SUMMARY

The research work being reported in this thesis has been divided into three parts.

PART - I

ACTION OF N-BROMOSUCCINIMIDE ON FRIEDELIN AND TRITERPENOIDS OF FRIEDELIN SKELETON IN DIMETHYLSULFOXIDE.

Part - I has been divided into three Chapters.

CHAPTER - I

This chapter comprises a short review of the action of N-bromosuccinimide in dimethyl sulfoxide.

CHAPTER - II

This chapter contains the action of N-bromosuccinimide on friedelin : Section A; Cerin: Section B & Cerin acetate : Section C.

SECTION - A

Friedelin (I) taken in dimethyl sulfoxide with N-bromosuccinimide afforded six products : A —— F.

Compound A identified as 2β, 23-dibromo-friedelin (2); molecular formula $C_{30}H_{48}OBr_2$, m.p. 214-15^{o}C; responded Beilstein test for halogen and gave no yellow colouration with tetranitro methane (TNM); IR : 1735 cm^{-1} (C = O); ^{1}H NMR : δ = 0.73, 0.85,

0.96, 0.997, 0.999, 1.04, 1.18 (7s, 3H each), 1.65 (dd, J = 3 & 13 Hz, 1H), 2.05 (AB_q, J = 13 & 26 Hz, 1H), 2.63 (ddd, J = 3, 7 & 13 Hz, 1H), 2.83 (d, J = 3 & 10 Hz, 1H), 3.38 (dd, J = 3 & 10 Hz, 1H), 3.78 (d, J = 10 Hz, 1H), 3.78 (d, J = 10 Hz, 1H), 4.68 (dd, J = 7 & 13 Hz, 1H).

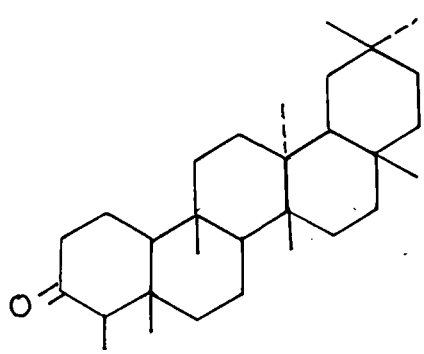
Compound B identified as 2α, 23-dibromofriedelin (3), molecular formula $C_{30}H_{48}OBr_2$, m.p. 222-23°C, responded Beilstein test for halogen and no yellow colouration with (TNM); IR : 1725 cm^{-1} (C = 0); ^1H NMR : δ = 0.73, 0.85, 0.96, 0.996, 1.00, 1.08, 1.18 (7s, 3H each), 1.6 (dd, J = 3 & 10 Hz, 1H), 2.02 (dd, J = 3 & 10 Hz, 1H), 2.18 (dd, J = 3 & 10 Hz, 1H), 3.37 (d, J = 3 & 10 Hz, 1H), 3.64 (d, J = 10 Hz, 1H), 3.68 (t, J = 10 Hz, 1H), 4.46 (t, J = 3 Hz, 1H).

Compound C identified as 2α-bromofriedelin (4), molecular formula $C_{30}H_{49}OBr$, m.p. 210°C, responded Beilstein test for halogen and no yellow colouration with (TNM); IR : 1725 cm^{-1} (C = 0); Mass : m/e 506.

Compound D identified as 2,2-dibromofriedelin (5), molecular formula $C_{30}H_{48}OBr_2$, m.p. 233-34°C, responded Beilstein test for halogen and no yellow colouration with (TNM), IR : 1730-40 cm^{-1} (C = 0); ^1H NMR : δ = 0.72, 0.90, 0.97, 1.01, 1.02, 1.08, 1.19 (7s & 3H each), 1.02 (d, J = 7 Hz, 3H), 1.87 (dd, J = 15 Hz, 1H), 2.70 (dd, J = 15 & 13 Hz, 1H), 2.93 (dd, J = 5 & 3 Hz, 1H), 3.23 (q, J = 7 Hz, 1H).

