

CHAPTER - IIIEXPERIMENTAL

Melting points are uncorrected. The petroleum used throughout the investigation had b.p. 60-80°. All optical rotations were determined in chloroform solution unless stated otherwise. NMR spectra were determined on Varian A-60, HA-100 and CFT-20 spectrophotometer using chloroform-d solution containing tetramethyl silane as reference. The IR spectra were recorded ^{in nujol} on Pye Unicam-SP-300S and Beckmann IR-20 spectrophotometers. UV absorption spectra were taken in Shimad-Zu UV-240 and UV Beckmann DU-2 spectrophotometers in 95% ethanol solution unless stated otherwise. TLC was done on chromatoplate of silica gel G (E. Merck) and the spots were developed in iodine vapour chamber. The mass spectra were determined with Jeol JMS-D-300 mass spectrophotometer, using direct sample introduction into the ion source. GLC spectra were taken in Chemito 3800 spectrophotometer using cholestane as internal reference.

Extraction of Xanthoxylum Budrunca : Isolation of Lupeol 12 :

Dried and powdered trunk bark of Xanthoxylum budrunca (2 kg) was extracted with benzene in a Soxhlet apparatus for 20 hours. Benzene was distilled off and the gummy residue (10 gm) was taken up in ether (1.5 litre). The ether solution was washed with 10% aqueous sodium hydroxide solution (3 x 300 ml). The aqueous alkaline layer was thoroughly shaken with ether to remove

any neutral material that might be present. The ether portion was washed with water till neutral and then dried (Na_2SO_4). Ether was removed when a gummy residue (3 gm) of lupeol 12 was obtained. This residue dissolved in benzene (30 ml) was placed over a column of silica gel (100 gm) developed with petroleum and was eluted with following solvents (Table - III).

Table - III

Eluent	Fraction 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether : Benzene (4:1)	5-8	Nil
Petroleum ether: Benzene (3:2)	9-12	Solid m.p. 212°

Further elution with more polar solvent was not continued.

Fractions 9-12 (2 gm) were combined and crystallised from a mixture of chloroform and methanol. The compound 12 m.p. 215° , $[\alpha]_D + 33^\circ$ obtained was the same as the authentic sample of lupeol through m.m.p. and CO-TLC.

Hydrogenation of Lupeol 12 : Preparation of Lupanol 13 :

Lupeol (5 gm) dissolved in a mixture of ethyl acetate and acetic acid (80 ml each) was shaken in an atmosphere of hydrogen in presence of PtO_2 catalyst (0.2 gm) for three hours

until absorption of hydrogen ceased. Ethyl acetate was removed by distillation and the solution was diluted with water whereby a white solid (4.5 gm) separated out which was collected by filtration. Crystallisation from a mixture of chloroform and methanol furnished colourless plates of 13 m.p. 204° , $[\alpha]_D - 15^{\circ}$. This compound 13 was found to be identical with an authentic sample of lupanol (m.m.p. and IR).

Jones Oxidation of Lupanol 13 : Preparation of Lupanone 14 :

To a solution of Lupanol (5 gm) in pure acetone (500 ml) was added Jones' reagent 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 (Na_2SO_4) and the ether evaporated. The residue (3.5 gm) dissolved in benzene was chromatographed over a column of silica gel (100 gm). The chromatogram was developed with petroleum and then eluted with the following solvents (Table - IV).

Table - IV

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether: Benzene (4:1)	5-8	Solid m.p. $208-10^{\circ}$

Further elution with more polar solvent did not afford any material.

Fractions 5-8 (3.5 gm) were combined and crystallised from a mixture of chloroform and methanol. The crystallisation furnished colourless needles of 14 m.p. 208° , $[\alpha]_D + 15^{\circ}$.

Found : C 84.11 H 11.82%

Calculated for : C 84.52 H 11.74%
 $C_{30}H_{50}O$

IR (Nujol) : 1710 cm^{-1} (CO) (Fig. 1)

Hydrazone of Lupanone 14 : Preparation of Lupanone Hydrazone 15 :

To the Lupanone 14 (1 gm) in anhydrous diethylene glycol (50 ml) hydrazine hydrate (10 ml) was added and refluxed for 3 hours. Then the reaction mixture was cooled and poured into water. Solid precipitate was obtained and washed with water thoroughly. Extracted with ether. The solid colourless compound 15 m.p. 340° was found.

