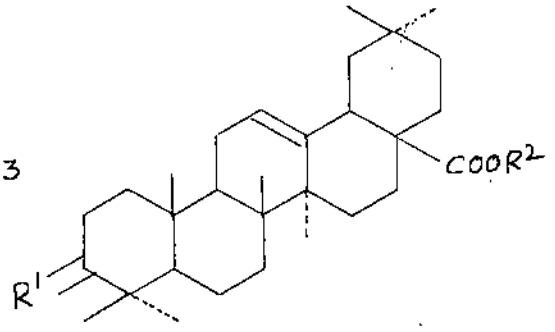
vi) Methyl aleuritolate 49, on reduction with lithium-ethylenediamine affords aleuritolic acid 49a, $C_{30}H_{48}O_3$, m.p. 300-301°; IR : 3450 (-OH), 1700 cm^{-1} (-COOH).

The structures of these acids have been confirmed by preparing their acetyl derivatives and by direct comparison with authentic specimens.



45, R=O

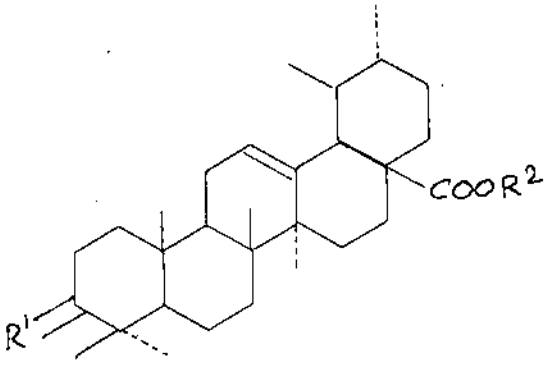
45a, R= 



46, R^1=O, R^2=CH_3

46a, R^1=

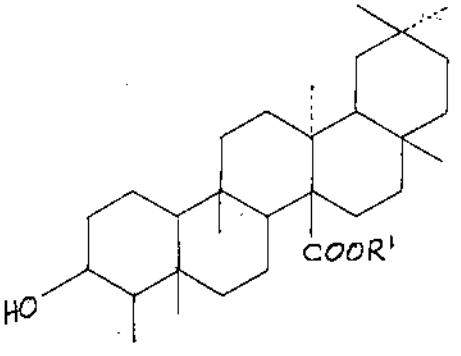
, R^2=H



48, R^1=O, R^2=CH_3

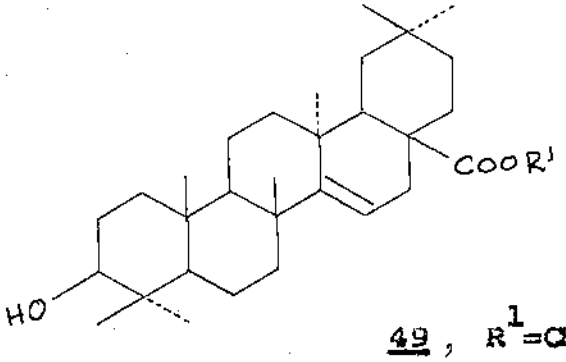
48a, R^1= 

, R^2=H



47, R^1=CH_3

47a, R^1=H



49, R^1=CH_3

49a, R^1=H

SECTION B

This section constitutes the study on reduction of steroid and triterpenoid α,β-unsaturated ketones.

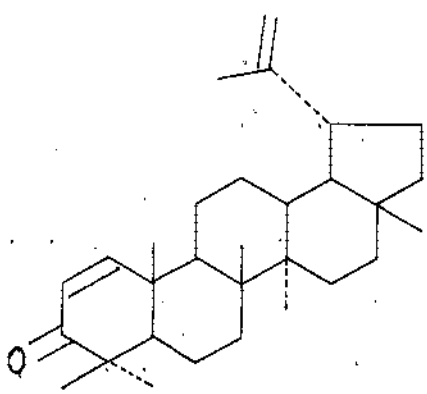
Reaction of less sterically hindered ketone, glochidone 50 with lithium in presence of ethylenediamine leads to the reduction of the double bond to give lupanone 32, $C_{30}H_{50}O$, m.p. 209-10°; IR : 1705 cm^{-1} (carbonyl) followed by that of the carbonyl group to afford thermodynamically stable alcohol, lupanol 32a, m.p. 204-5°. Cholest-4-en-3-one 51 on reduction with lithium-ethylenediamine affords cholestan-3β-ol 52, $C_{27}H_{48}O$, m.p. 140-41°, confirmed by preparing acetyl derivative and by direct comparison with authentic specimen.

