

## SUMMARY.

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

### PART-I

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

Part-I has been divided into three chapters

#### CHAPTER-I

This chapter comprises a short review of oxidations with selenium dioxide in presence of hydrogen peroxide.

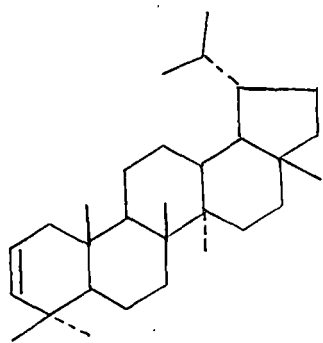
#### CHAPTER-II

This chapter contains the discussion part on oxidation of Lup-2(3)-ene (1), 2,3 dehydro methyl dihydro betulinate (4), Friedel-3(4)-ene (6), and 3,4 dehydro friedel 27→15-olide (9), in tertiary butanol containing hydrogen peroxide.

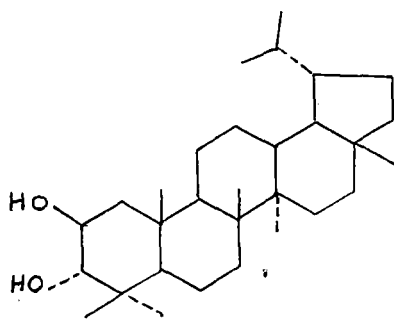
#### SECTION -A :

Lup-2(3)-ene 1, on refluxing with selenium dioxide in tertiary butanol containing hydrogen peroxide afforded a single product characterised as lupan 2 $\beta$ ,3 $\alpha$ -diol 2, M.P. 245-6<sup>o</sup>C, which was isolated after acetylation as lupan 2 $\beta$ ,3 $\alpha$ -diyl acetate 3, M.P. 221-2<sup>o</sup>C; molecular formula C<sub>34</sub>H<sub>56</sub>O<sub>4</sub>; IR : 1750, 1270 and 1250 cm<sup>-1</sup> (-CO-CH<sub>3</sub>); Mass : m/e 528 (M<sup>+</sup>, 86%);

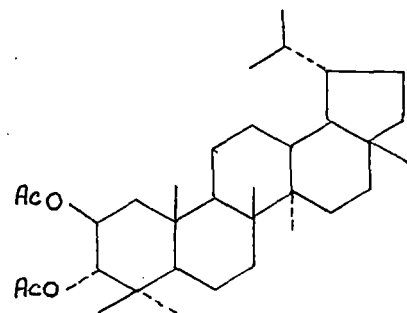
The structure 3, is established from spectral studies ( <sup>1</sup>H NMR , Mass and IR ). The mode of reaction mechanism and formation of 2 and 3 has also been discussed.



1



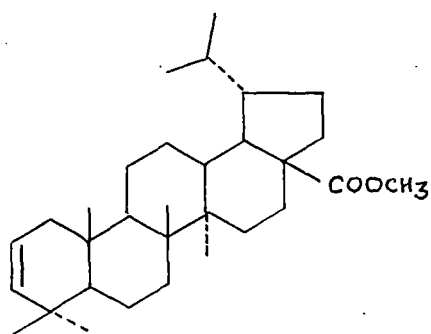
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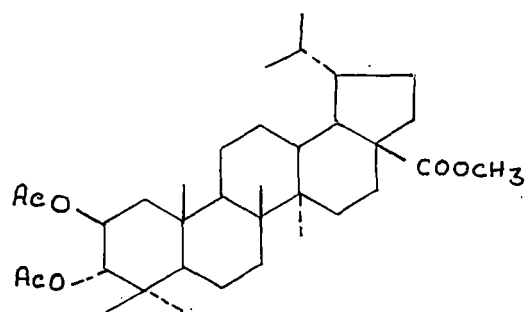
3

SECTION-B :