Compound E identified as 2α-bromo-4(23)-dehydrofriedelin (6), molecular formula $C_{30}H_{47}OBr$, m.p. 200-201°C, responded Beilstein test for halogen and produced yellow colouration with (TNM); IR : 1750 cm^{-1} (C = O), 3040, 1640, 980 cm^{-1} (= CH_2); ^1H NMR : δ = 0.71, 0.87, 0.965 (3s& 3H each), 1.005 (3s, 9H), 1.12 (s, 3H), 4.4 (t, 1H), 5.3 (s, 1H), 5.805 (s, 1H).

Compound F identified as 2 keto-friedel-3(4)-en-3-ol (7), molecular formula $C_{30}H_{48}O_2$, m.p. 272°C; IR : 3360 cm^{-1} (-OH), 1640 cm^{-1} (α,β-unsaturated C = O), 1710 cm^{-1} (C = O); ^1H NMR : δ = 0.95, 0.96, 0.99, 1.01, 1.02, 1.10, 1.20, 1.83 (8s & 3H each), 2.41 (dd, J = 17 & 12 Hz, 1H), 2.51 (dd, J = 12 & 2 Hz, 1H), 5.98 (s, 1H).



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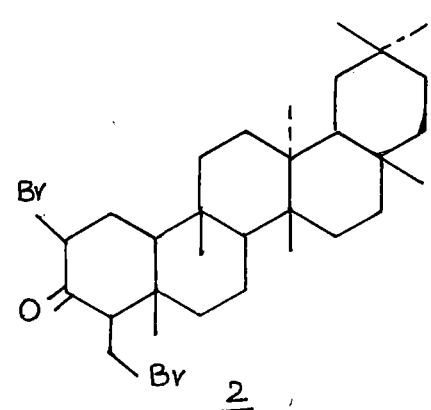

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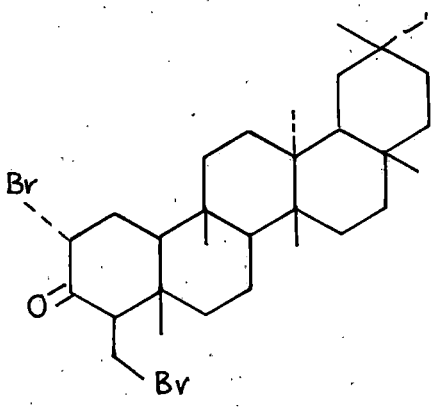

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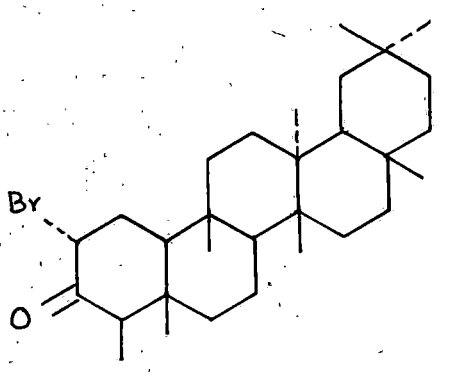

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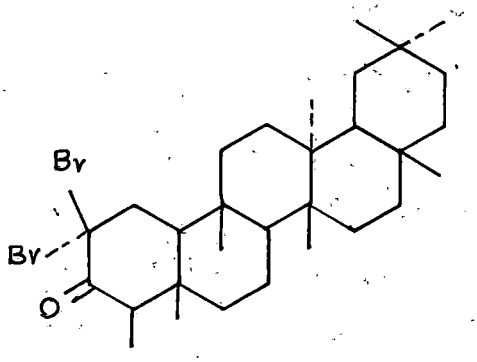

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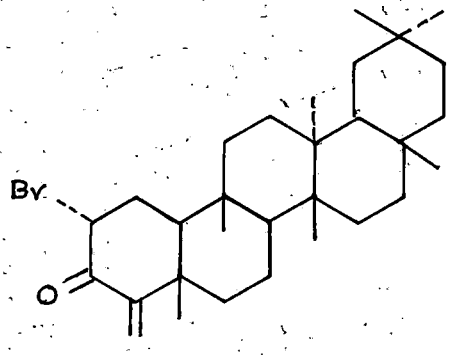

