

Melting points are uncorrected. The petroleum ether used throughout the investigation had B.P. of 60-80°C. The INFRARED spectra were recorded in BECKMAN IR-20 spectrophotometer. The UV absorption spectra were taken in BECKMAN DU-2 spectrophotometer. Mass spectra were determined with an MS-9 mass spectrometer. <sup>1</sup>H NMR spectra were recorded with VARIAN A-60 or HA-100 spectrometer using deuterated chloroform solution containing tetramethylsilane as reference. Silica gel used for column chromatography was of 60-120 mesh (B.D.H. and Glaxo). TLC was done on chromatoplates prepared on glass strips with silica gel using benzene-petrol mixture as solvents and the spots were developed in an iodine chamber.

#### ISOLATION OF LUPEOL 69 FROM XANTHOXYLUM BUDRUNGA.

About five kilogram of air dried finely powdered bark of *Xanthoxylum budrunga*<sup>32</sup> was extracted with benzene in a Soxhlet extractor for 48 hours. The extract was cooled and the solvent was distilled off. The residual gummy mass was then dissolved in minimum volume of benzene, chromatographed over silica gel column and elution with petrol-benzene (4:1) mixture furnished lupeol 69 (10 gm.). Lupeol was further purified by repeated crystallisation from chloroform-methanol mixture, M.P. 215-6°C,  $[\alpha]_D = -33^\circ$ , found to be identical with authentic sample of lupeol (Co-tlc, M.M.P. and Co-IR).

#### HYDROGENATION OF LUPEOL TO LUPANOL 70.

5.0 gm. of lupeol was dissolved in 250 ml of distilled ethyl acetate and 1.6 gm. of palladised charcoal (E. Merck) was added. Then it was reduced with hydrogen at atmospheric pressure. The catalyst was then filtered off, the solvent was distilled out and the residue on crystallisation from chloroform-methanol mixture gave fine crystals of lupanol (4.5 gm.), M.P. 207-8°C,  $[\alpha]_D = -17.8^\circ$ , identical with authentic lupanol (Co-IR, M.M.P.).

DEHYDRATION OF LUPANOL TO 2,3-DEHYDRO LUPANE 71.

2.5 gm. of lupanol was dissolved in 10 ml of distilled pyridine (Py) and 5 ml of distilled phosphorus oxychloride ( $\text{POCl}_3$ ) was added. The mixture was then heated over water bath for 4 hours. It was then cooled, diluted with water cautiously to destroy excess  $\text{POCl}_3$  and extracted with ether. Then it was repeatedly washed with water till neutral, dried with anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) and finally the ether was distilled off giving a yellowish white gummy mass.

The gummy substance was then dissolved in minimum volume of benzene and chromatographed over silica gel (100 gms.) column developed with petroleum ether and eluted with solvents as shown in the table below -

TABLE-I

Eluent.	Fraction of 50 ml each.	Residue on distillation.	M.P.
petrol	1-5	oil	
petrol-benzene (4:1)	6-12	solid 1.4 gms.	181-2°C

Further elution with more polar solvents did not afford any solid material.

Fractions 6-12 were combined together. This on crystallisation with  $\text{CHCl}_3$ -MeOH afforded needle shaped crystals of lup- $\Delta^2$ -ene 71. M.P. 186-7°C,  $[\alpha]_D = +13.4^\circ$ ,  $\nu_{\text{max}}$  730 and 1640  $\text{cm}^{-1}$ , produced yellow colour with tetra nitro methane (TNM).

OXIDATION OF LUP- $\Delta^2$ -ENE 71 WITH SELENIUM DIOXIDE IN TERTIARY BUTANOL CONTAINING HYDROGEN PEROXIDE.

A solution of lup  $\Delta^2$ -ene (1.0 g) dissolved in tertiary butanol (t-BuOH) 150 ml. containing selenium dioxide ( $\text{SeO}_2$ ) 0.8 g and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) 2 ml. (30%) was refluxed over water bath. After 40 hours, black selenium metal separated out indicating the

completion of the reaction. It was cooled and poured in ice cold water when a white solid appeared which was extracted with ether and the ether layer was washed with 5%  $\text{Na}_2\text{CO}_3$  solution three times followed by water repeatedly till neutral. The ether layer was then dried over anhy.  $\text{Na}_2\text{SO}_4$  and the filtered solution on evaporation to dryness yielded a gummy residue (0.5 g).