In this section the oxidation product of 2,3 dehydro methyl dihydro betulinate (4), is discussed. 4 on oxidation with selenium dioxide in tertiary butanol containing hydrogen peroxide furnished a single product isolated after acetylation as 2 $\beta$ ,3 $\alpha$ -diacetoxy methyl dihydro betulinate 5, molecular formula  $C_{35}H_{56}O_6$ , M.P. 209-10 $^{\circ}$ C; IR : 1730, 1710 and 1230  $cm^{-1}$  (-CO-CH<sub>3</sub> and -COOCH<sub>3</sub>) ; Mass : m/e 572 (M<sup>+</sup>, 4%) ; The structure 5 is based on spectral analysis ( <sup>1</sup>H NMR , IR and Mass)



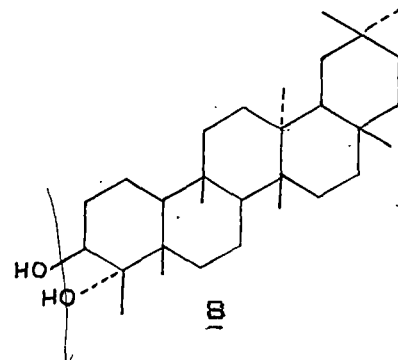
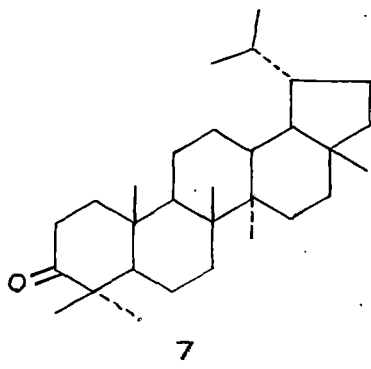
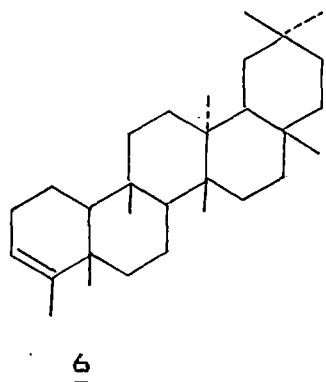
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SECTION-C :

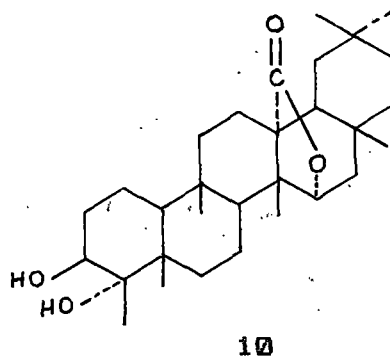
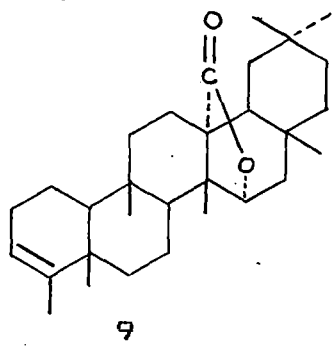
Friedel-3(4)-ene (6) on prolong heating with selenium dioxide in tertiary butanol containing hydrogen peroxide furnished two products isolated and characterised as lupanone 7,  $C_{30}H_{50}O$ , M.P. 207-8 $^{\circ}$ C; IR : 1715  $cm^{-1}$  (-CO); Mass : m/e 426 (M<sup>+</sup>, 14%) and friedelan-3 $\beta$ ,4 $\alpha$ -diol 8,  $C_{30}H_{52}O_2$ , M.P. 235-6 $^{\circ}$ C, IR : 3340 and 3380  $cm^{-1}$  (-OH), Mass : m/e 444 (M<sup>+</sup>, 72%), from <sup>1</sup>H NMR, Mass and IR spectral studies.



Their formation and probable mechanism are also suggested in this section.