Sterically hindered α,β-unsaturated ketones : (a) 11-oxo-olean-12(13)-en-3β-yl acetate 53 on reduction with lithium-ethylenediamine furnishes three compounds which are characterized as β-amyrane 54, $C_{30}H_{52}$, m.p. 174-5°; IR : No absorption between 780 to 900, 1600 to 1750 and 3000 to 3600 cm^{-1}; olean-9(11), 12(13)-dien-3β-ol 55, $C_{30}H_{48}O$, m.p. 210-11°, mass : m/z 424 (M^+); IR : 3340 (-OH) cm^{-1} and olean-3β, 11α-diol 54a, $C_{30}H_{52}O_2$, m.p. 240-42°, IR : 3300-3350 cm^{-1} (-OH); (b) Reduction of 11-oxo-olean-12(13), 15(16)-dien-3β-yl acetate 56 with lithium in presence of ethylenediamine affords three compounds which are identified as olean-12(13), 15(16)-diene 56a, $C_{30}H_{48}$, m.p. 202-03°; mass : m/z 408 (M^+); IR : 820, 795, 780, 760 cm^{-1} (olefinic double bond); olean-12(13), 15(16)-dien-3β-ol 56b, $C_{30}H_{48}O$, m.p. 235-36°; mass : m/z 424 (M^+);

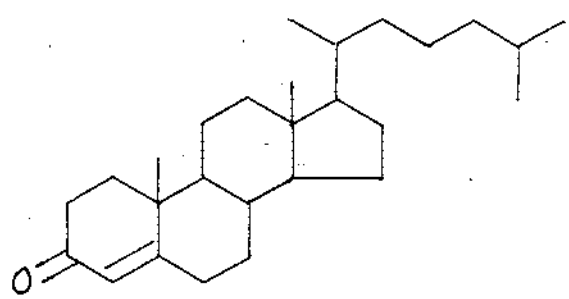
IR : 3200-3500 (-OH), 830, 800, 760, 750, 730 cm^{-1} (olefinic double bond); olean-15(16)-en-11α -ol 57, $C_{30}H_{50}O$, m.p. 205-6°; mass : m/z 426 (M^+); IR : 3470 (-OH), 780, 760 cm^{-1} (olefinic double bond) respectively.

Reduction of 7-oxo-cholesteryl acetate 58 and cholest-3, 5-dien-7-one 60 with lithium in presence of ethylenediamine furnish same product cholest-4(5)-en-7β -ol 59, $C_{27}H_{46}O$, m.p. 115-16°; IR : 3340 cm^{-1} (-OH) in both cases.

The structures of these reaction products have been established on the basis of analytical data, spectral data (IR, ^1H NMR, mass and ^{13}C NMR) and by direct comparison with authentic specimens.



50



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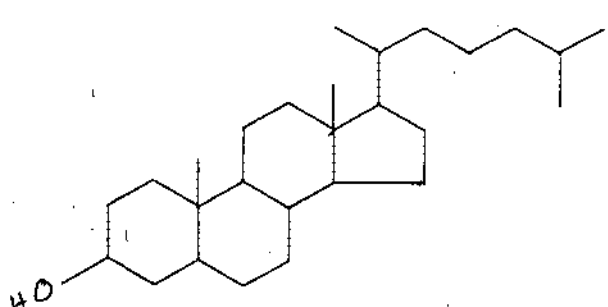

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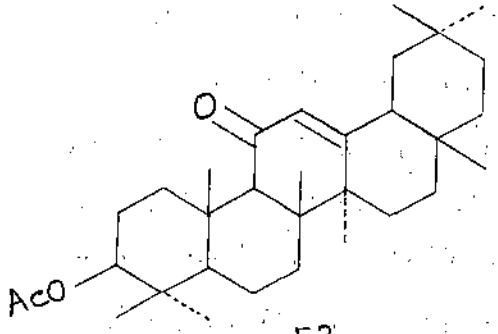