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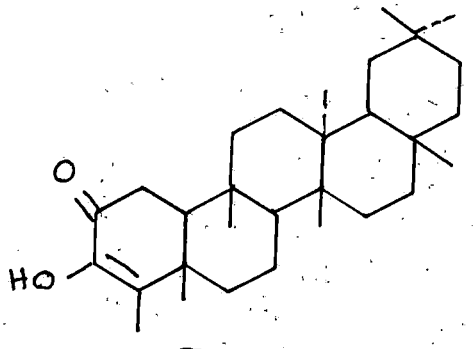

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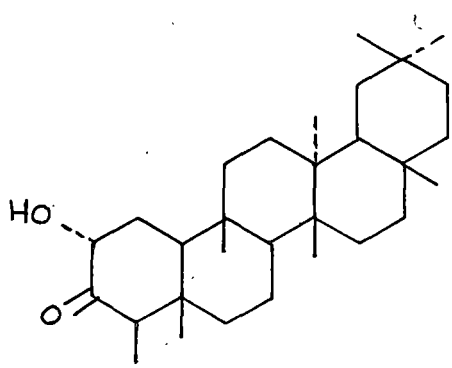
SECTION - B

Cerin (8) taken in dimethyl sulfoxide on reaction with N-bromosuccinimide afforded two products : A and B.

Compound A identified as 1,1-dibromo-2-keto friedel-3(4)-en-3-ol (9), molecular formula $C_{32}H_{48}O_3Br_2$, m.p. 234-35°C, responded Beilstein test for halogen and ferric chloride test for phenolic -OH group showing the presence of enol functional group, IR : 1655 cm^{-1} (α,β-unsaturated C = O) and (-OH) group, UV : λ_{max}^{MeOH} 292 nm, ^1H NMR : δ = 0.95, 1.00, 1.04, 1.07, 1.09, 1.19, 1.25, 1.84 (8s & 3H each), 3.09 (dd, J = 5, 12 Hz, 1H), 3.24(s, 1H), 6.62 (s, 1H).



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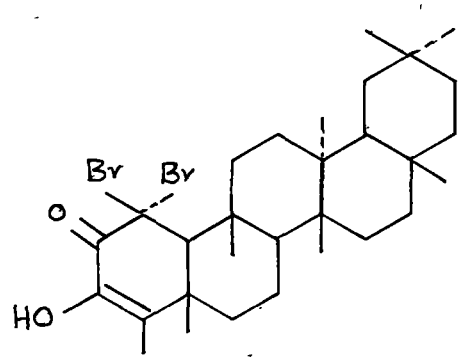
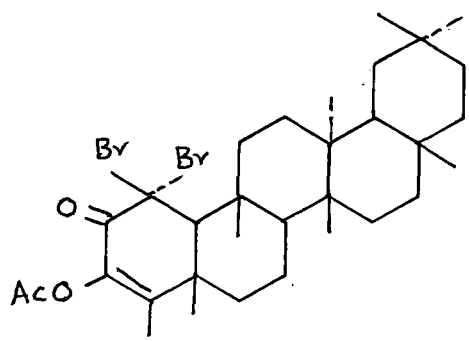


9

Acetylation of compound (9) produced the Acetate 10 identified as 1,1-dibromo-3-acetoxylfriedel-2 keto-3-ene (10), molecular formula $C_{32}H_{48}O_3Br_2$, m.p. 242-43°C, responded Beilstein test for halogen; IR :1750 cm^{-1} (enol-acetate), 1614-1680 cm^{-1} (α,β-unsaturated C = O), ^1H NMR : δ = 0.96, 1.00, 1.05, 1.08, 1.19, 1.21, 1.26, 1.81 (8s, 24H), 2.39(s, 3H), 3.03(dd, J = 3 & 12 Hz, 1H), 3.4 (s, 1H).