The alkali-wash was kept aside for further treatment.

ISOLATION OF LUPAN 2,3 DIOL 72.

The neutral gummy mass (0.5 g) was dissolved in minimum volume of benzene and chromatographed over silica gel (40 g). The chromatograph was developed with petrol and eluted with solvents as in table-

TABLE-II

Eluent	Fractions of 50 ml. each.	Residue on distillation.
1. petrol	1-4	oil.
2. petrol-benzene (3:2)	5-10	oil.
3. petrol-benzene (1:4)	11-15	oil.
4. benzene-chloroform (4:1)	16-20.	solid.

Further elution with more polar solvents did not furnish any more solid material.

The fraction (16-20) were combined and crystallised from  $\text{CHCl}_3$ -MeOH,  $M.P. 245-46^\circ\text{C}$ ; its IR spectrum showed a broad peak at  $3540\text{ cm}^{-1}$  indicating the presence of hydroxy group and hence it was acetylated.

ACETYLATION OF FRACTION (16-20) TO LUPAN 2 $\beta$ ,3 $\alpha$  DIYL ACETATE 73.

The compound 72. (0.4 g) was dissolved in 4 ml. pyridine (Py.) and 4 ml. of acetic anhydride ( $\text{Ac}_2\text{O}$ ) was added. The mixture was than kept over

water bath for 4 hours and then poured in ice cold water when a white solid separated out. It was filtered through suction, washed with water and dried. The dried mass was then chromatographed over silica gel column with the following solvents as shown in the table below:-

TABLE-III.

Eluent.	Fraction of 50 ml. each.	Residue on distillation.
1. petrol	1-3	nil.
2. petrol-benzene (4:1)	4-6	nil.
3. petrol-benzene (3:2)	7-10	white solid. (0.35 g)

Further elution did not afford any more solid.

The fractions 7-10 were collected together and crystallised from  $\text{CHCl}_3$ -MeOH mixture giving colourless crystals, M.P.  $220-21^\circ\text{C}$ ,  $[\alpha]_D^{25} = +23.4^\circ$ , identified as lupan  $2\beta,3\alpha$  diyl acetate 73.

ANALYSIS REPORT

Found : C 77.13 ; H 10.01.  
 Calculated for  $\text{C}_{34}\text{H}_{56}\text{O}_4$  : C 77.27 ; H 10.61.

IR (Nujol):  $\nu_{\text{max}}$  1750, 1270 and 1250  $\text{cm}^{-1}$   
 (  $2 \times \text{CH}_3\text{-CO-O-}$  )  
 fig.1.

MS : m/e 528 ( $\text{M}^+$ , 86), 513 (30), 488 (43), 468 (78), 408 (100), 393 (88), 365 (52.5), 231 191 (86), 187 (98), 123 (94)  
 fig.2.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  
 (  $\delta$  in ppm.) 0.77 and 0.84 (dd, 6H,  $\text{CH}_3\text{-CH-CH}_3$ )

0.76, 0.91, 0.95, 0.98, 1.03 and  
 1.07 (6s, 18H, 6x t-CH<sub>3</sub>).  
 2.01 and 2.07 (2s, 6H, 2x -OCOCH<sub>3</sub>)  
 4.96 (dd, 3H, AcO-CH-CH<sub>2</sub>-)  
 5.07 (d, 2H, AcO-CH-CH-OAc)  
 fig. 3.

TREATMENT OF THE ALKALI WASH.  
 .....

The alkali wash, that remained after separation of neutral part was treated with 20% HCl till whole solution was slightly acidic. Since no solid material separated out, the solution was rejected.

ISOLATION OF BETULINIC ACID FROM BISCHOFIA JAVANICA.  
 .....

Five Kg. of air dried finely powdered bark of *Bischofia Javanica*<sup>33</sup> was extracted with benzene in a soxlet extractor and distillation of the solvent gave a gummy residue, which was taken up in ether. Then the ether solution was treated with aqueous alkali (20% NaOH) and the alkali layer was separated from ether layer. (The ether layer containing neutral compounds was rejected.) The alkali layer on acidification with dil HCl yielded solid betulinic acid 74, which was filtered through suction, washed repeatedly with water till neutral and dried properly for further work.