Found : C 81.56 H 11.79%

Calculated for : C 81.82 H 11.82%
 $C_{30}H_{52}N_2$

IR (Nujol) : 3380, 3240 (NH),
 1640 cm^{-1} (C = N) (Fig. 2)

Acetylation of Lupanone hydrazone 15 : Preparation of N-acetyl derivative of Lupanone hydrazone 16:

The Lupanone hydrazone 15 (500 mg) was acetylated with acetic anhydride (15 ml) and pyridine (15 ml). The reaction mixture was kept on water bath for 7 hours. The solid obtained by usual work up was dissolved in benzene (20 ml) and chromatographed on a column of silica gel (20 gm) and eluted with the following solvents (Table - V).

Table - V

Eluent	Fraction 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether: Benzene (2:1)	5-8	Solid m.p. 146°

Further elution with more polar solvents did not give any material.

Fractions 5-8 (300 mg) were combined and crystallised from a mixture of chloroform and methanol. Crystallisation furnished colourless needles of 16 m.p. 148°.

Found	:	C	79.51	H	11.23%
Calculated for	:	C	79.67	H	11.21%
$C_{32}H_{54}N_2O$					

IR (Nujol) : 3310, 3190 (NH), 1660 cm^{-1} (CONH)

(Fig. 3)

Lead (IV) acetate oxidation of Lupanone hydrazone 15 and subsequent hydrolysis :

The Lupanone hydrazone 15 (1 gm) in dichloromethane (100 ml) was treated at 20°C with lead (IV) acetate (2.2 gm). There was immediate precipitation of lead diacetate and evolution of nitrogen. When nitrogen evolution was complete, the mixture was filtered. Ethane diol (20 ml) was added to neutralise excess $\text{Pb}(\text{OAc})_4$ and then the mixture was poured into water. The organic layer was separated and the aqueous layer was extracted with ether (3 x 50 ml). The combined solution was washed with aqueous sodium bicarbonate (2 x 50 ml) until neutral and water (2 x 50 ml), dried (Na_2SO_4) and evaporated. The solid compound obtained was dissolved in benzene (20 ml). 5% methanolic potassium hydroxide (20 ml) was added to it and refluxed for two hours. The mixture was poured into water and the product was extracted with ether in the usual way. The crude product in benzene was chromatographed on silica gel column. Chromatogram was eluted with the following solvents (Table - VI).

Table - VI

Eluent	Fraction 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether	5-8	Solid m.p. 190°
Petroleum ether: Benzene (9:1)	9-12	Solid m.p. 154-5°
Petroleum ether: Benzene (3:2)	13-16	Solid m.p. 195°

Further elution with more polar solvent did not afford any material.

Fractions 5-8 (250 mg) were combined and rechromatographed on a silver nitrate (15%) impregnated silica gel column and eluted with petroleum ether. The compound isolated in petroleum ether was crystallised from a mixture of chloroform and methanol and furnished the compound 17 m.p. 198°, $[\alpha]_D - 19.7^\circ$, yield 25%.

Found : C 87.69 H 11.99%

Calculated for : C 87.81 H 12.2%
C₃₀H₅₀

Mass : M⁺ 410, 395, 367, 327, 189, 122 m/z

(Fig. 4)

G.L.C. : Single peak

(Fig. 5)

¹H NMR (100 Mc) : δ 0.71 - 1.17 (6 methyls), δ 1.73,

δ 1.65 ($\text{C} = \underset{\text{CH}_3}{\text{C}} - \text{CH}_3$) (Fig. 6)

Fractions 9-12 (250 mg) were combined and crystallisation from a mixture of chloroform and methanol furnished colourless compound 19b m.p. 154-57°, yield 25%.

Found : C 84.1 H 12.01%

Calculated for : C 84.12 H 12.15%
 $C_{30}H_{52}O$

IR (Nujol) : 3360 cm^{-1} (OH) (Fig. 10)

Fractions 13-16 (300 mg) were combined and crystallised from chloroform and methanol to furnish colourless compound 19a m.p. 196°, $[\alpha]_D - 16^\circ$. This compound was found to be identical with an authentic sample of lupanol (m.m.p. and IR).

Dehydration of lupanol 13 by phosphorus oxy-chloride ($POCl_3$):

The compound lupanol 13 (500 mg) was dissolved in pyridine (10 ml). Freshly distilled $POCl_3$ (2 ml) was added on it slowly and heated gently on the steam bath for 2 hours and then refluxed for 5 min. The reaction mixture was well cooled and poured into crushed ice. The precipitate was filtered and washed with water, dried and dissolved in minimum amount of benzene (10 ml) and chromatographed on silica gel (15 g) and eluted with the following solvents (Table - VII).