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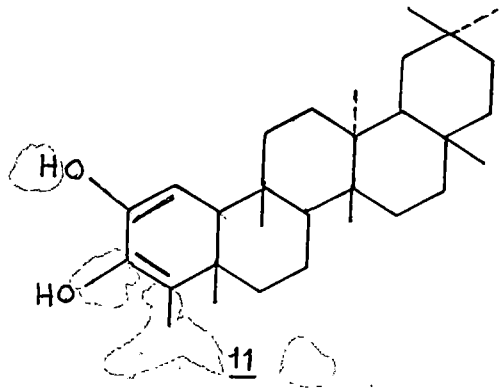
Compound B identified as friedel-1,3-diene-2,3-diol (11), molecular formula $C_{30}H_{48}O_2$, m.p. 172-73°C, negative Beilstein test for halogen, ferric chloride test positive for enolic hydroxyl group, UV : λ_{max} 292 nm in MeOH and 340 nm in alkali, IR : 3380-3460 cm^{-1} (-OH), ^1H NMR : δ = 0.96, 0.98 (2s, & 3H each), 1.01 (bs, 9H), 1.06, 1.19, 1.85 (3s & 3H each), 2.69 (d, J = 3 Hz, 1H), 6.1 (d, J = 3 Hz, 1H).

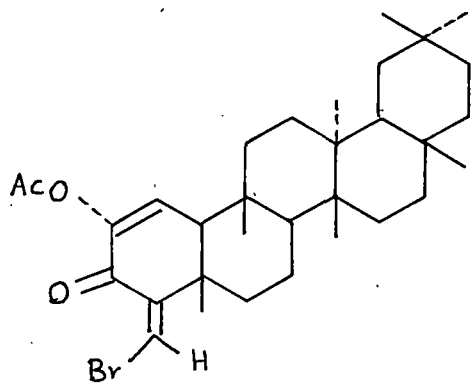


11

SECTION - C

Cerin acetate (14) taken in dimethyl sulfoxide afforded on treatment with N-bromosuccinimide three products : C, D and E.

Compound C identified as 23-bromo-2α-acetoxy friedel-1(2), 4(23)-dien-3-one (12), molecular formula $C_{32}H_{47}O_3Br$, m.p. 177-78°C responded Beilstein test for halogen, IR : 1700 cm^{-1} (α,β-unsaturated C = O); ^1H NMR : δ = 0.96, 0.99 (2s, 6H), 1.00 (bs, 6H), 1.04, 1.06, 1.2 (3s, 9H), 2.3 (s, 3H), 5.83 (s, 1H), 2.69 (d, J = 3 Hz, 1H), 6.1 (d, J = 3 Hz, 1H).



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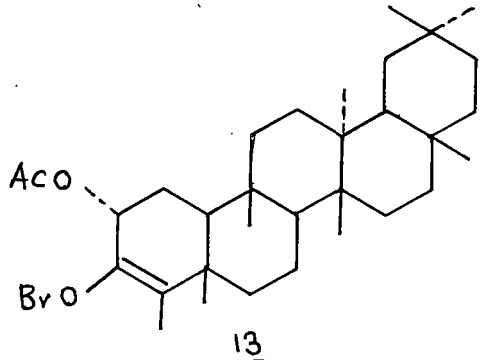
Compound D identified as 2α-acetoxy friedel-3(4)-en-3-hypobromite (13), molecular formula $C_{32}H_{51}O_3Br$, m.p. 164-65°C, responded Beilstein test for halogen, IR : 1740, 1230 cm^{-1} ($-OCOCH_3$, C = O), 710 cm^{-1} (tetra substituted double bond); ^1H NMR : = 0.90, 0.97, 0.98 (3s & 3H each), 1.01 (bs, 6H), 1.09 (s, 3H), 1.19 (s, 3H), 1.72 (s, 3H), 2.13 (s, 3H), 5.19 (dd, J = 3 & 5 Hz, 1H).