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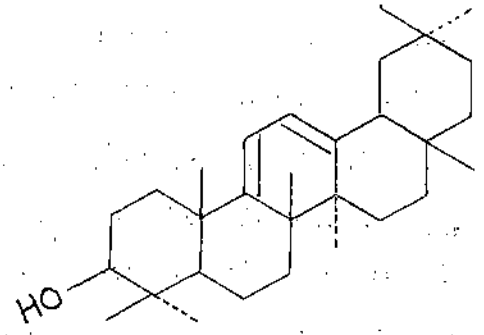

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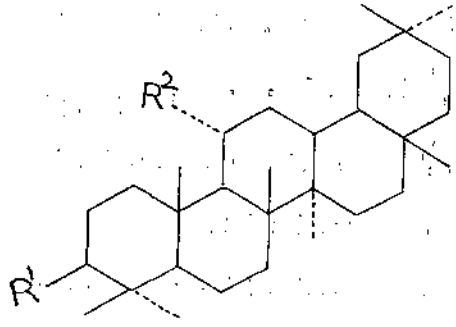
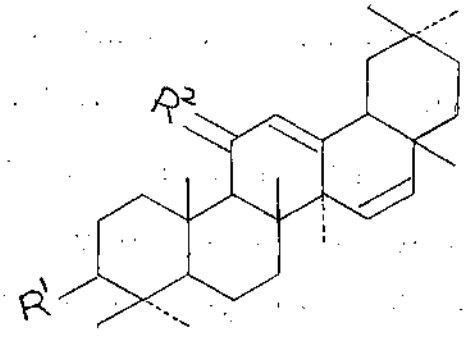


54, $R^1=R^2=H$

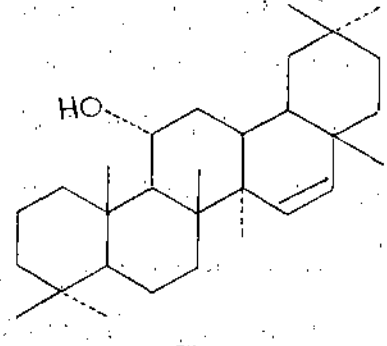
54a, $R^1=R^2=OH$



56, $R^1=OAc$, $R^2=O$

56a, $R^1=H$, $R^2=H_2$

56b, $R^1=OH$, $R^2=H_2$



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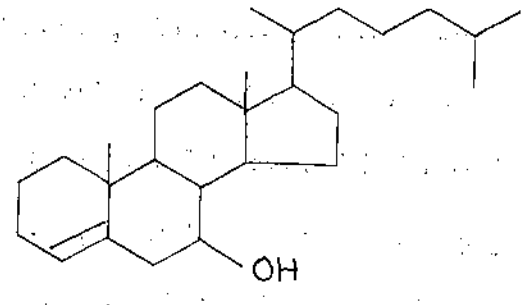

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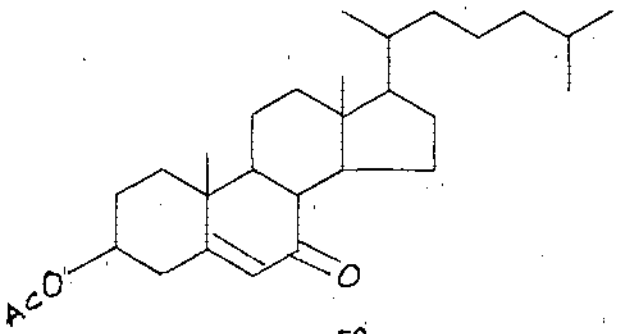
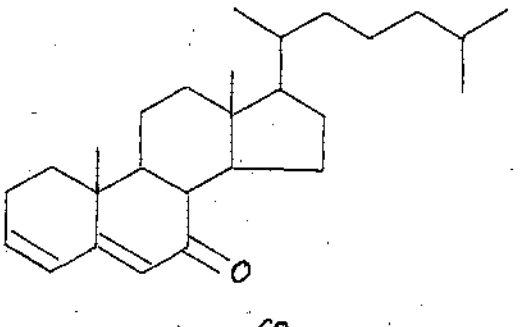


58



60

The possible mode of formation of these products have also been discussed.

