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SUMMARY

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

PART I

STUDIES ON THE ACTION OF N-BROMOSUCCINIMIDE IN DIMETHYL SULFOXIDE ON 3-KETO AND 3-OXIMINO TRITERPENOIDS AND THE TRANSFORMATIVE REACTIONS OF THEIR BROMO DERIVATIVES

Part I has been divided into five chapters.

CHAPTER I

This chapter comprises a short review on the action of N-bromosuccinimide on triterpenoids and steroids.

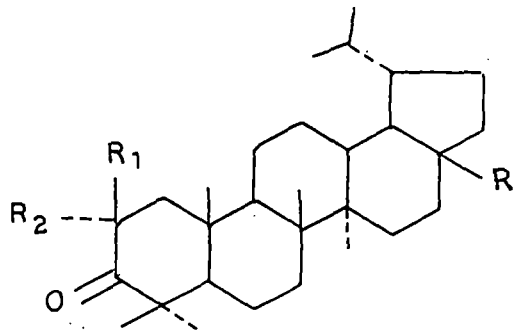
CHAPTER II

This chapter deals with the studies on the action of N-bromo succinimide in dimethyl sulfoxide on 3-keto triterpenoids.

(a) Studies on the action of N-bromosuccinimide in dimethyl sulfoxide on lupanone 1.

Reaction of lupanone 1, with NBS in DMSO furnishes two products characterized as 2,2-dibromo lupanone 2, $C_{30}H_{48}OBr_2$, m.p. 210-11°; mass : m/z 586, 584, 582 $[M]^+$ (1:2:1); IR : 1722 cm^{-1} (CO), CD : $\lambda_{max}^{CHCl_3}$ 239 nm (ϕ = +4590.18) and 320 nm (ϕ = -8977.85) and 2α-bromo lupanone 3, $C_{30}H_{49}OBr$, m.p. 224-25°; mass : m/z 506, 504 $[M]^+$ (1:1) IR : 1720 cm^{-1} (CO);

CD : $\lambda_{max}^{CHCl_3}$ 295 nm ($\emptyset$ = +2620.82). The structure of 2 and 3 are based on spectral data (IR, UV, ^1H NMR, Mass and ^{13}C NMR).



1, $R_1 = R_2 = H$, $R = CH_3$
2, $R_1 = R_2 = Br$, $R = CH_3$
3, $R_1 = H$, $R_2 = Br$, $R = CH$
4, $R = COOMe$, $R_1 = R_2 = H$
5, $R_1 = COOMe$, $R_1 = R_2 = Br$
6, $R = COOMe$, $R_1 = H$, $R_2 = Br$

(b) Studies on the action of NBS in DMSO on methyl-dihydrobetulonate 4.

The products isolated are characterized as 2,2- dibromo methyl dihydrobetulonate 5, $C_{31}H_{48}O_3Br_2$, m.p. 160-62°; mass: m/z 628, 626, 624 $[M^+]$ (1:2:1); IR : 1725 (-COOMe) and 1705 (C=O) cm^{-1} and 2 α-bromo methyl dihydrobetulonate 6, $C_{31}H_{49}O_3Br$, m.p. 125-27°; mass: m/z 550, 548 $[M]^+$ (1:1) IR : 1725 (-COOMe) and 1705 ($>C = O$) cm^{-1}. The structures 5 and 6 have been established on the basis of spectral analysis (IR, UV, Mass, ^1H and ^{13}C NMR). The possible mode of formation of 2, 3, 5 and 6 have also been discussed.

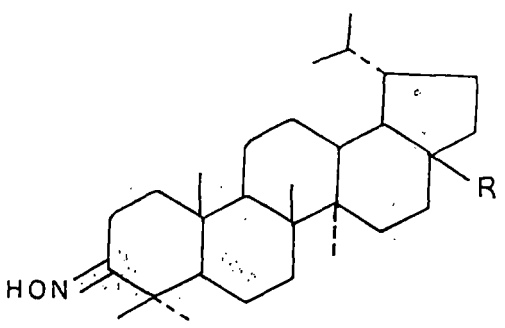
CHAPTER III

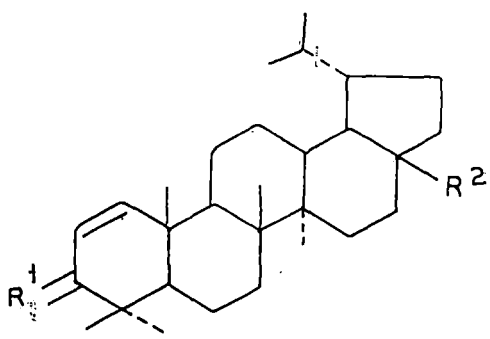
This chapter contains isolation and characterization of products formed on NBS oxidation of (a) oxime derivative 7 of lupanone 1, (b) oxime derivative 9 of methyl dihydrobetulonate 4 and (c) oxime derivative 11 of friedelin 10 in DMSO.

Section A : This section constitutes the oxidation of 3-oximino triterpenoids containing gem dimethyl group at C-4 position, with NBS-DMSO. (a) The oxime derivative 7 of lupanone on oxidation with NBS in DMSO furnishes two compounds which are characterized as 2,2-dibromo lupanone 2 and 3-oximino -lup-1(2)-ene 9, $C_{30}H_{49}ON$, m.p. 290-92°; mass : m/z 439 $[M]^+$; IR : 3180-3420 cm^{-1} (-OH), 948, 807 cm^{-1} ($\rangle C = C \langle$) UV : 235 nm (ϵ = 11,800).