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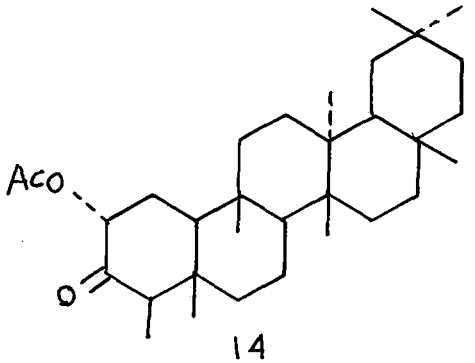
Compound E identified as 2α-acetoxy friedelin (14), molecular formula $C_{32}H_{52}O_3$, m.p. 252-53°C, responded no Beilstein test for halogen; IR : 1740 cm^{-1}, 1220 cm^{-1} ($-OCOCH_3$), 1705 cm^{-1} (C = O); ^1H NMR : δ = 0.70, 0.84, 0.96, 1.00, 1.07, 1.19 (6s & 3H each), 0.89 (d, J = 7 Hz, 3H), 2.67 (AB_q, 1H), 2.12(s, 3H), 4.94 (t, J = 3 Hz, 1H). The probable mechanism for the formation of compounds are also discussed in this cahpter.



14

CHAPTER - III

This chapter constitutes the experimental details of work described in CHAPTER - II.

PART - II

OXIDATION OF PENTACYCLIC TRITERPENOIDS HAVING DOUBLE BONDS AT C-2 AND C-3 POSITIONS WITH SELENIUM DIOXIDE-HYDROGEN PEROXIDE MIXTURE IN TERTIARY BUTANOL.

Part - II comprises of three chapters.

CHAPTER - I

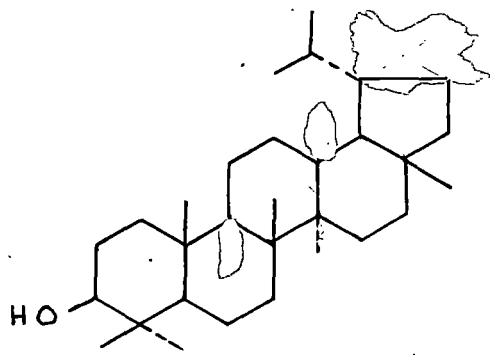
This chapter contains a short review of oxidation with a mixture of selenium dioxide-hydrogen peroxide in tertiary butanol.

CHAPTER - II

This chapter contains the results and discussion part on oxidation of lupan-2(3)-ene (70), 28-carbomethoxy lupan-2(3)-ene (73), friedel-3(4)-ene (76) and friedel 3(4)-en-27⟶15-olide (81).

SECTION - A

Lupan-2(3)-ene (16) on refluxing with selenium dioxide-hydrogen peroxide in tertiary butanol afforded a product identified as lupan-2β, 3α-diol (17), m.p. 240-46°C, IR : 3300-3450 cm^{-1} and its corresponding acetate (18), m.p. 221-22°C, molecular formula $C_{34}H_{56}O_4$, IR : 1750, 1270 and 1250 cm^{-1} ($-COOCH_3$). The structure of 72 has been established from spectral studies. ^1H NMR of (17) & (18) : δ = 0.77 & 0.84 (dd, J = 7 Hz, 6H), 0.76, 0.91, 0.95, 0.98, 1.03 & 1.07 (6s & 18H), 2.01 & 2.07 (2s & 6H), 4.96 (dd, J = 7 & 13 Hz, 3H), 5.07 (d, J = 7 Hz & 2 H). The mode of reaction mechanism and formation of (17) and (18) has been discussed in this chapter.



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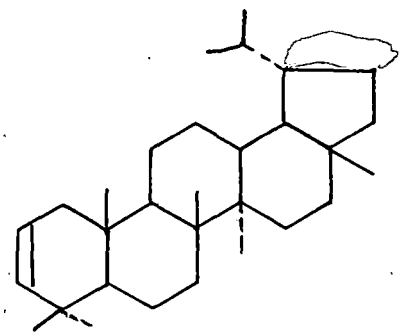

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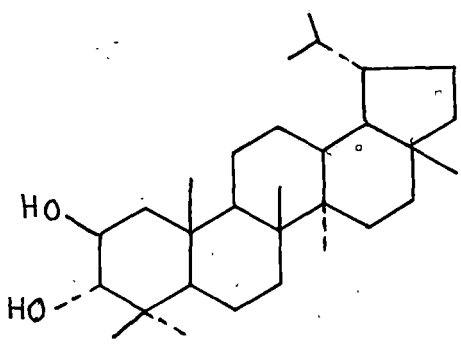