Table - VII

Eluent	Fractions of 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether	5-8	Solid m.p. 188°

Further elution with more polar solvent did not afford any materials.

Fractions 5-8 (300 mg) were combined and crystallisation from a mixture of chloroform and methanol furnished the colourless compound lup-2-ene 27 m.p. 188°, $[\alpha]_D + 13.6^\circ$

Found	:	C	87.73	H	12.01%
Calculated for $C_{30}H_{50}$:	C	87.80	H	12.20%
Mass	:	M^+ 410, 395 ($M^+ - 15$), 367, 328 m/z (Fig. 7)			
IR (Nujol)	:	1620, 740 cm^{-1} (cis disubstituted double bond) (Fig. 8)			
G.L.C.	:	Single peak			(Fig. 9)

Dehydration of lupanol 13 by phosphorus pentachloride :

A mixture of lupanol (300 mg), PCl_5 (600 mg) in dry light petroleum (100 ml) was stirred (45 min, N_2) at 0°. The product obtained (250 mg) after usual work up²⁰ showed on TLC

(AgNO₃ - SiO₂ gel; solvent : light petroleum) two spots (one is minor). This mixture was subjected to AgNO₃ impregnated (15%) silica gel chromatography and the single compound 17 (150 gm) was isolated by petroleum ether which was identical with the olefin obtained from Pb(OAc)₄ reaction, m.p. 197°, [α]_D - 19.7°.

Found : C 87.74 H 12.21%

Calculated for C₃₀H₅₀ : C 87.80 H 12.2%

IR (Nujol) : No peak in the region 690-90 cm⁻¹
(tetra substituted alkene)

NMR (100 MHz) : δ .71 - 1.17 (6 saturated methyls),
1.73, 1.65 (CH₃ - C = C,
|
CH₃)
2 vinyl methyls)

Meerwein-Ponndorf reaction on Lupanone 14 :

A mixture of lupanone 14 (1 gm), Al-isopropoxide (1.5 gm) in dry isopropanol (25 ml) was distilled slowly with the addition of isopropanol to maintain constant volume. After 5 hours the distillate no longer contained acetone and the solution was concentrated to a small volume. The reaction mixture was diluted with water followed by 10% H₂SO₄ (20 ml) and the extracted with chloroform. The product obtained after removal of chloroform was dissolved in benzene and chromatographed on a column of silica gel (20 gm). The compound 19b (700 mg) obtained with the

eluent (Petroleum ether : Benzene :: 9:1) was crystallised from a mixture of chloroform and methanol and ^{shown to be} ~~showed~~ identical with the compound 19b (obtained from $\text{Pb}(\text{OAc})_4$ reaction) m.p. 156° , IR (Nujol) : 3362 cm^{-1} (OH).

Acetylation of the compound 19b: Preparation of Epi-Lupanol acetate 18b:

The compound 19b (300 mg) was acetylated with acetic anhydride (10 ml) and pyridine (10 ml). The reaction mixture was kept over night at room temperature. The solid obtained by usual work up was dissolved in benzene (10 ml) and chromatographed in a column of silica gel (20 gm) and eluted with the following solvents (Table - VIII).

Table - VIII

Eluent	Fractions of 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether : Benzene (4:1)	5-8	Solid m.p. 145°

Further elution with more polar solvents did not give any materials.

Fractions 5-8 (150 mg) were combined and crystallised from a mixture of chloroform and methanol. The compound 18b was obtained, m.p. 146° , $[\alpha]_D - 45^\circ$.

Found : C 81.52 H 11.5%
 Calculated for : C 81.7 H 11.49%
 $C_{32}H_{54}O_2$

IR (Nujol) : 1730, 1250 cm^{-1} (acetate) (Fig. 11)

Mercuric Oxide (HgO) oxidation of lupanone hydrazone 15

The lupanone hydrazone 15 (500 mg) in diglyme (25 ml) was treated at 100°C with mercuric oxide (HgO) and refluxed for 2 hours. Then the mixture was cooled, filtered and poured into water. The mixture was taken in ether and washed thoroughly. Ether was removed and the gummy residue was dissolved in benzene, (15 ml) chromatographed and eluted with the following solvents (Table - IX).

Table - IX

Eluent	Fractions of 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether	5-8	Solid m.p. 182°

Further elution with more polar solvent did not afford any materials.