SECTION-D :

3(4)-dehydro friedelan 27→15-olide (9), on similar treatment under identical condition afforded a single product isolated and characterised as friedelan 3 $\beta$ ,4 $\alpha$ -dihydroxy 27→15-olide 10, C<sub>30</sub>H<sub>48</sub>O<sub>4</sub>, M.P. 270-1°C; IR : 3500, 3440 (-OH) and 1760 cm<sup>-1</sup> ( $\gamma$ -lactone), Mass : 472 (M<sup>+</sup>, 22%).



The structure 10 is based on Mass, IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectral analysis.

CHAPTER-III

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

## PART-II

### ACTION OF N-BROMOSUCCINIMIDE ON PENTACYCLIC TRITERPENOIDS OF LUPANE AND FRIEDELANE SKELETON IN DIMETHYL SULFOXIDE.

Part-II has been divided into three chapters.

#### CHAPTER-I.

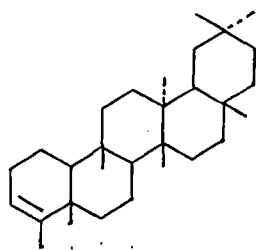
This chapter constitutes a brief review of previous related works done with N-bromosuccinimide.

#### CHAPTER-II

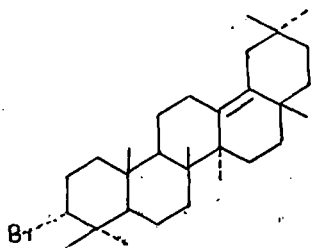
Studies on the action of N-bromosuccinimide on friedel-3(4)-ene (11), 30-bromolupenyl acetate (14), lupan 20(29)-ene,3 $\beta$ ,28-diol (16), lupan 20(29)-ene,3 $\beta$ ,28-diyl acetate(18) and lupan 20(29)-ene,3 $\beta$ ,30-diyl acetate (21) taken in dimethyl sulfoxide.

#### SECTION-A :

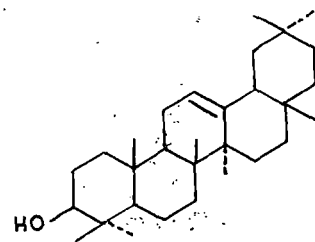
Friedel-3(4)-ene (11) was taken in dimethyl sulfoxide and kept in dark for 24 hours with N-bromosuccinimide. After the reaction two products were isolated and characterised as 3 $\alpha$ -bromo olean-13(18)-ene 12, molecular formula  $C_{30}H_{49}Br$ , M.P. 200-1 $^{\circ}$ C; responded to Beilstein test for halogen and gave yellow colouration with tetranitromethane (TNM), Mass : m/e 490 ( $M_1^+$ , Br<sup>79</sup>), and 488 ( $M_2^+$ , Br<sup>77</sup>) and 3 $\beta$ -hydroxy olean-12(13)-ene 13,  $C_{30}H_{50}O$ , M.P. 229-30 $^{\circ}$ C, TNM test positive but Beilstein test for halogen negative, IR : 3380  $cm^{-1}$  (-OH), Mass : m/e 411 ( $M^+$ , 11%).



11



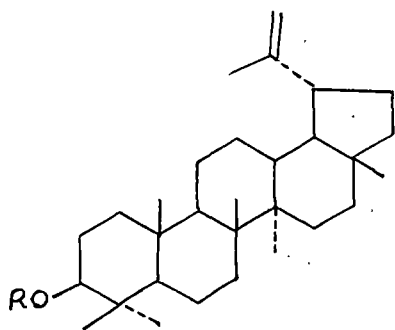
12



13

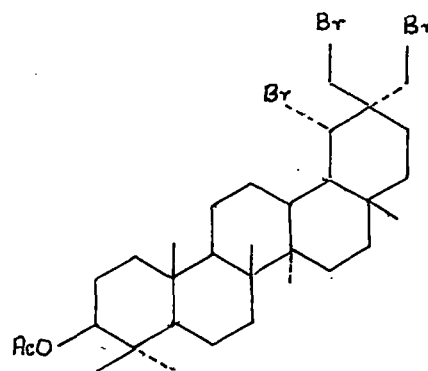
SECTION-B :