(b) Oxidation of oxime derivative 8 of methyl dihydrobetulonate 4 with NBS-DMSO affords two compounds which are identified as 2,2-dibromo methyl dihydrobetulonate 5 and 28-carbomethoxy-3-oximino lup-1(2)-ene 12, $C_{31}H_{49}ON$, m.p. 246-47°; mass : m/z 483 $[M]^+$; IR : 3420 (-OH), 1720 (CO_2Me), 940 and 800 cm^{-1} ($\rangle C = CH_2$).

The structures 9 and 12 have been established on the basis of spectral analysis (IR, UV, Mass, ^1H NMR and ^{13}C NMR) and by direct comparison with authentic specimens prepared from 1(2)-dehydro derivatives 9a and 12a of lupanone 1 and methyl dihydrobetulonate 4 respectively.





7, R = Me

8, R = COOMe

9, R^1 = NOH, R^2 = Me

9a, R^1 = O, R^2 = Me

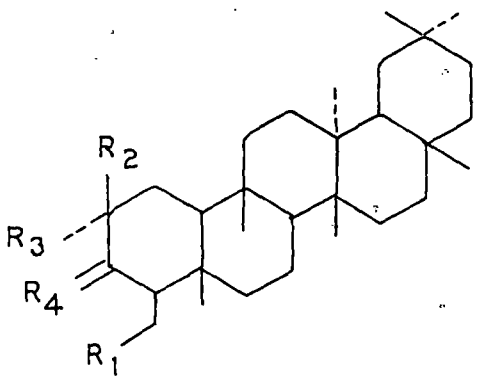
12, R^1 = NOH, R^2 = COOMe

12a, R^1 = O, R^2 = COOMe

The mode of formation of 2, 9, 5 and 12 have been discussed.

Section B: This section describes the isolation and characterization of products obtained on oxidation of oxime derivative 11 of friedelin 10, a triterpenoid containing only one methyl at C-4 position, with NBS in DMSO.

The products isolated are characterized as 2β, 23-dibromo friedelin 13, $C_{30}H_{48}OBr_2$, m.p. 214-15°; mass : m/z 586, 584, 582 $[M]^+$ (1:2:1); IR : 1735 cm^{-1} (>C = O), CD : $\lambda_{max}^{CHCl_3}$ 290 nm (Ø =-5809) and 2α-bromo friedelin 14, $C_{30}H_{49}OBr$, m.p. 210°; mass : m/z 506, 504 $[M]^+$(1:1); IR : 1725 cm^{-1} (>C = O). The structures 13 and 14 have been established on the basis of spectral analysis (IR, CD, Mass ^1H NMR and ^{13}C NMR).



10, $R_1 = R_2 = R_3 = H$, $R_4 = O$
11, $R_1 = R_2 = R_3 = H$, $R_4 = NOH$
13, $R_1 = R_2 = Br$; $R_3 = H$, $R_4 = O$
14, $R_1 = R_2 = H$; $R_3 = Br$, $R_4 = O$

Chapter IV

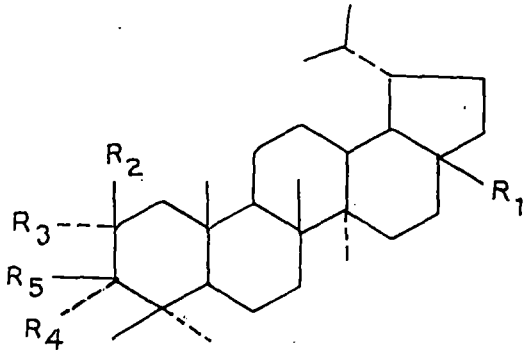
This chapter deals with the studies on the transformative reactions of 2α-bromo and 2,2-dibromo-3-keto triterpenoids of lupane skeleton.

Section A: Reaction with lithium aluminium hydride

This section constitutes the studies on the reaction of Lithium aluminium hydride.

(1) 2α-bromo methyl dihydro betulonate 6 on reduction with LAH at room temperature furnishes two compounds which are characterised as 2α-bromo-3α-hydroxy methyl dihydro betulanate 15, $C_{31}H_{51}O_3Br$, m.p. 200-201°; mass : m/z 552, 550 $[M]^+$ (1:1); IR : 3200-3600 cm^{-1} (-OH), 1720 cm^{-1} (COOMe) and methyl dihydro betulinate 16.

(b) 2α-bromo lupanone 3 on similar treatment with LAH affords two compounds which are identified as 2α-bromo-3α-



15, R_1 = COOMe, R_2 = R_5 = H, R_3 = Br, R_4 = OH

16, R_1 = COOMe, R_2 = R_3 = R_4 = H, R_5 = OH

17, R_1 = Me, R_2 = R_5 = H, R_3 = Br, R_4 = OH

18, R_1 = Me, R_2 = R_3 = R_4 = H, R_5 = OH

19, R_1 = Me, R_2 = R_5 = OH, R_3 = R_4 = H

hydroxy lupane 17, $C_{30}H_{51}OBr$, m.p. 222°; mass : m/z 508, 506 $[M]^+$ (1:1); IR : 3600 cm^{-1} (OH) and lupanol 18.

