Friedel-3(4)-ene **54** was prepared from friedelin by the same method as discussed in experimental section of part -I in this thesis.

OXIDATION OF FRIEDEL-3(4)-ENE **54** *BY N-BROMOSUCCINIMIDE* (NBS) *IN DIMETHYL SULFOXIDE* (DMSO).

1.0 g of friedel-3(4)-ene **54** was dissolved in 10 ml of $CHCl_3$ and 100 ml of DMSO was added. Then 1.0 g of NBS was added in small lots of 0.1 g each and the mixture was kept in dark for 24 hours. It was then diluted with $CHCl_3$, taken in a separating funnel and was washed with water till there was no smell of DMSO. It was then dried over anhydrous Na_2SO_4 and the solvent was distilled off yielding a gummy solid which showed two distinct spots in tlc plates.

The gummy mass was dissolved in minimum volume of benzene and subjected to column chromatography the result of which are given in tabular form below :-

TABLE-I

Eluent	Fraction of 50 ml each.	Residue on distillation.
1. petrol	1-4	solid, (0.2 g)
2. petrol-benzene (4:1)	5-10	solid, (0.4 g)

further elution did not yield any more solid.

The fractions 1-4 were crystallised from $CHCl_3$-MeOH, *M.P.* 200-1°C; showed positive Beilstein test for halogen and gave yellow colouration with TNM. It was identified as 3α-bromo-Olean $\Delta^{13(18)}$-ene **55** from spectral analysis.

ANALYSIS REPORT.

Found :	C 73.0 ; H 9.7%
Calculated for $C_{30}H_{49}Br$:	C 73.6 ;: H 10.02%

Mass : m/e	490 (M_1^+,Br^{79}),488 (M_2^+,Br^{77}) 475, 473, 410, 408, 395, 274, 257, 218, 205, 109, 95(100). fig.1.
^1H NMR : ($CDCl_3$) (δ in ppm)	0.79,0.81,0.83,0.84,0.86, 0.94 and 1.08(bs) (6s,3H each & one 6H,8X t-Me) 1.81 (td,1H,J=3 & 13 Hz, C_9-αH) 5.16 (bs, $W_{1/2}$=8 Hz, C_3-βH). fig.2.

The fractions 5-10 were combined and crystallised from $CHCl_3$-MeOH, *M.P.*229-30^oC; did not respond to Beilstein test for halogen but gave yellow colour with TNM. It was identified as 3β-hydroxy olean $\Delta^{12(13)}$-ene **56** from spectral datas.

ANALYSIS REPORT.

Found :	C 83.9 ; H 11.2%
Calculated for $C_{30}H_{50}O$:	C 84.5 ; H 11.73%

IR (Nujol) : ν_{max}	3380 cm^{-1} (-OH) fig.3.
Mass : m/e	426 (M^+), 411, 408, 395, 393, 255, 229, 205, 173, 145, 125, 123, 95(100). fig.4.

^{1}H NMR : ($CDCl_3$)	0.79,0.81,0.82,0.87,0.94,
(δ in ppm)	0.99 and 1.06(bs)
	(6s,3H each & one 6H,8X t-Me)
	4.08 (bs,1H, C_3-βH)
	5.53 (t,1H, C_{12}-H)

fig.5.

BROMINATION OF LUPENYL ACETATE **57a** *BY BROMINE IN ACETIC ACID*

1.0 g. of lupenyl acetate **57a** was dissolved in 100 ml of acetic acid and allowed to cool at -5^oC with freezing mixture. Than 8 ml of bromine was added dropwise with constant shaking. The mixture was than poured in ice cold water, extracted with ether, washed with water repeatedly, dried with anhydrous sodium sulphate and finally the solvent ether was distilled off yielding a yellowish solid mass. It was dissolved in minimum benzene and chromatographed over silica gel column. On elution with petrol a crystalline white solid compound (0.3 g) was obtained. It was recrystallised from $CHCl_3$-MeOH, M.P.225-6^oC, identified as 3β-acetyl oleanan 19α,29,30 tribromide **59**.