ESTERIFICATION OF BETULINIC ACID 74.  
 .....

About 5 gm. of betulinic acid was dissolved in ether and alkaline ethereal solution of N-nitroso N-methyl urea (8.0 gm.) was added. The ether solution was kept for one night in a freeze. It was acidified with few ml. of acetic acid to destroy excess diazomethane, washed with water till neutral and the solvent was evaporated to give crude methyl ester of betulinic acid. The crude ester was dissolved in minimum volume of benzene and chromatographed over silica gel column with eluents as shown in tabular form.

TABLE-IV.

Eluent.	Fraction on 50 ml. each.	Residue on distillation.
1. Petrol	1-3	nil
2. Petrol-benzene. (4:1)	4-7	nil
3. Petrol-benzene (3:2)	8-15	white solid. (0.4 g)

Further elution with more polar solvents did not afford any solid.

The fractions 8-15 were combined and crystallised from  $\text{CHCl}_3$ -MeOH, *M.P.* 223-4°C,  $[\alpha]_D^{20} = +5^\circ$ ; IR: 3520 (-OH), 1735, 1260 ( $-\text{COOCH}_3$ ), 1660, 870  $\text{cm}^{-1}$ . ( $=\text{CH}_2$ ), which were identical with authentic sample of methyl betulinate 75. (Co. tlc, & *M.M.P.* ).

#### HYDROGENATION OF METHYL BETULINATE 75.

3.0 g of methyl betulinate dissolved in distilled ethyl acetate was reduced with hydrogen gas in presence of palladised charcoal catalyst at atmospheric pressure. The catalyst was filtered off, solvent was removed and the residue obtained was crystallised from  $\text{CHCl}_3$ -MeOH to give fine crystals of methyl dihydro betulinate 76. *M.P.* 236-7°C, IR : 3500 (-OH), 1735, 1250 ( $-\text{COOCH}_3$ )  $\text{cm}^{-1}$ . identical with authentic sample (CO-tlc & *M.M.P.*).

#### DEHYDRATION OF METHYL DIHYDRO BETULINATE 76.

3.0 g of methyl dihydro betulinate was dehydrated with dry Pyridine (8 ml.) and distilled  $\text{POCl}_3$  (4 ml.). After usual work up, the gummy residue was chromatographed over silica gel. On elution with petrol-benzene (4:1) a solid was obtained, which was crystallised from  $\text{CHCl}_3$ -MeOH yielding white crystals of 2,3 dehydro methyl dihydro betulinate 77. *M.P.* 228-9°C, IR : 1730, 1260 ( $-\text{COOCH}_3$ ), 1640, 850 ( $-\text{CH}=\text{CH}-$ ), gave yellow colour with TNM, identical with authentic sample (Co-tlc & *m.m.p.*)

OXIDATION OF 2,3 DEHYDRO METHYL DIHYDRO BETULINATE 77 WITH  $\text{SeO}_2$  IN  
 TERTIARY BUTANOL CONTAINING  $\text{H}_2\text{O}_2$ .

1.0 g of the compound was dissolved in 150 ml. of t-BuOH and refluxed with a mixture of  $\text{SeO}_2$  (0.8 g) and  $\text{H}_2\text{O}_2$  (30%, 2 ml.) for 40 hours. After usual workup, the gummy residue obtained from the neutral ether layer was chromatographed over silica gel column. On elution with solvents of increasing polarity, a mixture of benzene- $\text{CHCl}_3$  (1:1) gave a gummy solid difficult to crystallise. The IR spectrum of the crude product indicated the presence of hydroxy function and hence it was acetylated with  $\text{Ac}_2\text{O}$ -Py. mixture. The alkali layer was acidified with 20% HCl till slightly acidic and since no solid material separated out, it was rejected.

ACETYLATION OF THE GUMMY SOLID : ISOLATION OF 2 $\beta$ ,3 $\alpha$ -DIACETOXY METHYL DIHYDRO BETULINATE 79.

The gummy solid (0.6 g) was acetylated with Py. (10 ml.) and  $\text{Ac}_2\text{O}$  (10 ml.). The solid material obtained on usual workup was chromatographed over silica gel column and on elution with benzene-petrol (4:1) mixture yielded a white solid. It was crystallised from  $\text{CHCl}_3$ -MeOH to afford white crystals identified as 2 $\beta$ ,3 $\alpha$ -diacetoxy methyl dihydro betulinate 79. M.P. 209-10 $^\circ$ C from spectral studies.