(c) Reduction of 2,2-dibromo methyl dihydro betulonate 5 with LAH at room temperature affords two compounds which are identified as 2α-bromo methyl dihydro betulonate 6 and methyl dihydro betulinate 16.

(d) Treatment of 2,2-dibromo lupanone 2 with LAH under similar condition furnishes three compounds which are characterized as 2α-bromo lupanone 3, lupanol 18 and lupan-2β, 3β-diol 19, $C_{30}H_{52}O_2$, m.p. 215-16°; mass : m/z 444 $[M]^+$, IR : 3200, 3400 cm^{-1} (-OH).

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

Section B: Reaction with sodium borohydride

This section deals with the studies on the action of sodium borohydride on the bromo compounds 2 and 3.

(a) Reduction of 2α-bromo lupanone 3 with $NaBH_4$ in dioxan-methanol mixture furnishes two compounds which are characterized as 2α-bromo-3α-hydroxy lupane 17 and lupanol 18.

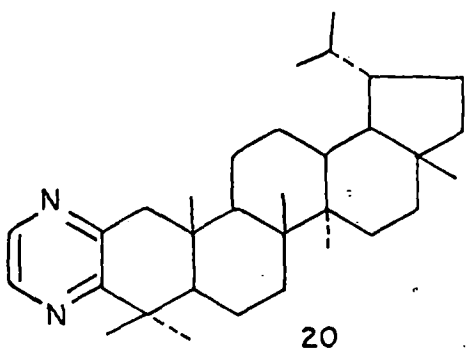
(b) 2,2-dibromo lupanone 2 on similar treatment furnishes lupanone 1 and lupanol 18. The structures of these compounds have been established on the basis of analytical data, spectral data (^1H NMR, Mass and IR) and by direct comparison with authentic specimens.

Section C : Studies on the action of lithium-ethylene diamine on 2,2-dibromo and 2α-bromo ketone.

This section constitutes the study on the action of lithium-ethylene diamine on 2-bromo lupanone 2 and 3.

Reaction of 2,2-dibromolupanone 2 and 2α-bromo lupanone 3 with lithium in presence of ethylenediamine furnish same compounds which are characterized as lupanone 1 and pyrazine derivative 20 of lupane 21, $C_{32}H_{50}N_2$, m.p. 220°; IR : 1650, 1430, 1120 cm^{-1}, mass : m/z 462 $[M]^+$.

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



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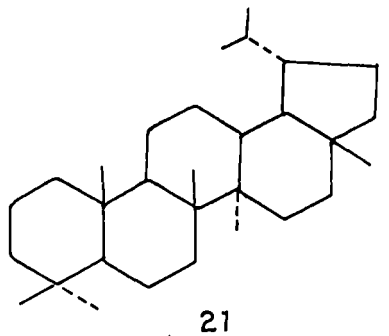
Section D : Wolff Kishner Reduction

This section comprises the studies on Wolff-Kishner reduction of 2-bromo lupanone 2 and 3. Wolf-Kishner reduction of 2,2-dibromo lupanone 2 and 2α-bromo lupanone 3 furnish same product lupane 21, $C_{30}H_{52}$, m.p. 187-88°. Mass : m/z 412 $[M]^+$ in both cases. The structure of which is established

on the basis of spectral data (IR, Mass) and by direct comparison with authentic specimen.



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Section E : Reaction with lithium bromide in N,N-dimethyl formamide

This section deals with the studies on the action of LiBr-DMF on 2-bromo-3-keto triterpenoids.

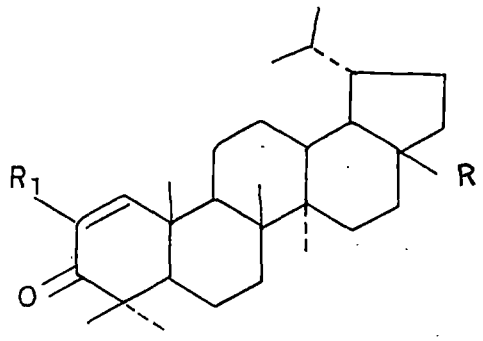
(a) Reaction of 2,2-dibromo methyl dihydro betulonate 5 with LiBr-DMF furnishes 2-bromo-28-carbomethoxy-lup-1(2)-en-3-one 22, $C_{31}H_{47}O_3Br$, m.p. 135-36°; IR: 1730, 1680 cm^{-1}; UV : 258 nm (ϵ = 19000); mass : m/z 548, 546 $\lceil M \rfloor^+$ (1:1).

(b) Reaction of 2α-bromo methyl dihydro betulonate 6 with LiBr-DMF gives 28-carbomethoxy-lup-1(2)-en-3-one 23, $C_{31}H_{48}O_3$, m.p. 186-87°; IR : 1735, 1670 cm^{-1}; UV : 228 nm (ϵ = 18000); mass : m/z 468 $\lceil M \rfloor^+$.

(c) 2,2 dibromo lupanone 2 on similar treatment with LiBr-DMF affords 2-bromo-lup-1(2)-en-3-one 24, $C_{30}H_{47}OBr$, m.p. 241-42°; IR : 1690 cm^{-1}, UV : 257 nm (ϵ = 19000); mass : m/z 504, 502 $\lceil M \rfloor^+$ (1:1).