BROMINATION OF LUPENYL ACETATE **57a** *WITH* NBS *IN CARBON TETRACHLORIDE.*

1.0 g of lupenyl acetate **57a**, *M.P.*212-3^oC, was dissolved in 100 ml of carbon tetrachloride and refluxed over waterbath with 1.0 g of NBS for 4 hours. It was than kept overnight and unreacted NBS was filtered, solvent was distilled off and the product obtained was chromatographed which on elution with petrol-benzene (4:1) gave white crystals, recrystallised from chloroform-methanol, M.P. 225-6^oC, gave yellow colouration with TNM and responded to Beilstein test for halogen; IR : 1725, 1255 (-OCOCH_3), 3015, 1640 and 880 cm^{-1} (C=CH_2); identified as 30-bromo lupenyl acetate **58**, *M.P.*235-6^oC ; [Lit.*M.P.* 235-6^oC] by comparison with authentic sample (prepared earlier).

ANALYSIS REPORT

Found :	C 54.02 ;	H 7.10
Calculated for $C_{32}H_{51}O_2Br_3$:-	C 54.08 ;	H 7.18

IR (Nujol) : ν_{max}	1690 and 1255 cm^{-1} ($-OCOCH_3$)
	fig.6
Mass : m/e	710 (M^+),708,706,648,646,626 568,566,633,487,466,376,362 267,231,189,175,135,95,82, 80 (100).
	fig.7
^1H NMR : ($CDCl_3$) (δ in ppm)	0.84,0.85,0.86,0.94,0.95,1.06 (6s,18H.6 X t-CH_3)
	2.05 (s,3H,$-OCOCH_3$)
	3.5-3.9 (AB_q, J=10 Hz,$-CH_2Br$)
	3.8-4.6 (AB_q,J=11.5 Hz,$-CH_2Br$)
	4.24 (d,1H, C_{19}-βH)
	4.48 (m,1H, C_3-αH)
	fig.8
^{13}C NMR :	fig.9

Betulinic acid was isolated and esterified by same method as discussed in the experimental section of part-I of this thesis.

LAH REDUCTION OF METHYL BETULINATE : PREPARATION OF LUPAN 20(29)-EN-3β,28-DIOL **60**.

3.0 g of methyl betulinate was dissolved in 400 ml dry ether and 8.0 g of LAH was added cautiously to the cold ethereal solution. The mixture was than refluxed for 6 hours over heating mentle. It was than cooled to room temperature and excess LAH was destroyed with saturated solution of sodium sulfate when a white inorganic salt coagulated. The supernatant solution was decanted and the residue was washed with fresh chloroform. The decanted and chloroform solution was washed with water, dried and the solvent was distilled off. The solid obtained (2.4 g) was crystallised from $CHCl_3$-MeOH mixture to furnish white crystals of lupan 20(29)-ene 3β,28-diol **60** (Betulin), *M.P.* 258°C, $[\alpha]_D$=+ 17°, IR : 3350, 3370 (-OH) and 890 cm^{-1} (C=CH_2),TNM test +ve; identical with authentic sample (*M.M.P.* and CO-tlc)

Found :	C 81.25% ; H 10.95%	
Calculated for $C_{30}H_{50}O_2$:	C 81.45% ; H 11.31%	

OXIDATION OF LUPAN 20(29)-EN-3β,28-DIOL BY N-BROMOSUCCINIMIDE IN DIMETHYL SULFOXIDE.

1.0 g of lupan 20(29)-en-3β,28-diol **60** was dissolved in 7-8 ml of $CHCl_3$ and 35 ml of DMSO was added. Than 1.0 g of NBS was added in small lots of 0.1 g each with constant shaking and it was kept in dark for 24 hours. The mixture was then poured in ice cold water when a solid material separated out which was extracted with excess $CHCl_3$. The $CHCl_3$ layer was washed with water repeatedly till free from DMSO, dried over anhydrous sodium sulfate and finally the solvent was distilled off to furnish a gummy mass (0.85 g). Tlc of the latter showed a single spot indicating the presence of at least one new product. The gummy mass was dissolved in minimum volume of benzene and chromatographed over silica gel column.