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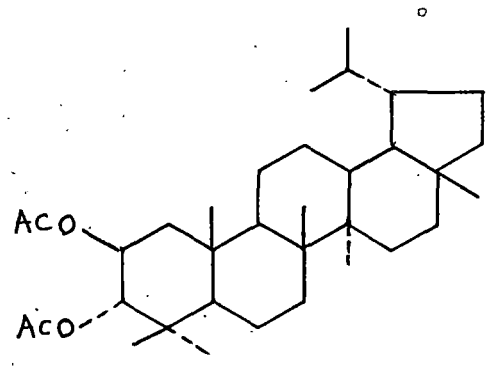
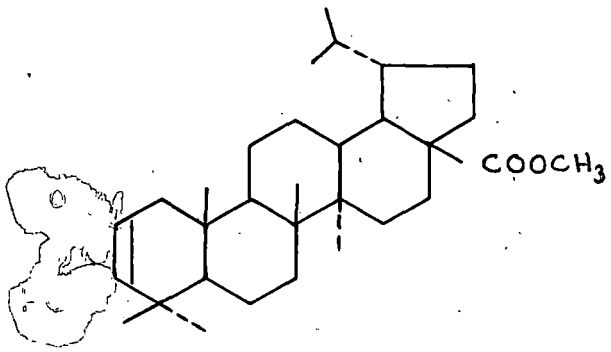


18

SECTION - B

In this section oxidation product of 28-carbomethoxy lupan-2(3)-ene (19) is discussed. 19 on oxidation with Selenium dioxide-hydrogen peroxide mixture in tertiary butanol furnished a product isolated after acetylation as 2β, 3α-diacetoxy methyldihydro betulinate (20), molecular formula $C_{35}H_{56}O_6$, m.p. 209-10°C, IR : 1730, 1710 and 1230 cm^{-1} ($-OCOCH_3$ and $-COOCH_3$), ^1H NMR : δ= 0.74 & 0.85 (2d, J = 7 Hz, 6H), 0.90 (s, 6H), 0.95, 0.96, 1.05, 2.01, 2.05, 3.64 (s & 3H each), 4.76 (dd, J = 13 & 7 Hz, 1H), 5.06 (d, J = 7 Hz, 1H).



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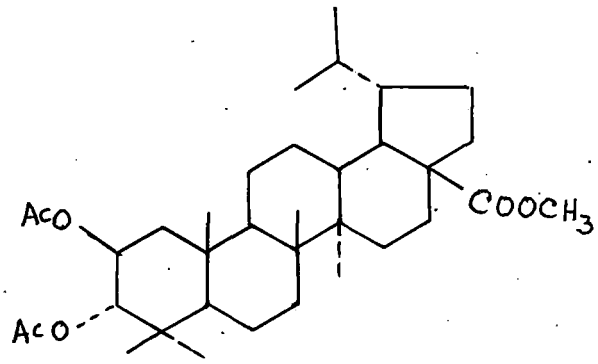

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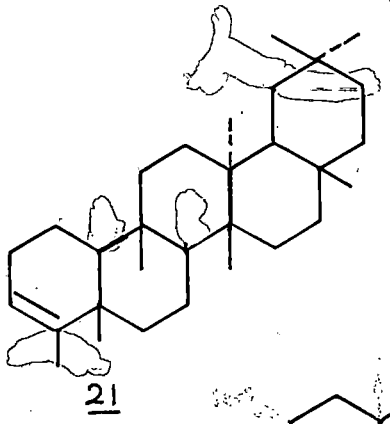
SECTION - C

Friedel-3(4)-en (21) on prolong refluxing with selenium dioxide-hydrogen peroxide mixture in tertiary butanol furnished two products, isolated and identified as lupanone (22), molecular formula $C_{30}H_{50}O$, m.p. 207-8°C, IR : 1715 cm^{-1} (C = O) and friedelan

-3β, 4α-diol (23) molecular formula $C_{30}H_{52}O_2$, m.p. 235-6°C, IR : 3340 and 3380 cm^{-1} (-OH).