(d) Reaction of 2α-bromo lupanone 3 with LiBr-DMF furnishes lup-1(2)-en-3-one 25, $C_{30}H_{48}O$, m.p. 198-99°; IR : 1680 cm^{-1},

UV : 228 nm (ϵ = 18000); mass : m/z 424 $[M]^+$.



22, R = COOMe, R_1 = Br
23, R = COOMe, R_1 = H
24, R = Me, R_1 = Br
25, R = Me, R_1 = H

The structures of these compounds have been established on the basis of spectral analysis (IR, UV, Mass, ^{1}H NMR and ^{13}C NMR). The possible mode of formation of 22, 23, 24 and 25 have also been discussed.

Section F: Reaction with N, N-dimethyl aniline

This section contains isolation and characterisation of product formed by the action of N, N-dimethyl aniline on 2-bromo lupanone.

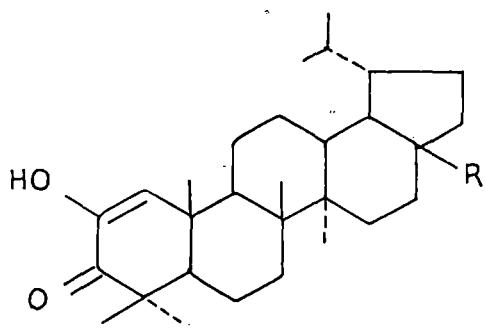
Reaction of 2,2-dibromo lupanone 2 and 2α-bromo lupanone 3 with N, N-dimethyl aniline furnish same product lupanone 1, m.p. 207-8°, IR : 1710 cm^{-1} in both cases, confirmed by comparison with authentic specimen.

Section G : Treatment with alcoholic potassium hydroxide

This section deals with the isolation and characterisation of products formed by the hydrolysis of 2,2-dibromo-3-keto triterpenoids with methanolic KOH.

(a) 2,2-dibromo lupanone 2 on treatment with methanolic potassium hydroxide affords diosphenol 26, $C_{30}H_{48}O_2$, m.p. 210-213°; IR : 3640, 1670, 1650, 860 cm^{-1}, UV : 270 nm (ϵ = 7932), 310 nm (alkali shift); Mass: m/z 440 [M]$^+$.

(b) 2,2-dibromo methyl dihydro betulonate 5 on similar treatment with methanolic KOH furnishes diosphenol 27, $C_{31}H_{48}O_4$, m.p. 131-33°; IR : 3460, 1670, 1650, 860 cm^{-1}, UV : 269 nm (ϵ = 7532) 310 (alkali shift).



26, R = Me

27, R = COOMe

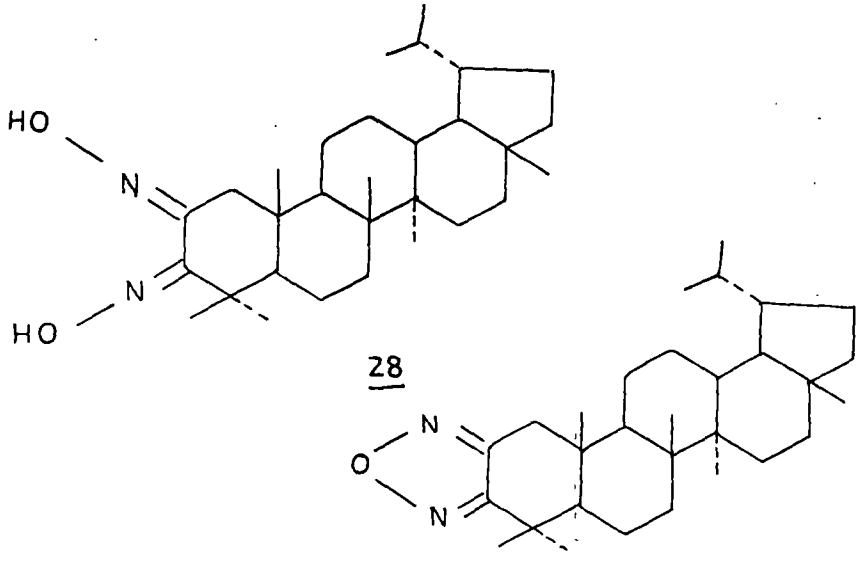
The structures of 26 and 27 have been established on the basis of analytical data, spectral data (IR, ^{1}H NMR and Mass) and by direct comparison with authentic sample.

Section H : Treatment with hydroxyl amine hydrochloride in pyridine:

This section deals with the preparation of dioximino lupane 28 from 2,2-dibromo lupanone 2 and the subsequent cyclisation of the dioximino derivative 28 with DMF to furazan derivative 29.

2,2-dibromo lupanone on treatment with NH_2OH-HCl in pyridine affords 2,3-dioximino lupane 28, $C_{30}H_{50}O_2N_2$, m.p. 193°; IR : 3200-3450, 1640 cm^{-1} UV : 220 nm (ϵ = 7892), 279 nm (alkali shift); Mass : m/z 469 $[M]^+$.