ANALYSIS REPORT.

Found :	C 72.8 ;	H 9.10.
Calculated for $\text{C}_{35}\text{H}_{56}\text{O}_6$ :	C 73.4 ;	H 9.79.

IR : (Nujol)  $\nu_{\text{max}}$  1730, 1230  $\text{cm}^{-1}$ . (-CO- $\text{CH}_3$ ).  
 1720, 1220  $\text{cm}^{-1}$ . (-CO-O- $\text{CH}_3$ ).  
 fig.4.

Mass : m/e 572 ( $\text{M}^+$ ), 513, 512, 470, 452,  
 437, 411, 393, 377, 203, 191,  
 187 (100%).

fig.5.

$^1\text{H NMR (CDCl}_3\text{):$	0.74 & 0.85 (dd, 6H, $\text{CH}_3\text{-CH-CH}_3$ )
( $\delta$ in ppm.)	0.90, 0.95, 0.96, & 1.05
	(4s, 15H, 5x t- $\text{CH}_3$ )
	2.01 & 2.06 (2s, 6H, 2x-O-CO- $\text{CH}_3$ )
	3.64 (s, 3H, -CO-O- $\text{CH}_3$ )
	4.76 (dd, - $\text{CH}_2\text{-CH-OAc}$ )
	5.06 (d, AcO- $\text{CH-CH-OAc}$ )

fig. 6.

ISOLATION OF FRIEDELIN FROM THE BARK OF QUERCUS SUBER, CORK.

5 kg. of finely powdered dry cork, the bark of Quercus suber<sup>34</sup>, was extracted with benzene in a soxlet extractor for 48 hours. After removal of the solvent, a white solid separated out. The solid was dissolved in minimum volume of benzene and chromatographed over silica gel. Elution of the column with petrol-benzene (4:1) mixture gave friedlin, which was crystallised from chlorform-methanol to give crystals of friedlin **80**, *M.P.* 262-3°C,  $[\alpha]_D = -48.7^\circ$ , IR : 1715  $\text{cm}^{-1}$ . for saturated ketone.

REDUCTION OF FRIEDELIN WITH SODIUM BOROHYDRIDE IN DIOXANE

3.0 g of friedlin was dissolved in 200 ml. of dioxane and 150 ml. of methanol was added. Then 4.0 g of  $\text{NaBH}_4$  was added to the mixture and it was kept at room temperature for 12 hours. The mixture was then diluted with water and acidified with dil HCl (1:4) till slightly acidic. The solid separated out was filtered with suction, washed with water till neutral and dried. It was then crystallised from  $\text{CHCl}_3\text{-MeOH}$  giving needle shaped crystals of friedelan  $3\beta\text{-ol}$  **81**, *M.P.* 268-9°C, IR : 3540  $\text{cm}^{-1}$ . (-OH), identified by comparison with authentic sample (Co-tlc, & *M.M.P.*).

DEHYDRATION OF FRIEDELIN  $3\beta\text{-ol}$  **81** BY PHOSPHORUS OXYCHLORIDE-PYRIDINE MIXTURE.

2.5 g of friedelan- $3\beta\text{-ol}$  was dissolved in 10 ml. of pyridine and



5 ml. of phosphorus oxychloride was added. The mixture was than heated in water bath for 4 hours. After usual workup, the gummy mass obtained was chromatographed. On elution with petrol, a white solid material (1.3 g) was obtained, which was repeatedly crystallised from petrol- $\text{CHCl}_3$  to furnish white crystals of 3(4)-dehydro friedlin 82, *M.P.* 263°C IR : 1650 and 800  $\text{cm}^{-1}$ . gave yellow colour with TNM.

Found :	C	87.60%	:	H	12.01%
Calculated for $\text{C}_{30}\text{H}_{50}$ :	C	87.73%	:	H	12.26%

OXIDATION OF 3(4)-DEHYDRO FRIEDELIN 82 WITH SELENIUM DIOXIDE IN TERTIARY BUTANOL CONTAINING HYDROGEN PEROXIDE.