Elution with petrol furnished a solid mass, designated as compound E, *M.P.*232-3°*C*; identified as 3-keto-oleanan-28-19-oxo-29,30-dibromide **61**.

ANALYSIS REPORT.

Found :	C 60.0% ; H 7.4%
Calculated for $C_{30}H_{46}O_2Br_2$:	C 60.1% ; H 7.6%

IR (Nujol) : ν_{max} 1720 cm^{-1} (C=O)

fig **10**

Mass : m/e 599 (M^+),519, 517, 488, 439, 423, 407, 293, 283, 267, 189, 107, 95, 81, 55(100)

fig.**11**

^1H NMR : ($CDCl_3$) (δ in ppm)

0.93, 1.03, 1.10, 1.14 and 1.21 (5s,15H, t-CH_3)
2.68 (m,2H,-$COCH_3$)
3.69 (AB_q, J=5 Hz, -C_{28}-H_2-)
3.50-3.71 (AB_q, 10 Hz,-CH_2Br)
3.59-3.82 (AB_q, 10 Hz,-CH_2Br)
3.98 (d,J=3 Hz, -C_{19}-H)

fig.**12**

ACETYLATION OF BETULIN,60 ; PREPARATION OF BETULIN DIACETATE,62.

1.5 g of betulin, **60** was dissolved in 10 ml pyridine and 15 ml of acetic anhydride was added. The mixture was heated over water bath for 6 hours. After usual workup and chromatography, a solid material was obtained with eluent petrol-benzene mixture (4:1) which was crystallised from $CHCl_3$-MeOH to afford white crystals of betulin diacetate, *M.P.* 222-3°C, $[\alpha]_D$= +21°; IR : 1740,1250 ($-O-COCH_3$) and 1650,900 cm^{-1} ($C=CH_2$).

Found :	C	77.36%	;	H	10.06%
Calculated for $C_{34}H_{54}O_4$:	C	77.56%	;	H	10.26%

OXIDATION OF BETULIN DIACETATE 62 BY NBS IN DMSO

0.5 g of betulin diacetate **62** was dissolved in minimum $CHCl_3$ containing 25 ml of DMSO. Then 0.75 g of NBS was added in small lots and the mixture was kept in dark for 24 hours. On usual workup, the gummy product obtained was dissolved in minimum volume of benzene and chromatographed over silica gel column. The solvent used are shown in table below :-

TABLE-II.

	Eluent	Fraction of 50 ml each.	Residue on distilation.
1.	Petrol	1-4	nil
2.	petrol-benzene (4:1)	5-8	nil
3.	petrol-benzene (3:2)	9-11	nil
4.	petrol-benzene (2:3)	12-15	solid,(0.2 g)
5.	petrol-benzene (1:4)	16-18	nil
6.	benzene	19-23	solid,(0.2 g)

Further elution did not afford any more solid.

Fractions 12-15 were crystallised together from $CHCl_3$-MeOH; *M.P.* 169-70°C, identified as 30-bromo lup-20(29)-en-3β,28-diyl acetate **63.**

ANALYSIS REPORT

Found :	C 67.3 ;	H 8.90%
Calculated for $C_{34}H_{54}O_4Br$:	C 67.33 ;	H 8.91%

IR (Nujol) : ν_{max} 1730 and 1240 cm^{-1} ($-OCOCH_3$)

fig.**13**

Mass : m/e 606(M^+),604,593,592, 577,546,531,511,466, 465,451,405,267,201, 189(100)

fig.**14**

^{1}H NMR : ($CDCl_3$) (δ in ppm.)

0.83,0.85,0.98,1.05 and 1.26 (5s,15H,5 X t-CH_3)

2.03 and 2.07 (2s,6H,2 X $-COCH_3$)

3.91 (s,2H,$-CH_2OAc$)

3.84 and 4.26 (dd,2H,$-CH_2Br$)

5.03 and 5.12 (2s,2H, $C=CH_2$)

fig. **15**

Fractions 19-23 were crystallised together from $CHCl_3$-MeOH, *M.P.* 202-3°C, identified as 30-bromo lup-20(29)-en$\not$-3β,28-diol **64.**