SECTION C

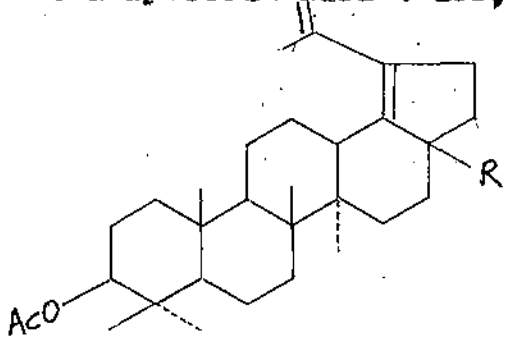
This section contains the action of lithium in presence of ethylenediamine on triterpenoid conjugated dienes.

Olean-9(11), 12(13)-dien-3β-ol 55 on treatment with lithium in presence of ethylenediamine results the recovery of starting material 55.

The reduction of lup-18(19), 20(29)-dien-3β-yl acetate 61 with lithium in presence of ethylenediamine furnishes lup-18(19)-en-3β-ol 63, $C_{30}H_{50}O$, m.p. 220-22°; IR : 3400-3450 cm^{-1} (-OH). The structure 63 has been confirmed by preparing acetyl derivative, comparison with authentic specimen and by spectral analysis (IR, mass, NMR, ^{13}C NMR).

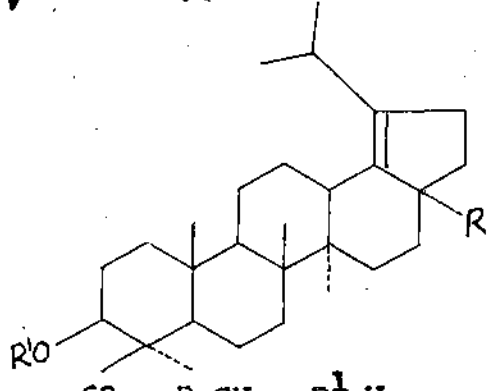
The reaction of methyl-3β-acetoxy-lup-18(19), 20(29)-dien-28-oate 62 with lithium in presence of ethylenediamine affords four compounds which are characterized as 28-nor-lup-17(18)-en-3β-ol 64, $C_{29}H_{48}O$, m.p. 186-87°; mass : m/z 412(M^+);

IR : 3400 cm^{-1} (-OH); the structure 64 has been established by preparing acetyl derivative, direct comparison with authentic specimen and spectral analysis (IR, mass, ^{1}H NMR, ^{13}C NMR); lupan-28-oic acid 65, $C_{30}H_{50}O_2$, m.p. 290-92°; mass : m/z 442 (M^+); IR : 3300-2900 (broad), 1690 cm^{-1} (-COOH); the structure 65 has been confirmed by preparing ester derivative, direct comparison with authentic specimen, elemental and spectral analysis (IR, mass); lup-18(19)-en-3β, 28-diol 63a, $C_{30}H_{50}O_2$, m.p. 208-9°; mass : m/z 443 (MH^+); IR : 3320-3200 cm^{-1} (-OH); the structure 63a has been established by preparing acetyl derivative, direct comparison with authentic specimen, analytical and spectral data (IR, mass); lup-18(19)-en-3β-ol-28-oic acid 63b, $C_{30}H_{48}O_3$, m.p. 275-77°; IR : 3500-3400 (-OH), 1710 cm^{-1} (-COOH); the structure 63b has been ascertained by preparing ester derivative, direct comparison with authentic specimen, analytical and spectral data (Mass, IR, NMR, ^{13}C NMR).