A solution of friedel  $\Delta^3$ -ene (1.0 g) dissolved in t-butanol (150 ml.) containing selenium dioxide (0.8 g) and hydrogen peroxide (30%, 2 ml.) was refluxed for 40 hours. After workup, the residual gummy mass obtained from the neutral part was chromatographed. The column was eluted with solvents as shown in table-V.

The alkali wash on acidification did not afford any solid material and hence it was rejected.

TABLE-V.

Eluent.	Fraction 50 ml. each.	Residue on distillation.
1. petrol	1-8	oil
2. petrol-benzene (4:1)	9-12	solid, (0.15 g)
3. " " (3:2)	13-16	solid, (0.12 g)
4. " " (1:1)	17-20	nil
5. benzene-chloroform (4:1)	21-25	solid, (0.4 g)

Further elution did not afford any more compound.

Fractions 9-12 were collected together and crystallised from petrol-

$\text{CHCl}_3$ , *M.P.* 263-4°C., which were unreacted compound identified by comparison with authentic sample (*m.m.p.* & Co-tlc).

Fractions 13-16 on crystallisation from  $\text{CHCl}_3$ -MeOH afforded needle shaped crystals, *M.P.* 207-8°C,  $[\alpha]_D^{20} +16^\circ$ , IR : 1715  $\text{cm}^{-1}$ . identified as lupanone 83, from spectral analysis ( $^1\text{H}$  NMR & Mass) and comparison with authentic lupanone (*M.M.P.*, Co-tlc and Co-IR)

ANALYSIS REPORT.

Found : C 83.8 ; H 12.0%.  
Calculated for  $\text{C}_{30}\text{H}_{52}\text{O}$  : C 84.12; H 12.14%.  
IR (Nujol) :  $\nu_{\text{max}}$  1715  $\text{cm}^{-1}$ .  
fig.7

Mass : m/e 426 (M)<sup>+</sup>, 411, 383, 355, 206  
205, 163, 109, 107 (100)  
fig.8

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  
( $\delta$  in ppm.) 0.75 and 0.83 (dd, 6H,  $\text{CH}_3$ -CH- $\text{CH}_3$ )  
0.75, 0.98, 0.93, 1.02 and 1.07  
(5s, 18H, 6X - $\text{CH}_3$ )  
1.88 and 2.44 (2m, - $\text{CH}_2$ - $\text{CH}_2$ -C=O)  
fig.9

Fractions 21-25 were combined and than crystallised from  $\text{CHCl}_3$ -MeOH, *M.P.* 235-6°C,  $[\alpha]_D^{20} +14.1^\circ$ , IR : 3340, 3480  $\text{cm}^{-1}$ . (-OH), identified as friedelan 3 $\beta$ ,4 $\alpha$  diol 84, from  $^1\text{H}$  NMR and Mass analysis.

ANALYSIS REPORT.

Found : C 80.21; H 11.10% ;  
Calculated for  $\text{C}_{30}\text{H}_{52}\text{O}_2$  : C 81.08 ; H 11.71%  
IR (Nujol) :  $\nu_{\text{max}}$  3340 and 3480  $\text{cm}^{-1}$ . (-OH)  
fig.11.

Mass : m/e 444 (M)<sup>+</sup>, 429, 426, 411, 341,  
273, 218, 208 163 and 161.  
fig.12

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.88, 0.97, 0.99, 1.00, 1.02, 1.12  
 (δ in ppm.) 1.17 and 1.24 (8s, 24H, 8X-CH<sub>3</sub>)  
 3.56 (AB<sub>q</sub>, -CH-CH<sub>2</sub>-, J = 3 &  
 7 Hz.)

fig. 13

The compound **B4**, on acetylation with Ac<sub>2</sub>O-Py mixture furnished the corresponding mono acetate **B5**, *M.P.* 245-6<sup>0</sup>C, [α]<sub>D</sub> = +24<sup>0</sup>, IR: 3500 (-OH) 1720, 1280 cm<sup>-1</sup>. (-OCOCH<sub>3</sub>); Mass: 486 (M)<sup>+</sup>; PMR: (δ) 0.9-1.3 (8s, 24H, 8X t-CH<sub>3</sub>), 2.1 (s, 3H, -OCOCH<sub>3</sub>), 4.75 (t, 1H, J = 3 Hz.)

OXIDATION OF FRIEDELIN 3β,4α DIOL **B4** BY JONES' REAGENT.