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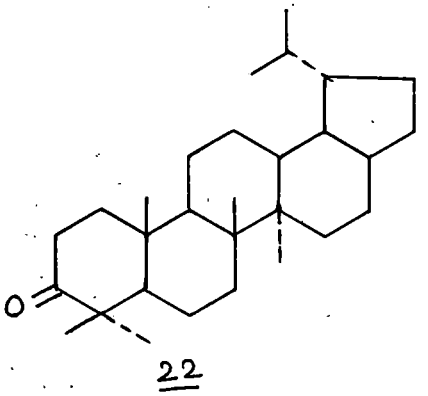

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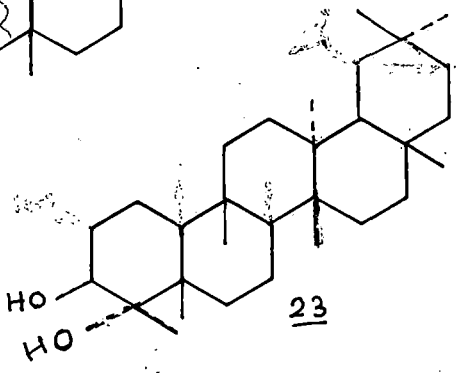

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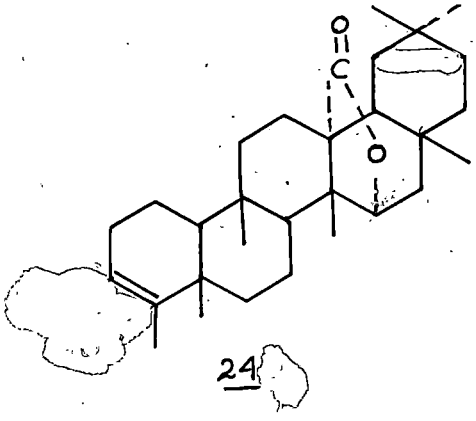
SECTION - D

Friedelin-3(4)-en-27 $\longrightarrow$ 15 olide (24) on similar treatment under identical condition afforded a single product and identified as friedel-3β-4α-diol 27$\longrightarrow$15 olide (25), molecular formula $C_{30}H_{48}O_4$, m.p. 271°-72°C, IR : 3500 and 3440 cm^{-1} (2-OH), 1760 cm^{-1} (C = 0), ^{1}H NMR : δ = 0.86, 0.94, 0.96, 1.02, 1.05 & 1.21(t.d), 2.02 (J = 3 & 13.5 Hz), 3.54 (t, J = 3 Hz), 4.34 (J = 3 Hz).



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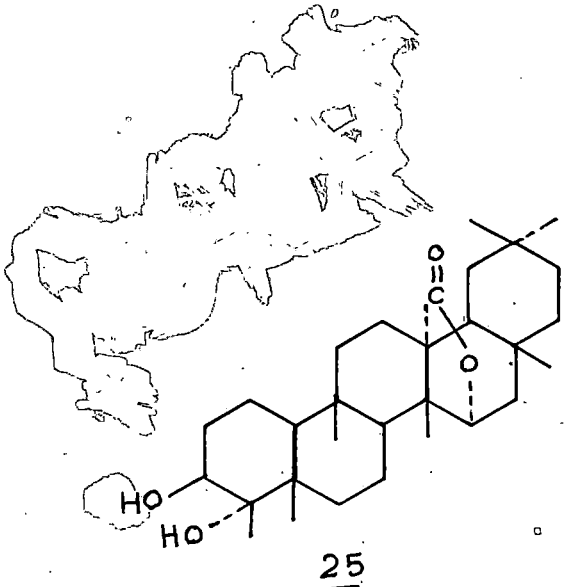


25

CHAPTER - III

This chapter constitutes the experimental details of work described in CHAPTER - II.

PART - III

ACTION OF META CHLOROPERBENZOIC ACID IN CHLOROFORM ON TRITERPENOID DERIVATIVES.