ANALYSIS REPORT

Found :	C 68.8 ;	H 9.50%
Calculated for $C_{30}H_{50}O_2Br$:	C 68.97 ;	H 9.57%

IR (Nujol) : ν_{max}	3390 cm^{-1} (broad) (-OH)

fig.**16**

Mass : m/e	442,440,425,409,369, 207,189,135,107,91, 55(100)

fig.**17**

^{1}H NMR : ($CDCl_3$) (δ in ppm)	0.76,0.82,0.96,0.98 and 1.02 (5s,15H,5 X t-CH_3)
	3.19 (m,1H, C_3-αH)
	3.15 and 3.78 (dd, J=10 and 10 Hz,-CH_2Br)
	4.12 (bs,2H,-CH_2OH)
	4.90 and 4.95 (2s,2H,-CH_2=C)

fig.**18**

ACETYLATION OF LUPEOL : PREPARATION OF LUPENYL ACETATE **57a**.

1.0 g of lupeol **57** was dissolved in 15 ml of pyridine and 20 ml acetic anhydride was added. The mixture was heated over waterbath for 4 hours and poured in ice cold water when a white solid of lupenyl acetate **57a** separated out. It was filtered through suction, washed with water and dried in air. *M.P.* 212-13°C, [lit. *M.P.*213-14°C]

OXIDATION OF LUPENYL ACETATE **57a** *IN ACETIC ACID WITH* SeO_2 *: PREPARATION OF LUPAN 20(29)-EN-30-AL,3β-YL ACETATE* **65**

1.0 g of lupenyl acetate was dissolved in 150 ml of acetic acid and refluxed with 1.0 g of SeO_2 over heating mentle for 1 hour. Then it was poured in ice cold water when solid crystals of lupan 20(29)-en-30-al-3β-yl acetate **65** separated out. It was filtered, washed with water till neutral and dried,*M.P.* 224-5°C, [lit. *M.P.* 224-25°C] IR : 1730,1700 and 1255 cm^{-1}, gave yellow colouration with TNM.

REDUCTION OF LUPAN 20(29)-EN-30-AL-3β-YL ACETATE **65** *WITH LAH : PREPARATION OF LUPAN 20(29)-EN-3β,30-DIOL* **66**.

1.0 g of lupan 30-al- 3β-yl acetate **65** was dissolved in dry ether and 1.5 g of LAH was added. The mixture was then refluxed for 5 hours over heating mentle and allowed to cool at room temperature. After usual workup, the product was extracted with ether, washed, with water, dried and the ether was distilled off giving a white solid (0.7 g). It was crystallised from $CHCl_3$-MeOH, *M.P.* 231-2°C, produced yellow colouration with TNM; IR : 3400 and 3320 cm^{-1} (-OH) identified as lupan 20(29)-en-3β,30-diol **66**.

ACETYLATION OF LUPAN 20(29)-EN-3β,30-DIOL **66** *: ISOLATION OF LUPAN-20(29)-EN-3β,30- DIYL-ACETATE* **67**

0.6 g of lupan 20(29)-en,3β,30-diol **66** was heated over waterbath with of 10 ml pyridine and 15 ml of acetic anhydride. It was than poured in ice cold water when white crystals of lupan 20(29)-ene-3β,30-diyl acetate **67** was separated out. It was filtered, washed with water and dried in air, *M.P.* 253-4°C, IR : 1750,1740,1250 and 1230 cm^{-1}.

OXIDATION OF LUPAN-20(29)-EN-3β,30-DIYL ACETATE **67** *WITH NBS IN DMSO :-*

0.5 g of lupan-20(29)-en-3β,30-diyl actate **67** was dissolved in minimum volume of $CHCl_3$ followed by 20 ml of DMSO and than 0.75 g of NBS was added. The mixture was than kept in dark for 24 hours and than usual workup gave a gummy yellow product which was chromatographed in silica gel column.

TABLE-III

Eluent	Fraction of 50 ml each	Residue on distillation.
1. petrol	1-3	nil
2. petrol-benzene	4-6	nil

(4:1)		
3. petrol-benzene (3:2)	7-10	nil
4. Petrol-benzene (2:3)	11-13	nil
5. benzene	14-18	solid, (0.35 g)

The fractions 14-18 were crystallised from $CHCl_3$-MeOH, *M.P.* 224-5^{o}C; TNM test positive, identified as lupan 20(29)-en-30-al,3β-yl acetate **65**.