0.2 g of friedelan 3β,4α diol **B4**, was dissolved in acetone (100 ml.) and Jones reagent was added dropwise with shaking until a faint orange colour persisted. The mixture was kept at room temperature for 1 hour, diluted with water and extracted with ether. The ether layer was washed thoroughly with water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and the ether on evaporation gave a residue, which was chromatographed. On elution with petrol-benzene (2:3) mixture, a solid mass was obtained which was crystallised from CHCl<sub>3</sub>-MeOH to give white crystals, *M.P.* 252-3<sup>0</sup>C; IR: 1715 (C=O) and 3470 cm<sup>-1</sup>. (-OH), identified as friedelan 3-oxo 4α-ol from spectral analysis.

ANALYSIS REPORT.

IR (Nujol) : ν<sub>max</sub> 3470 (-OH), 1715 cm<sup>-1</sup>. (C=O)  
 fig. 14

Mass : m/e 442 (M<sup>+</sup>), 436, 407, 365, 281,  
 267, 239, 225, 211, 146, 85.

fig. 15

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.80, 0.87, 0.95, 1.00, 1.05, 1.16, 1.17  
 (δ in ppm.) (7s, 3H each and one 6H, 24H, 8-Me)  
 2.105 (dd, J = 3 Hz. and J = 8 Hz.)  
 2.23 and 2.96 (2m)

fig. 16

DEHYDRATION OF FRIEDELAN 3-OXO 4 $\alpha$ -OL 86 BY POCl<sub>3</sub>-Py :

0.2 g of friedelan 3-oxo 4 $\alpha$ -ol 86, was dissolved in Py. (4 ml) and POCl<sub>3</sub> (1 ml) was added. The mixture was then heated over waterbath for 4 hours. After usual workup, the gummy mass was chromatographed and on elution with petrol, a solid mass was obtained which was crystallised from petrol, *M.P.* 208-9<sup>o</sup>C; UV : 220 nm. (fig. 17) for (CH<sub>2</sub>=CH-C=O), IR : 1690, 1550 and 850 cm<sup>-1</sup>. identified as friedelan 4(24)-ene 3-one 87.

ISOLATION OF FRIEDELAN 3-OXO 27  $\rightarrow$  15 $\alpha$  OLIDE (ODOLACTONE) FROM THE BARK OF GYNOCARDIA ODORATA.

About 5 kg. of dry finely powdered bark of *Gynocardia odorata*<sup>35</sup>, was extracted with benzene in a soxlet extractor for 48 hours. After the removal of solvent, the gummy mass was dissolved in minimum volume of benzene and chromatographed over silica gel. Elution of column with petrol-benzene (4:1) afforded a keto lactone, *Odolactone*<sup>35</sup> which was friedelan 3-oxo 27  $\rightarrow$  15 $\alpha$  olide, 88. It was crystallised from CHCl<sub>3</sub>-MeOH; *M.P.* >320<sup>o</sup>C,  $[\alpha]_D = -47.06^o$ . Found : C 79.0% ; H 10.13% , calculated for C<sub>30</sub>H<sub>46</sub>O<sub>3</sub> : C 79.30% ; H 10.13%.

REDUCTION OF ODOLACTONE BY NaBH<sub>4</sub> IN DIOXANE CONTAINING METHANOL.

3.0 g of odolactone was reduced with NaBH<sub>4</sub> (6 g) in dioxane 200 ml. and methanol 150 ml. After usual workup, the reduced gummy product was dissolved in minimum volume of benzene and chromatographed. On elution with petrol-benzene (1:4) gave a solid material which was crystallised from CHCl<sub>3</sub>-MeOH to give epi-odolactone (3 $\beta$ -hydroxy friedelan 27  $\rightarrow$  15 $\alpha$  olide) 89. *M.P.* >320<sup>o</sup>,  $[\alpha]_D = -2.48^o$ ,

IR (Nujol) :  $\nu_{max}$  3520 (-OH) and 1740 cm<sup>-1</sup> ( $\gamma$ -lactone)

Found : C 78.90; H 10.52 % .  
Calculated for C<sub>30</sub>H<sub>48</sub>O<sub>3</sub> : C 78.95; H 10.53 % .