Fractions 5-8 (300 mg) were combined and ^{on} crystallisation with a mixture of chloroform and methanol furnished the colourless compound, 27, m.p. 188°, $[\alpha]_D + 13.6^\circ$.

Mass : M^+ 410, 395 (M^+ - 15), 367, 189 m/z .
 IR (Nujol) : 740 cm^{-1} (disubstituted double bond).

Extraction of ground Cork : Isolation of friedelin 20 :

Dried and powdered ground cork (2 kg) was extracted with petroleum ether in a Soxhlet apparatus for 20 hours. Petroleum ether was distilled off and the gummy residue (10 gm) was taken up in minimum amount of benzene and was placed over a dry column of silica gel (200 gm) developed with petroleum and was eluted with the following solvents (Table - X).

Table - X

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether	5-10	Solid m.p. 267°

Further elution with more polar solvent was not continued.

Fractions 5-10 (7 gm) were combined and crystallization from chloroform-methanol afforded pure friedelin 20, m.p. 269°.

$[\alpha]_D - 45^\circ$ which was identical with an authentic sample of friedelin.

Found : C 84.35 H 11.91%
 Calculated for : C 84.44 H 11.81%
 $C_{30}H_{50}O$

IR (Nujol) : 1720 (C = O) cm^{-1} (Fig. 12)

Preparation of friedelin hydrazone 21:

Friedelin 20 (1.5 gm) in anhydrous diethylene glycol (60 ml) was refluxed with hydrazine hydrate (12 ml) for 2 hours. Then the mixture was cooled and poured into ice-cold water. The solid white residue was filtered off, washed with water and dried (Na_2SO_4). The compound friedelin hydrazone, 21 m.p. 310° was characterized as the product.

Found : C 81.65 H 11.98%
 Calculated for : C 81.78 H 11.95%
 $C_{30}H_{52}N_2$

IR (Nujol) : 3340, 1650 cm^{-1} (-N-H stretching and bending vibration) (Fig. 13)

Acetylation of friedelin hydrazone 21 : Preparation ^{of} N-acetyl derivative of friedelin hydrazone 22 :

The compound 21 (300 mg) was acetylated with acetic anhydride and pyridine (10 ml each). The reaction mixture was kept on water bath for 6 hours. Then the mixture was cooled and poured into the crushed ice. The solid obtained by usual work up was dissolved in benzene (10 ml) and chromatographed in a

column of silica gel (20 gm) and eluted with the following solvents (Table - XI).

Table - XI

Eluent	Fractions of 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether : Benzene (4:1)	5-8	Solid m.p. 242°

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

Fractions 5-8 (140 mg) were combined and crystallization from chloroform-methanol afforded the compound 22, m.p. 245°.

Found	:	C	79.21%	H	11.48%
Calculated for	:	C	79.32%	H	11.32%
$C_{32}H_{54}N_2O$:				
IR (Nujol)	:	3380 cm^{-1} (N-H), 1640 cm^{-1} ($\begin{array}{c} -C - NH \\ \\ O \end{array}$)			

(Fig. 14)

Lead (IV) acetate oxidation of friedelin hydrazone 21 and subsequent hydrolysis :

The friedelin hydrazone 21 (1 gm) in dichloromethane (100 ml) was treated at 20°C with lead (IV) acetate (2 gm). There was immediate precipitation of lead diacetate and evolution of nitrogen. When nitrogen evolution was complete, the mixture was filtered. Ethane diol (15 ml) was added to neutralise excess $Pb(OAc)_4$ and the mixture was poured into water. Then the work up was same as described for the case of Lupanone hydrazone. The chromatography (silica gel, 20 g) with the following solvents are given below (Table - XII).

Table - XII

Eluent	Fractions of 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether	5-10	Solid, m.p. 265°
Petroleum ether: Benzene (4:1)	11-14	Nil
Petroleum ether: Benzene (2:3)	15-18	Solid, m.p. 302°

Further elution with more polar solvent did not afford any materials.

Fractions 5-10 (300 mg) were combined and crystallisation from chloroform-methanol afforded the white blades of compound 23, m.p. 268° , $[\alpha]_D + 49^{\circ}$, yield 30%.

Found	:	C	87.48%	H	12.52%
Calculated for	:	C	87.59%	H	12.41%
$C_{30}H_{50}$					
Mass	:	M^+	410, 395, 361, 219, 190	m/z	(Fig.15)
IR (Nujol)	:		820 cm^{-1}		(Tri substituted double bond)
G.L.C.	:		Single peak.		