Part - III comprises of three chapters.

CHAPTER - I

This chapter contains a short review of oxidative reactions by per acids and peroxides.

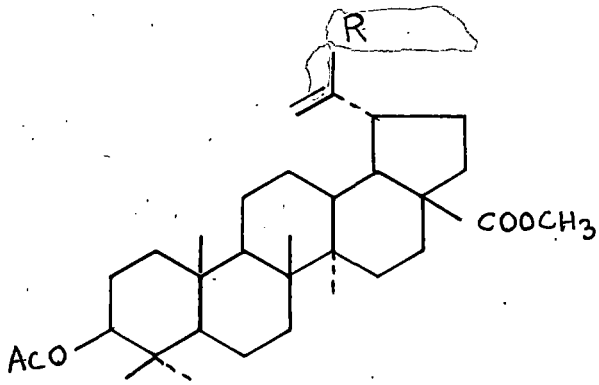
CHAPTER - II

This chapter contains the results and discussion part on the oxidation of acetyl methyl betulinate (26, Section - A) and lupenyl acetate (28, Section B) by metachloroperbenzoic acid in chloroform.

SECTION - A

Acetyl methyl betulinate (26) was refluxed with molar proportion of m-chloroperbenzoic acid in chloroform afforded a product identified as 30-hydroxy-acetyl methyl betulinate (27), m.p. 175-76°C, IR : 3400-3500 cm^{-1} (-OH) and 1710-1740 cm^{-1} and 1250 cm^{-1} ($-OCOCH_3$-$COOCH_3$), 910 cm^{-1} ($=CH_2$), UV : 220 to 300 nm

indicating no conjugated functional group. Molecular formula $C_{33}H_{52}O_5$, ^1H NMR : δ = 0.84 (s, 3H), 0.85(bs, 6H), 0.90(s, 3H), 0.97 (s, 3H), 2.04 (s, 3H), 2.8 (ddd, J = 4 Hz, 1H), 3.68 (s, 3H), 4.47 (m, 1H), 4.12 (6s, 2H), 4.93 (s, 1H), 4.97 (s, 1H).



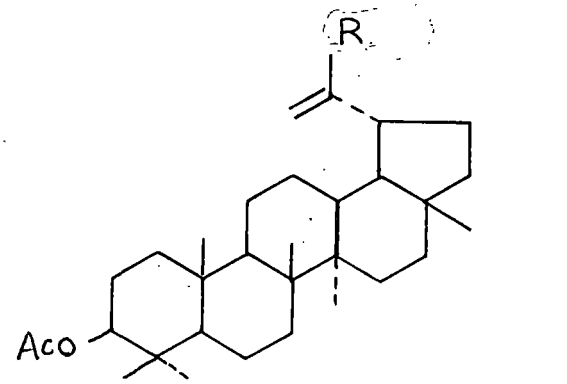
26 , R = CH_3

27 , R = CH_2OH

SECTION - B

Lupenyl acetate (28) was refluxed with molar proportion of m-chloroperbenzoic acid on chloroform afforded a product identified as 30-hydroxy lupenyl acetate (29), m.p. 245°C, IR : 3440-3450 cm^{-1} (-OH), 1730 cm^{-1}, 1260 cm^{-1} (O.$COCH_3$) and 900 cm^{-1} (disubstituted olefinic double bond), UV : 220 to 300 nm (absence of configurated functional group), molecular formula $C_{32}H_{52}O_3$, ^1H NMR : δ = 0.79 (s, 3H), 0.82 (s, 3H), 0.83 (s, 3H), 0.84 (s, 3H), 0.93 (s, 3H),

1.02(s, 3H), 2.04(s, 3H), 2.29 (ddd, J = 5 Hz, 1H), 4.12 (AB_q, J = 14 Hz, 2H), 4.48 (m, 1H), 4.9 (s, 1H), 4.94(s, 1H).



28, R = CH_3

29, R = CH_2OH

CHAPTER - III

This chapter constitutes the experimental details of work discussed in CHAPTER - II.