Further elution with petrol-benzene (1:1) gave another solid, which was crystallised from CHCl<sub>3</sub>-MeOH to give a pure compound identified

as odollactone (friedelan 3 $\alpha$ -hydroxy 27  $\rightarrow$  15 $\alpha$  olide) **90**, *M.P.* > 320 $^{\circ}$ ,  $[\alpha]_D^{25}$  = -12.14 $^{\circ}$ ; IR : 3480 (-OH) and 1758 cm $^{-1}$  ( $\gamma$ -lactone) by comparison with authentic sample. (Co-tlc & Co-IR)

of  
 DEHYDRATION 3 $\beta$ -HYDROXY FRIEDELAN 27  $\rightarrow$  15 $\alpha$  OLIDE **89** (EPI-ODOLLACTONE)

2.0 g of epi-odollactone was dissolved in pyridine 10 ml. and 4 ml. of POCl $_3$  added. The mixture was then heated for 4 hours over waterbath and after workup the gummy mass obtained was chromatographed over silica gel column. On elution with petrol-benzene (4:1) a solid was obtained which was crystallised from CHCl $_3$ -MeOH, *M.P.* > 300 $^{\circ}$ c ; IR : 800 cm $^{-1}$ . (-CH=CH-), gave yellow colour with TNM, identified as 3(4)-dehydro-friedelan 27  $\rightarrow$  15-olide **91**, from  $^1$ H NMR and Mass spectra.

OXIDATION OF 3,4 DEHYDRO ODOLACTONE **91** WITH SELENIUM DIOXIDE IN t-BuOH CONTAINING HYDROGEN PEROXIDE.

1.0 g of 3,4 dehydro odolactone **91**, was dissolved in t-butanol and 0.8 g of SeO $_2$  added followed by H $_2$ O $_2$  (30% , 4 ml.). The mixture was refluxed for 40 hours and after workup, the gummy product obtained from the neutral ether layer was chromatographed. The column was eluted with following solvents as shown in table-VI. The alkali layer was acidified like before and since no solid material separated out it was rejected.

TABLE-VI.

Eluent	Fraction 50 ml each.	Residue on distillation.
1. petrol	1-5	oil.
2. petrol-benzene (4:1)	6-10	solid. (0.1 g)
3. petrol-benzene (1:1)	11-15	nil.
4. benzene	16-20	nil.
5. benzene-chloroform	21-28	solid. (0.45 g)

(1:1)

.....  
Further elution did not afford any more solid.

Fractions 6-10 were collected and crystallised from  $\text{CHCl}_3$ -MeOH, which was found to be unreacted compound by comparison (CO-tlc & M.M.P.) with authentic sample.

Fractions 21-28 were combined and repeatedly crystallised from ethyl-acetate-petrol, M.P.  $270-71^\circ\text{C}$ , identified as friedelan  $3\beta,4\alpha$  dihydroxy  $27 \rightarrow 15\alpha$  olide 92 from spectral studies.

ANALYSIS REPORT.  
.....

Found : C 76.01 ; H 10.24%.  
Calculated for  $\text{C}_{30}\text{H}_{48}\text{O}_4$  : C 76.27 ; H 10.16%

IR (Nujol) :  $\nu_{\text{max}}$  3500 and  $3440 \text{ cm}^{-1}$ . (-OH)  
fig. 18.

Mass : m/e 472 (M, 22%), 436, 386,  
385 (100), 123.  
fig. 19.

$^1\text{H}$  NMR : ( $\text{CDCl}_3$ ) 0.86, 0.94, 0.96, 0.99, 1.02, 1.05  
( $\delta$  in ppm.) and 1.21 (7s, 21H, 7X t- $\text{CH}_3$ )  
2.02 (t, 1H, J= 3 & 13.5 Hz.)  
3.54 (t, 1H, J= 3 HZ.  $3\alpha$ -H)  
4.34 (t, 1H, J= 3 Hz.  $15\beta$ -H)  
fig. 20.

$^{13}\text{C}$  NMR : fig. 21

REFERENCES.  
.....