Further treatment of 28 with DMF furnishes lupan [2,3-c] -1', 2', 5'-oxadiazole 29, $C_{30}H_{48}ON_2$, m.p. 249-50°; IR : 1620, 1120, 980, 960, 890 cm^{-1}, UV : 220 nm (ϵ = 7932); mass : m/z 452 $[M]^+$. The structure of 28 and 29 have been established on the basis of analytical data, spectral data (IR, ^1H NMR, mass, UV).



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CHAPTER V

This chapter describes the experimental details of the works discussed in Chapter II, III and IV.

PART II

STUDIES ON THE ACTION OF SELENIUM-DIOXIDE-HYDROGEN PEROXIDE IN TERTIARY BUTANOL ON TRITERPENOIDS HAVING ISOPROPENYL GROUP.

Part II has been divided into three chapters.

CHAPTER I

This chapter constitutes (i) a short review of selective oxidation with selenium dioxide (Section A) and (ii) a short review on reactions of hydrogen peroxide in presence of selenium dioxide (Section B).

CHAPTER II

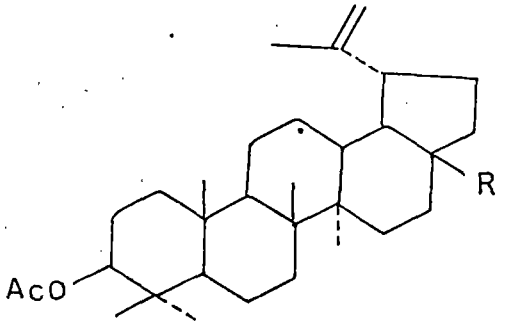
This chapter deals with the studies on the action of selenium dioxide containing hydrogen peroxide and tertiary butanol on triterpenoids containing isopropenyl group.

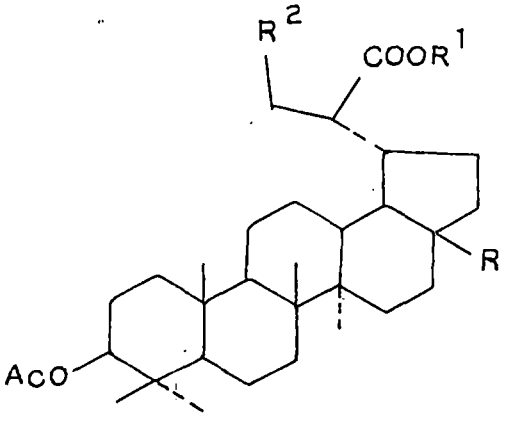
(a) Oxidation of lupenyl acetate 30 with selenium dioxide and hydrogen peroxide in tertiary butanol affords three compounds which are identified as (i) 30-carbomethoxy lupenyl acetate 31, $C_{33}H_{52}O_4$, m.p. 220-21°; IR : 1720-1740 , 1250 cm^{-1} (-COOMe and $OCOCH_3$), 1630, 1125, 990 and 825 cm^{-1} ($>C = CH_2$); mass: m/z 512 $[M]^+$, (ii) 30-carbomethoxy lupan-3β, 29-diyl acetate

32, $C_{33}H_{54}O_6$, m.p. 240-41°; IR : 1700-1750, 1235-1250 cm^{-1} (-COOMe and $OCOCH_3$); mass : m/z 512 $[M - CH_3COOH]^+$ and (iii) 29-carbomethoxy-lupan-3β-yl acetate 33, $C_{33}H_{54}O_4$, m.p. 237-38°; IR : 1730-40, 1252 cm^{-1} (-COOMe and $OCOCH_3$), mass : m/z 514 $[M]^+$.

(b) Methyl acetyl betulinate 34 on oxidation with selenium dioxide and hydrogen peroxide in t-butanol furnishes two products which are identified as (i) 28, 30-dicarbomethoxy lupenyl acetate 35, $C_{34}H_{52}O_6$, m.p. 150-51°; IR : 1730-40, 1250 cm^{-1} (-COOMe and $OCOCH_3$), 1640, 830 cm^{-1} ($\diagdown C=CH_2$), mass : m/z 556 $[M]^+$ and (ii) 28, 29 dicarbomethoxy lupan-3β-yl acetate 36, $C_{34}H_{54}O_6$, m.p. 185-86°; IR : 1730-40, 1250 cm^{-1} (-COOMe and $OCOCH_3$); mass : m/z 558 $[M]^+$.

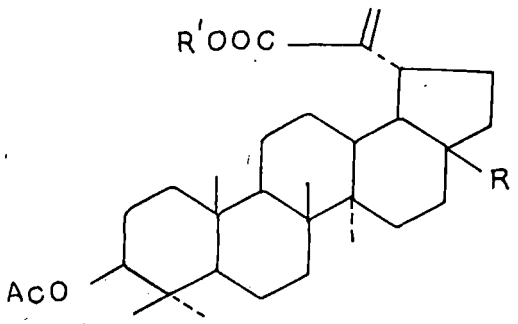
The structures of these reaction products have been established on the basis of analytical and spectral data (^1H NMR, Mass, ^{13}C NMR and IR).





30, R = Me
34, R = COOMe

32, R = R' = Me, R^2 = OAc
33, R = R' = Me, R^2 = H
36, R = COOMe, R' = Me, R^2 = H



31, R = R' = Me

35, R = COOMe

R' = Me

The mode of formation of products 31, 32, 33, 35 and 36 have been discussed.