ANALYSIS REPORT.

Found :	C 78.9% ; H 10.3%
Calculated for $C_{32}H_{50}O_3$:	C 79.6 ; H 10.37

IR (Nujol) : ν_{max} 1730, 1700 and 1255 cm^{-1} (-CHO, $-COCH_3$)
fig.**19**

Mass : m/e 482 (M^+),467,422,407,379, 297,249,203,189,149,135, 121,107 and 95 (100).
fig.**20**

^1H NMR : ($CDCl_3$) (δ in ppm)
0.82, 0.83, 0.84, 0.85 0.92 and 1.01 (6s,18H, 6X t-CH_3)
2.04 (s, 3H, $-COCH_3$)
5.93 and 6.31 (2s,2H, C=CH_2)
9.51 (s,1H, -CHO at C-30).
fig.**21**

REFERENCES.

1. A.Wohl et al, Ber.Dent.Chem.Ges. 32, 51, (1919); 54, 476, (1921); 74, 1243, (1943).

2. K.Ziegler and A.Spath, Justus Leibigs.Ann.Chem., 80, 551, (1942).

3. B.W.Finucane and J.B.Thomson, Chem.Commun. 1220, (1969).

4. B.W.Finucane and J.B.Thomson, J.C.S.Perkins-I 1856, (1972).

5. S.Corsano and G.Piancatelli, Ann.Chem. (Italy), 55, 742, (1965).

6. E.J.Corey and J.J.Ursprung, J.A.C.S. 78, 5041, (1956).

7. C.Djerassi, J.Osiecki, R.Rinikar and B.Rinikar, J.A.C.S. 80, 1216, (1958).

8. R.Stevenson and Fortune Kohen, J.Org.Chem. 30, 2479, (1965).

9a. V.V.Kane and R.Stevenson, Chem.Ind. (London), 1243, (1960)
b. V.V.Kane and R. Stevenson, Tetrahedron, 15, 223, (1961).

10. M.Rubin and B.H.Armbrecht, J.A.C.S. 75, 3513, (1963).

11. B.P.Pradhan and T.Ray, Ind.J.Chem. 27B, 846, (1988).

12. S.Corsano and G.Piancatelli, Ann.Chem. (Italy), 55, 742, (1965).

13. B.W.Finucane and J.B.Thomson, Chem.Commun. 1220, (1969).

14. B.W.Finucane and J.B.Thomson, J.Chem.Soc. Perkin-I, 1856, (1972).

15. K.Chattopadhaya, D.R.Misra and H.N.Khastigir, Ind.J.Chem, 14B, 403, (1976).

16. D.R.Dalton and W.G.Jones, Chem.Commun. 2875, (1967).

17. Ruzicka and Muller, Helv.Chem.Acta. 22, 758, (1939).

18. B.P.Pradhan, M.M.Mukherjee, D.K.Chakraborty and J.N.Shoolery, Ind.J.Chem. 22B, 12, (1983).

19. D.H.R.Barton and N.J.Holeness, J.Chem.Soc. 78, (1952).

20. B.P.Pradhan, D.K.Chakraborty, R.Ghosh, S.R.Dutta and A.Roy, Ind.J.Chem. 30B, 32-37, (1991).

21. J.Fried and J.E.Herz, Chem.Abst. 52, 5491, (1958).

22. A.K.Macbeth, B.Milligon and J.S.Shannon, J.Chem.Soc. 2574, (1953).

23. A.C.Cope, M.Brown and H.H.Lee, J.A.C.S. 80, 2855, (1958).

24. I.E.Marko and A.Mekhalfia, Tetrahedron Letters, 31, 49, 7237, (1990).

25. J.Simonsen and W.C.J.Ross, The Terpenes, Vol.IV, p-331, Cambridge University Press, (1957).

26. H.Budzikiewicz, J.M. Wilson and C.Djerassi, J.Am.Chem.Soc. 85, 3688, (1963).

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