Lupenyl acetate (14a), (prepared from lupeol, 14 see Experimental ) was dissolved in acetic acid cooled at  $0^{\circ}(-5)^{\circ}\text{C}$  and bromine was added. After the reaction a single product was isolated which was identified as  $3\beta$ -acetyl  $19\alpha,29,30$  tribromo oleanane 15, molecular formula  $\text{C}_{32}\text{H}_{51}\text{O}_2\text{Br}_3$ , M.P.  $225-6^{\circ}\text{C}$ , IR :  $1690$  and  $1255\text{ cm}^{-1}$  (  $-\text{COCH}_3$  ), Beilstein test for halogen was positive but did not respond to TNM test, Mass : m/e  $710$  ( $\text{M}_1^+$ ,  $\text{Br}^{79}$ ) and  $708$  ( $\text{M}_2^+$ ,  $\text{Br}^{77}$ ).



14, R = H

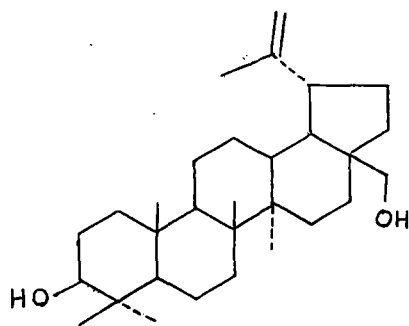
14a, R = Ac



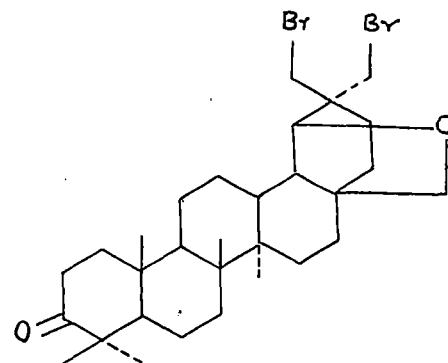
15

SECTION-C :

Lupan  $20(29)$ -en, $3\beta,28$ -diol (16), on similar treatment under identical condition furnished a product isolated and identified as 3-keto oleanan  $28-19$ -oxo, $29,30$  dibromide 17,  $\text{C}_{30}\text{H}_{46}\text{O}_2\text{Br}_2$ , M.P.  $232-3^{\circ}\text{C}$  IR :  $1720\text{ cm}^{-1}$  ( $-\text{C}=\text{O}$ ) ; Beilstein test for halogen was positive but TNM test negative ; Mass : m/e  $599$  ( $\text{M}_1^+$ ,  $\text{Br}^{79}$ , 2%) and  $597$  ( $\text{M}_2^+$ ,  $\text{Br}^{77}$ , 6%);



16

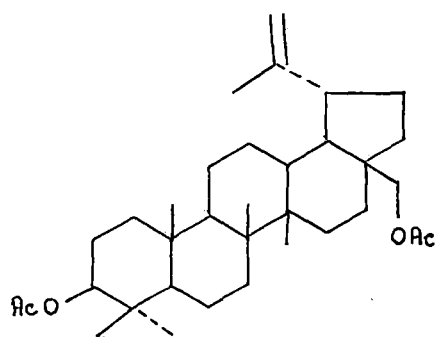


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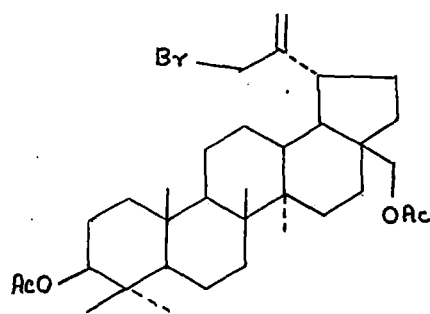
SECTION-D :

Lupan 20(29)-en,3 $\beta$ ,28-diyl acetate (18), on similar treatment under identical condition afforded two compounds 19 and 20.