CHAPTER III

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

PART III

STUDIES ON THE ACTION OF HYDROGEN PEROXIDE IN PRESENCE OF p-TOLUENE SULPHONIC ACID ON TRITERPENOID ALLYLIC ALCOHOLS.

Part III has been divided into three chapters.

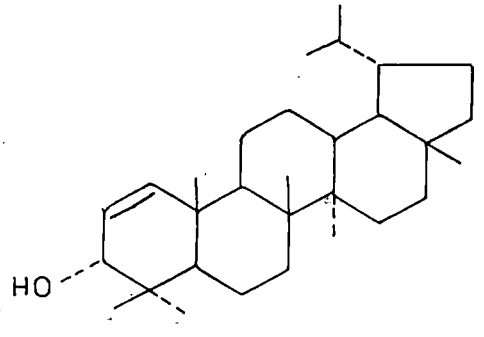
CHAPTER I

This chapter constitutes a short review on the oxidative transformation reactions of the pentacyclic triterpenes with hydrogen peroxide in acid medium.

CHAPTER II

This chapter deals with the oxidation of lup-1(2)-en-3α-ol 37 with hydrogen peroxide in tertiary butanol containing p-toluene sulphonic acid.

Treatment of 37 with hydrogen peroxide in t-butanol containing p-toluene sulphonicacid affords five compounds which are identified as (i) 3αt-butoxy-1α, 2α-epoxy lupane 38, $C_{34}H_{58}O_2$, m.p. 193-94°; Mass : m/z 482 $[M]^+$.
(ii) 3α-chloro-1α, 2α-epoxy lupane 39, $C_{30}H_{49}OCl$, m.p. 218-19°; IR : 880 cm^{-1} (epoxide ring); mass : m/z 462, 460 $[M]^+$ (1:3).
(iii) lup-1(2)-en-3-one 40, $C_{30}H_{48}O$, m.p. 198-99°; IR : 1680 (α,β-unsaturated ketone) cm^{-1}, UV 228 nm (ϵ = 18,000); mass : m/z 424 $[M]^+$.
(iv) lupan - 1α,2α-epoxy-3-one 41, $C_{30}H_{48}O_2$, m.p. 223-24°, IR : 1705 cm^{-1} (CO) and 880 cm^{-1} (epoxide ring), mass : m/z 440 $[M]^+$ and (v) lupan-1α, 2α- epoxy-3α-ol 42, $C_{30}H_{50}O_2$, m.p. 203-4°; IR : 3530 cm^{-1} (-OH) and 880 cm^{-1} (epoxide ring).



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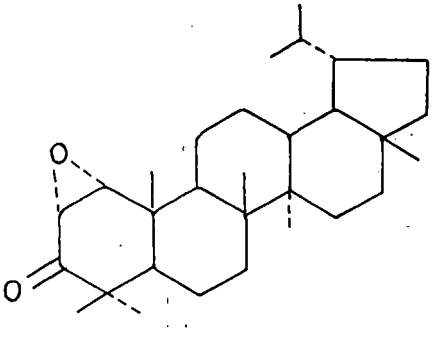

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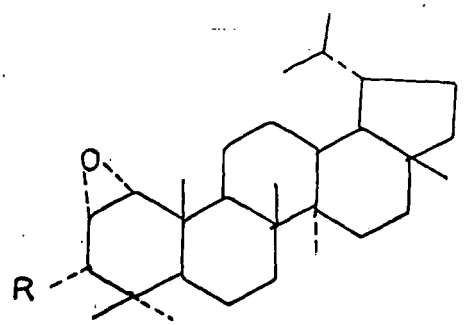
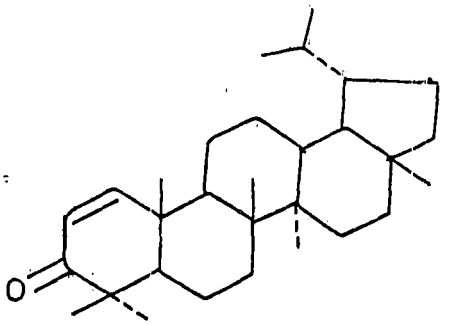


38, R = O-CMe$_3$

39, R = Cl

42, R = OH



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The structure of these reaction products have been established on the basis of analytical data, spectral data (IR, UV, ^{1}H NMR and ^{13}C NMR) and by direct comparison (40 and 41) with authentic specimen.

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

CHAPTER III

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

PART IV

STUDIES ON THE ACTION OF LEAD TETRA ACETATE ON SATURATED TRITERPENE ACID WHERE THE TERTIARY CARBOXY GROUP IS SITUATED AT THE RING JUNCTURE

Part IV has been divided into three chapters.

CHAPTER I

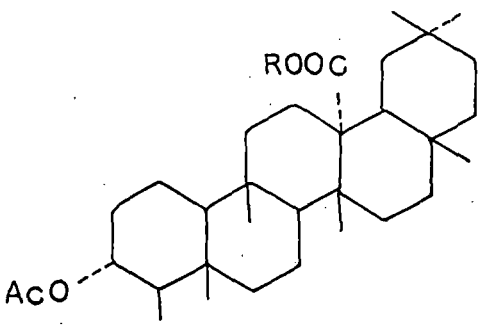
This chapter constitutes a short review on some oxidative reactions of lead tetracetate on triterpenoids.