61, R=CH_3

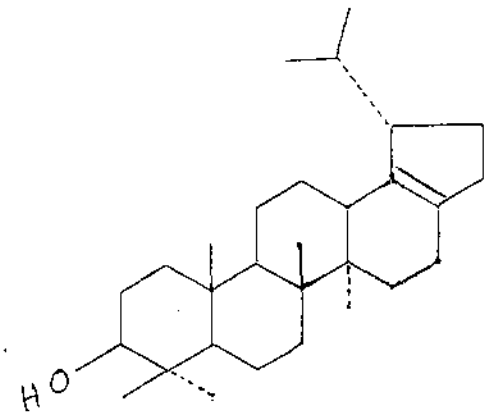
62, R=$COOCH_3$



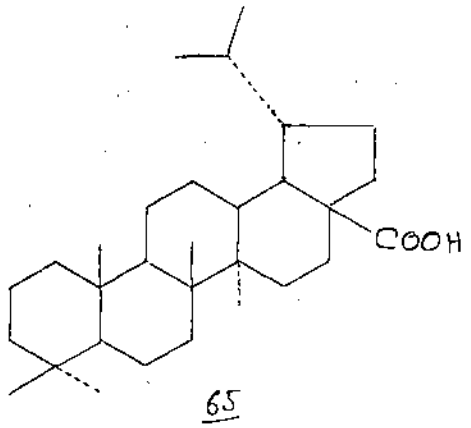
63, R=CH_3, R^1=H

63a, R=CH_2OH, R^1=H

63b, R=COOH, R^1=H



64



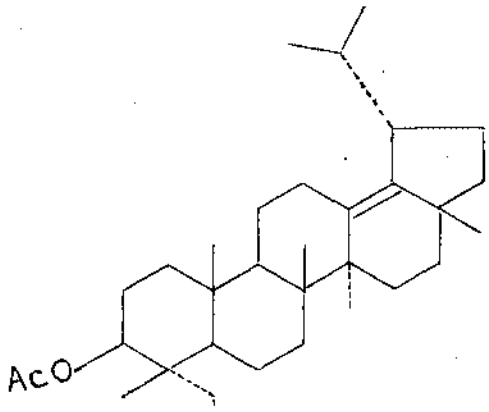
65

The possible mode of formation of products 65, 63a and 64 have been discussed.

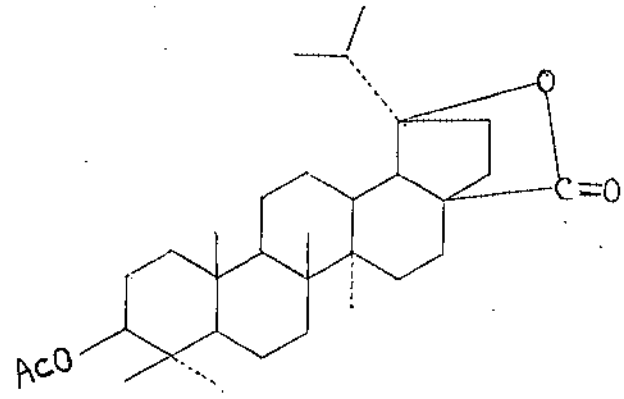
SECTION D

This section deals with isomerisation of 18(19) double bond in lupane skeleton. Lup-18(19)-en-3β-ol 63, on treatment with HCl-AcOH furnishes lup-13(18)-en-3β-yl acetate 66, $C_{32}H_{52}O_2$, m.p. 214-15°; mass : m/z 468 (M^+); IR : 1740, 1250 cm^{-1} (-OCOCH$_3$); the structure of the compound has been established on the basis of elemental and spectral data (IR, mass, ^{1}H NMR and ^{13}C NMR).

Treatment of lup-18(19)-en-3β-ol-28-oic acid 63b with HCl-AcOH results in two products. The first product is lup-28⟶19β-olide-3β-yl acetate 67, $C_{32}H_{50}O_4$, m.p. 299-300°; mass : m/z 498 (M^+); IR : 1770 (γ-lactone), 1725, 1245 cm^{-1} (-acetate); the structure of compound has been confirmed by direct comparison with authentic specimen; elemental analysis and spectral data (Mass, IR, NMR, ^{13}C NMR). The second product is the acetate derivative (68) of unisomerised acid 63b.



66



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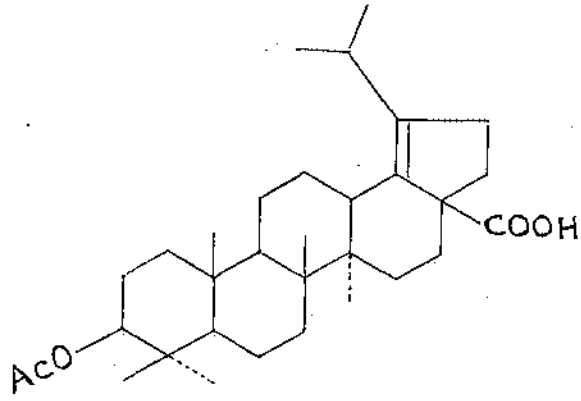

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CHAPTER III

This chapter describes the experimental details of the works contained in Chapter II.