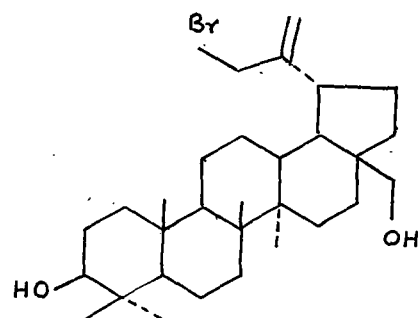
They were identified as 30-bromo lupan 20(29)-en-3 $\beta$ ,28-diyl acetate 19, C<sub>34</sub>H<sub>53</sub>O<sub>4</sub>Br, M.P. 169-70°C ; IR : 1730 and 1240 cm<sup>-1</sup> (-COCH<sub>3</sub>), Mass : m/e 606 (M<sub>1</sub><sup>+</sup>, Br<sup>79</sup>, 0.8%) and 604 (M<sub>2</sub><sup>+</sup>, Br<sup>77</sup>, 1.6%) and 30-bromo lupan 20(29)-en-3 $\beta$ ,28-diol 20, C<sub>30</sub>H<sub>50</sub>O<sub>2</sub>Br, M.P. 202-3°C ; Beilstein test was positive and produced yellow colouration with TNM, IR : 3390 cm<sup>-1</sup> (b,-OH); Mass : m/e 442 (M<sub>1</sub><sup>+</sup>) or 440 (M<sub>2</sub><sup>+</sup>) which was less than actual molecular ion mass probably due to loss of one HBr<sup>79</sup> or HBr<sup>77</sup> unit.



18



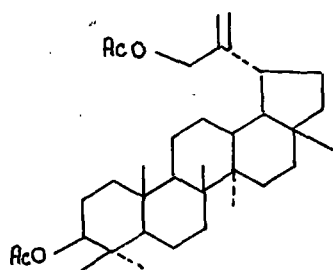
19



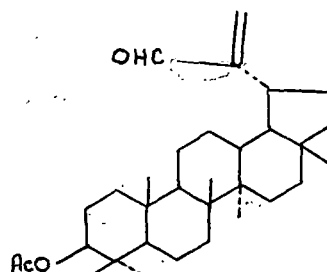
20

SECTION-E :

lupan 20(29)-en,3 $\beta$ ,30-diyl acetate (21), on similar treatment with N-bromosuccinimide in dimethyl sulfoxide furnished a compound identified as lupan 20(29)-en,30-al,3 $\beta$ -yl acetate 22, C<sub>32</sub>H<sub>50</sub>O<sub>3</sub>, M.P. 224-5°C, Beilstein test for halogen was negative but produced yellow colouration with TNM indicating presence of double bond. IR : 1730 cm<sup>-1</sup> (-CHO) and 1700, 1255 cm<sup>-1</sup> (-COCH<sub>3</sub>), Mass : m/e 482 (M<sup>+</sup>, 24%).



21



22

All the above structures are established from Mass, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral analysis.

### CHAPTER-III

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

### PART-III

OXIDATION OF PENTACYCLIC TRITERPENOID KETONE, LACTONE AND ESTER WITH META CHLOROPERBENZOIC ACID IN CHLOROFORM.

Part-III has been divided into three chapters.

#### CHAPTER-I

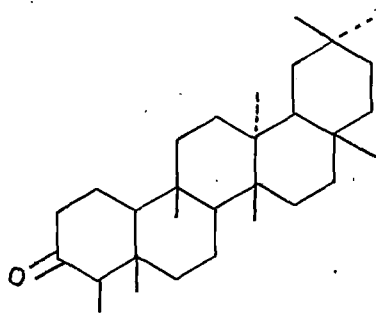
It contains a brief review of oxidation of triterpenoids with meta-chloroperbenzoic acid in different solvents.