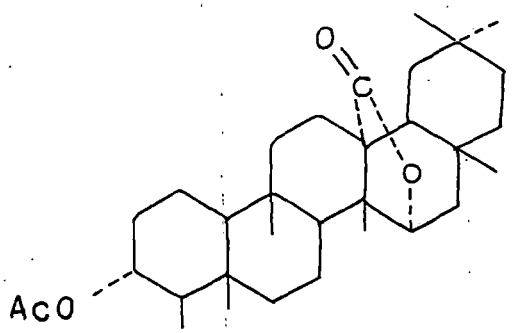
CHAPTER II

This chapter deals with the studies on the action of lead tetraacetate on saturated triterpene acid where the tertiary carboxy group is situated at the ring juncture (in this case at C-13).

Acetyl trichadenic acid 43 on treatment with LTA in glacial acetic acid furnishes three compounds which are identified as (i) acetyl methyl trichadenate 44, $C_{33}H_{54}O_4$, m.p. 224-25°; IR : 1730 (COOMe), 1740, 1250 cm^{-1} ($OCOCH_3$); mass : m/z 514 $[M]^+$, (ii) 3-Oα-acetyl friedal-27 $\longrightarrow$ 15α-olide 45, $C_{32}H_{50}O_4$, m.p. $>$ 320°; IR : 1750 cm^{-1} (γ-lactone), 1730, 1240 cm^{-1} ($OCOCH_3$); mass : m/z 498 $[M]^+$ and (iii) 3-Oα-acetyl friedal 27$\longrightarrow$16α-olide 46, $C_{32}H_{50}O_4$, m.p.$>$320°; IR : 1725 cm^{-1} (δ-lactone) 1740 and 1240 cm^{-1} ($OCOCH_3$), mass: m/z 498 $[M]^+$.

The structures of these products have been established on the basis of analytical data, spectral data (IR, ^1H NMR and Mass) and by direct comparison (44 and 45) with authentic sample.

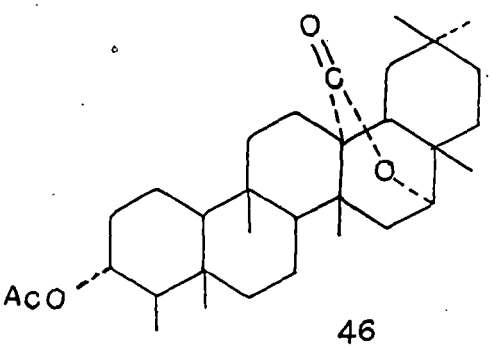




43, R = H

44, R = Me

45



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The mode of formation of products 44, 45 and 46 have been discussed.

CHAPTER III

This chapter describes the experimental details of the works.

PART V

STUDIES ON THE ACTION OF LITHIUM-ETHYLENE DIAMINE ON DIKETO COMPOUNDS.

This part 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

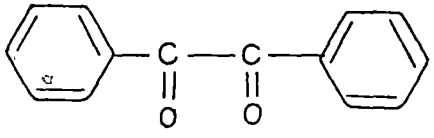
This chapter has been divided into two sections.

SECTION A: Studies on the action of lithium-ethylene diamine on 1,2-diketones

(a) Treatment of benzil 47 with lithium ethylene diamine furnishes a single compound which is identified as 2,3 diphenyl pyrazine 48, $C_{16}H_{12}N_2$, m.p. 119°; IR : 1600, 1110 cm^{-1}, UV : 263 nm (ϵ = 5711) and 385 nm (ϵ = 1009), mass : m/z 232 $[M]^+$.

(b) Lupenone diosphenol 49 on similar treatment with Li-EDA affords pyrazine derivative 50 of lupene 51, $C_{32}H_{48}N_2$, m.p. 213-14°; IR : 1650, 1430, 1120 cm^{-1}, UV : 272 nm (ϵ = 5700) and 278 nm (ϵ = 5600); mass : 460 $[M]^+$.

(c) Treatment of the diosphenol 53 of dihydro methyl betulonate 52 with Li-EDA gives pyrazine derivative 54 of dihydro methyl betulanate, $C_{33}H_{50}O_2N_2$, m.p. 220°; IR : 1710-20 cm^{-1} (COOMe), 1650-70, 1430, 1120 cm^{-1}. UV : 272 nm (ϵ = 5712) and 278 nm (ϵ = 5603); mass : m/z 506 $[M]^+$.



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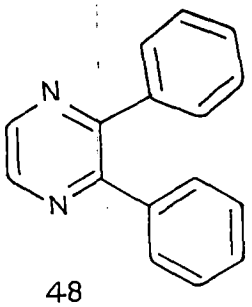

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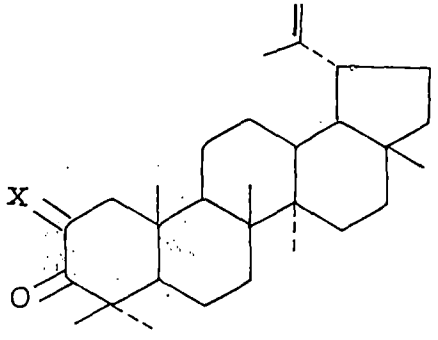
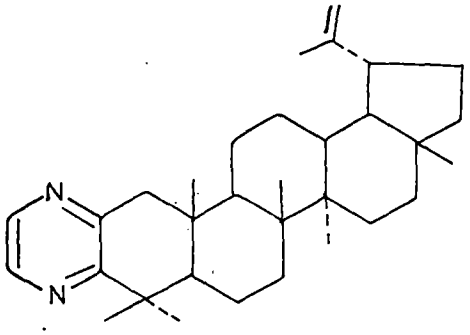


49 , X = O (diketo form of diosphenol)

51 , X = H , H .