1. Paul Seguin, Compt. Rend. 216, 667-8, (1943).
2. W.S.Curtis and T.H.Roy, J.Org.Chem. 22, 745, (1957).
3. G.B.Payne and Curtis W. Smith. J.Org.Chem. 22, 1680-2, (1957).
4. N.Sonoda and S.Tsutsumi, Bull.Chem.Soc. 32, 505, (1959).
5. F.J.Hughes and D.S.Martin Jr. J.Phy.Chem. 59, 410, (1955).
6. E. Caspi and S.N.Balasubramanyam, Tett. Letts. 745, (1963).
7. E.Caspi, Y.Shimizu and S.Balasubramanyam. Tetrahedron, 1271, (1964).
8. H.M.Hellman and R.A.Jerussi, Tetrahedron, 20, 741, (1964).
9. E.J.Corey, I.Ageta and A.G.Hortman, J.Org.Chem. 30, 1698, (1965).
10. I.Kitagawa et al, Tetrahedron Letts. 509, (1968).
11. I.Kitagawa, K.Kitazawa and I.Yosioka, Tett. Letts. 2643, (1968).
12. I.Kitagawa, K.Kitazawa and I.Yosioka, Tetrahedron, 28, 907, (1972).
13. O.Jeger, R.Borth and L.Ruzicka, Helv.Chem.Acta. 29, 1999, (1946).
14. J.Simonsen and W.C.J.Ross, The Terpenes, Vol.V, (Cambridge Univ. press, Cambridge.) 127, (1957).
15. P.L.Mazumder and M.Chakraborty, Tetrahedron, 35, 2397, (1979).
16. P.L.Mazumder and A.Bagchi, Tetrahedron, 39, 4, 649 (1983).
17. B.P.Pradhan and S.R.Dutta, Ind. J. Chem. 21B, 575, (1982).

18. B.P.Pradhan and S.R.Dutta, Ind. J. Chem. 22B, 680, (1983).
19. A.K.Ganguly and T.R.Govindacharia, Tetrahedron, 22, 1513, (1966).
20. S.Kundu, A.Chatterjee and A.S.Rao, Chem. Ber. 101, 3255, (1968).
21. J.Simonsen and W.C.J. Ross, The Terpenes, Vol.IV. (Cambridge Univ. press, Cambridge.) 336, (1957).
22. V.Anjaneyulu and G.Sambasiva Rao, Ind. J. Chem. 23B, 663, (1984).
23. B.P.Pradhan and S.R.Dutta, Ind. J. Chem. 23B, 565, (1984).
24. S.K.Talapatra, M.Bhattacharjee and B.Talapatra. Ind.J.Chem. 11, 977, (1973).
25. B.P.Pradhan, M.M.Mukherjee, D.K.Chakraborty and J.N.Shoolery. Tetrahedron, 39, 2619, (1983).
26. S.Chakraborty, Ph.D.thesis, North Bengal University Library, Raja Rammohanpur, Darjeeling.
27. B.P.Pradhan, S.Chakraborty and P.Weyerstahl, Ind.J.Chem. 26B, 405, 1987.
28. H.Kojima and H.Ogura, Phytochemistry, 6, 1703, (1989).
29. A.S.R.Anjaneyulu and M.N.Rao, Phytochemistry, 19, 1163, (1980).
30. H.Budzikiewicz, J.M.Wilson and C.Djerassi, J.A.C.S. 85, 3688, (1963).
31. P.Sengupta, B.Roy and S.Chakraborty, Ind.J.Chem. 11, 1249, (1973).



32. Dieterle, Arch. Pharm. 257, (1919); 260 (1921).
33. S.N.Bose and H.N.Khastgir, J.Ind.Chem.Soc. 46, 757, (1969).
34. E.J.Corey and J.J.Ursprung, J.A.C.S. 78, 5042, (1956).
- 35a.. B.P.Pradhan, A.Hassan and J.N.Shoolery, Tett.Letts. 25, 865, (1984).
- 35b. B.P.Pradhan, A.Hassan and J.N.Shoolery, Ind. J.Chem. 29B, 797, (1990).
36. D.P.Dantanarayana, N.S.Kumar, M.U.S.Sultanbawa and s.Balasubramanium, J.Chem.Soc.Perkins Trans-I, 2717, (1981).
37. W.Ammann, R.Richarz, T.Wirthlin and D.Wendish, Org.Mag.Chem. 20, 4, (1982).
38. "Steroid Reaction Mechanisms" by D.N.Kirk and M.P.Hartshorn page - 355, Elsevier Publishing Company, London, 1968.
39. The Chemistry of Natural Products - K.W.Bentely, Editor ; Vol.III, The Higher Terpenoids by P.de.Mayo, Interscience Publishers, INC, New York, 1959.