#### CHAPTER-II

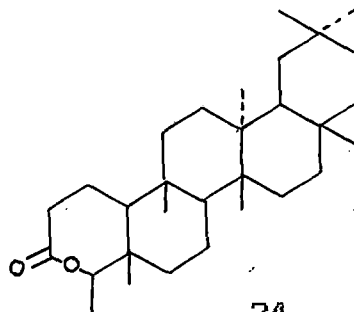
This chapter contains the discussion on oxidation of friedelin (23), 3-oxo friedelan 27 $\rightarrow$ 15-olide (25) and acetyl methyl betulinate (27) with meta-chloroperbenzoic acid.

#### SECTION-A :

Friedelin (23), was refluxed with meta-chloroperbenzoic acid in chloroform for 6 hours and after the reaction the single product obtained was identified as 3,4 seco friedelan 3 $\rightarrow$ 4-olide 24,  $\text{C}_{30}\text{H}_{50}\text{O}_2$ , M.P. 271-2 $^{\circ}\text{C}$ , IR : 1720  $\text{cm}^{-1}$  ( $\delta$ -lactone) ; Mass : m/e 442 ( $\text{M}^+$ , 30%).  
by comparing with authentic sample ( M.M.P. and Co-IR)



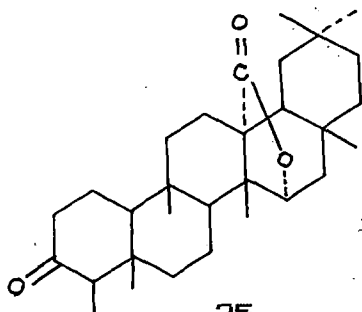
23



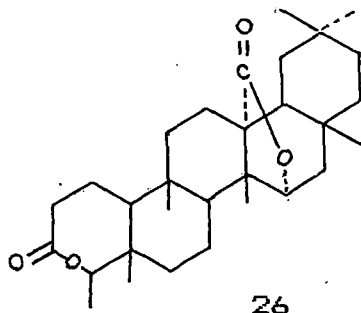
24

SECTION-B :

3-oxo friedelan 3 → 4-olide (25), (odolactone) on similar treatment afforded a single product, which was identified as friedelan 3→4,27→15-diolide 26,  $C_{30}H_{46}O_4$ , M.P. >300°C, IR : 1760 and 1730  $cm^{-1}$  ( $\epsilon$  and  $\gamma$ -lactone); Mass : 470 ( $M^+$ ).



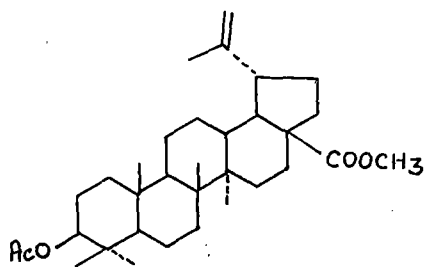
25



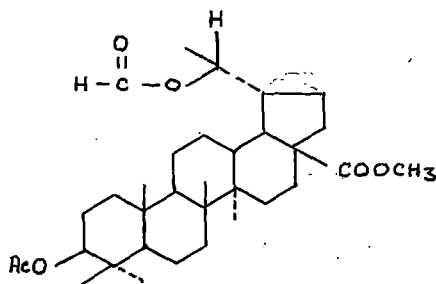
26

SECTION-C :

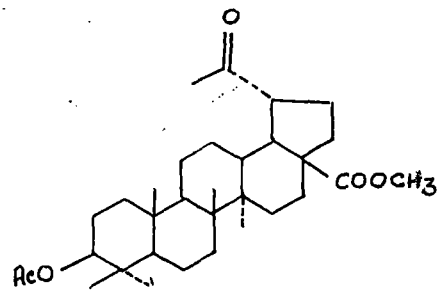
Acetyl methyl betulinate (27) on similar treatment under identical condition furnished two products characterised as 29-nor-3 $\beta$ -O-acetyl-lupan-20-O-formyl 28 methyl carboxylate 28,  $C_{33}H_{54}O_6$ , M.P. 151-2°C, did not respond to TNM test, IR : 1740, 1250  $cm^{-1}$  ( $-COCH_3$ ); Mass : m/e 544 ( $M^+$ ) and 29-nor acetyl methyl 20-oxo-betulinate 29,  $C_{32}H_{50}O_5$ , M.P. 211-2°C; IR : 1730, 1260  $cm^{-1}$  ( $-COCH_3$ ), did not produce yellow colouration with TNM. Mass : m/e 514 ( $M^+$ ).