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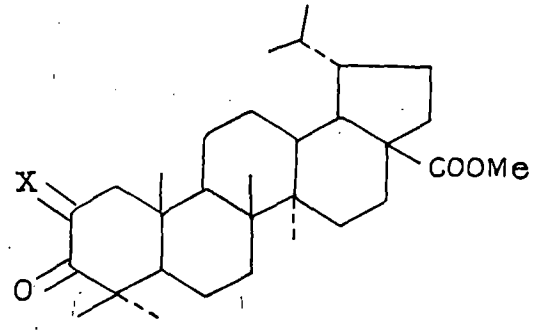
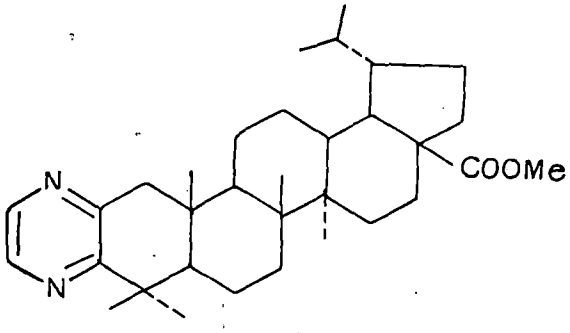


52 , X = H , H

53 , X = O (diketo form of diosphenol)



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

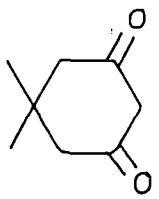
The mode of formation of 50 and 54 have been discussed.

SECTION B: Studies on the action of lithium-ethylene diamine on 1,3 and 1,4 diketone.

a) Action on 1,3 diketone: 2,2-dimethyl cyclohexan-1,3-dione (dimedone) 55 on treatment with Li-EDA furnishes a single compound which is identified as a furan derivative 56, $C_{16}H_{22}O_2$, m.p. 180-82°; IR : 3160, 1480, 1060, 1140, 860 cm^{-1}, UV : 275 nm (ϵ = 7500); mass : m/z 246 $[M]^+$.

b) Action on 1,4 diketone: Cholest-4(5)-en-3,6-dione 57 on similar treatment affords two different compounds which are identified as cholestane 58, $C_{27}H_{48}$, m.p. 81-82°, $[\alpha]_D$ + 27.9° and cholestan-3β-ol 59, $C_{27}H_{48}O$, m.p. 140-41, $[\alpha]_D$ + 24°; IR : 3400 cm^{-1}, confirmed by comparison with authentic specimen.

The structure of compound 56 has been established on the basis of analytical and spectral data (^{1}H NMR, ^{13}C NMR, Mass, IR and UV).



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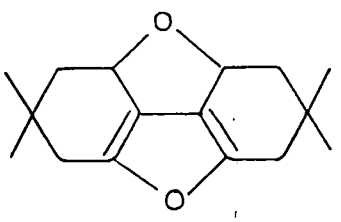
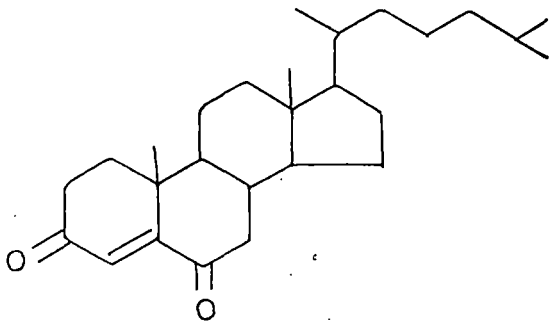


56



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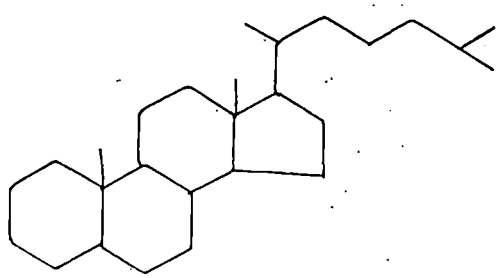

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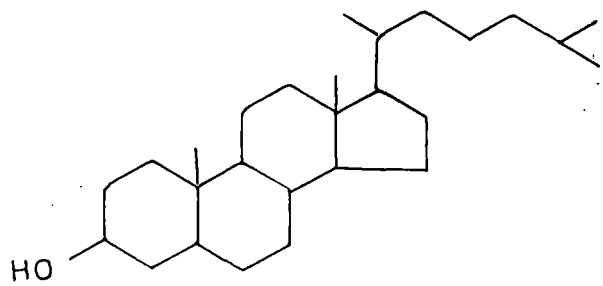

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The probable mode of formation of 56, 58 and 59 have been discussed.

CHAPTER III

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