27



28



29



All the 24, 26, 28 and 29 structures are based on  $^1\text{H}$  NMR, Mass and IR spectral studies.

### CHAPTER-III

Experimental details of work described in CHAPTER-II.

### PART-IV

REDUCTIVE CLEAVAGE OF SEVEN MEMBERED LACTONE RING WITH LITHIUM IN ETHYLENEDIAMINE.

This part is also divided in three chapters

#### CHAPTER-I

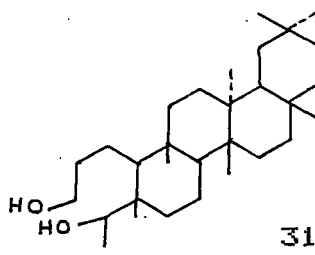
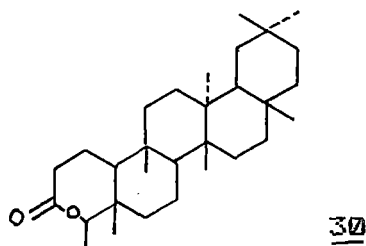
It constitutes a short review of lithium ethylenediamine as a reducing agent.

#### CHAPTER-II

This chapter contains studies on reductive cleavage of 3,4 seco friedelan 3 $\rightarrow$ 4-olide (30) and friedelan 3 $\rightarrow$ 4, 27 $\rightarrow$ 15-diolide (32) with lithium in ethylenediamine.

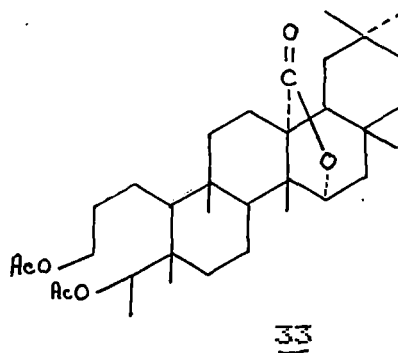
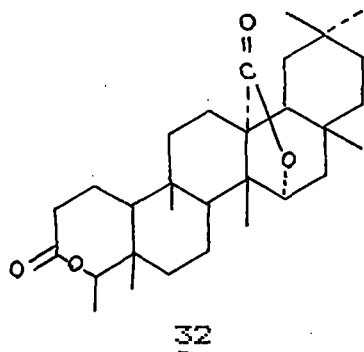
#### SECTION A :

3,4 seco friedelan 3 $\rightarrow$ 4-olide (30) was refluxed with lithium metal dissolved in dry ethylenediamine for 2 hours over heating mantle. After reaction the product obtained was identified as 3,4 seco friedelan 3,4 diol 31,  $\text{C}_{30}\text{H}_{50}\text{O}_2$ , M.P. 173-4 $^{\circ}$ C, IR : 3420  $\text{cm}^{-1}$  (broad) (-OH); Mass : m/e 428 ( $\text{M}-\text{H}_2\text{O}$ ) $^+$ .



SECTION-B :

Friedelan 3→4,27→15 diolide (32) was reduced with lithium metal dissolved in dry ethylenediamine at room temperature and the product obtained was isolated after acetylation. It was identified as friedelan 3,4 diacetoxo 27→15-olide 33,  $C_{34}H_{54}O_6$ , M.P. 241-2<sup>o</sup>C, IR :  $1750\text{ cm}^{-1}$  ( $-\text{COCH}_3$ ); Mass :  $m/e$  558 ( $M^+$ , 7%).



Both the structures 31 and 33 are established from  $^1\text{H}$  NMR, Mass and IR spectral analysis.

CHAPTER-III

The experimental details of the above two lactone cleavage are described in this chapter.