Fractions 15-18 (450 mg) were combined and crystallisation from chloroform-methanol afforded the crystalline compound 25, m.p. 302° , $[\alpha]_D + 16.2^{\circ}$, yield 45%.

Found	:	C	83.92%	H	12.56%
Calculated for	:	C	84.01%	H	12.27%
$C_{30}H_{52}O$					
Mass	:	M^+	428, 410 ($M^+ - H_2O$), 395, 219, 190	m/z	
IR (Nujol)	:		3400 cm^{-1}		(-OH).

Melting point of the acetylated product 24 of compound 25 was 315° . IR (Nujol) : 1740, 1260 cm^{-1} (acetate). The compound 25 was found to be friedelan-3 α -ol when compared with the authentic sample (m.m.p. and CO-TLC).

Mercuric Oxide (HgO) oxidation of friedelin hydrazone 21:

The friedelin hydrazone 21 (500 mg) in diglyme (25 ml) was treated at 100°C with mercuric oxide (HgO) and refluxed for 2 hours. Then the mixture was cooled, filtered and poured into water. The mixture was taken in ether and washed thoroughly. Ether was removed and the gummy residue was dissolved in benzene, (15 ml) chromatographed (silica gel, 14 g) and eluted with the following solvents (Table - XIII).

Table - XIII

Eluent	Fractions of 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether	5-8	Solid, m.p. 256°

Further elution with more polar solvent did not afford any materials.

Fractions 5-8 (250 mg) were combined and crystallisation from chloroform-methanol furnished the white compound 28, m.p. 254°
 $[\alpha]_D + 46^\circ$.

Found	:	C	87.51%	H	12.49%
Calculated for $C_{30}H_{50}$:	C	87.80%	H	12.20%
G.L.C.	:	Single peak			(Fig. 19)
Mass	:	M^+ 410, 395 (M^+-15), 342 ($M-68$) m/z			(Fig. 20)

Selenium dioxide (SeO_2) oxidation of Δ^3 friedelene 23 :

Preparation of friedel-3-ene-23 al 26 :

The Δ^3 -friedelene 23 (0.5 gm) was dissolved in 1 litre acetic acid. 0.8 gm selenium dioxide was added and refluxed for 4 hours. The hot solution was filtered, cooled and poured into water. Then the mixture was extracted with ether, washed with water until neutral and dried (Na_2SO_4). Then the residue was dissolved in minimum amount of benzene and chromatographed on a column of silica gel (12 gm) and eluted with the following solvents (Table XIV).

Table - XIV

Eluent	Fractions of 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether: Benzene (4:1)	5-8	Solid, m.p. 264° (800 mg)

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

Fractions 5-8 (800 mg) were combined and crystallization with chloroform-methanol furnished the crystalline compound 26, m.p. 265°.

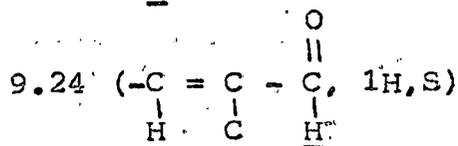
Found : C 84.73% H 11.51%

Calculated for : C 84.78% H 11.43%
 $C_{30}H_{48}O$

UV (ethanol) : 227 m μ , 330 m μ
 (α, β unsaturated aldehyde) (Fig. 16)

IR (Nujol) : 2720, 1680, 1640, 1420, 830 cm⁻¹
 (signals for α, β unsaturated aldehyde) (Fig. 17)

NMR (200 MHz) : δ .74 - 1.14 (7 methyls),
 6.52 (-C = C - CHO, 1H, m)



(Fig. 18)

Bamford Stevens reaction on lupanone tosyl hydrazone 29 of lupanone 14 in protic condition:

To lupanone (2 gm) dissolved in 50 ml ethanol 4 gm of p-toluene sulphonyl hydrazide (freshly prepared) was added and refluxed for 3 hrs. Then the mixture was kept overnight and the solid hydrazone was filtered off and washed with methanol and dried. Lupanone tosylhydrazone 29 thus obtained (1 gm) was taken in a mixture of sodium in ethylene glycol (1 gm Na in 10 ml ethylene glycol) and refluxed gently for 3 hrs.²¹ Then the mixture was poured in water, filtered and dried. The compound obtained was chromatographed on silica gel (20 gm) column. The petroleum ether fractions were combined (0.52 gm) and crystallisation from a mixture of chloroform and methanol furnished the compound 17 (500 mg), m.p. 195°. Mixed m.p. with the compound 17 which was found from $\text{Pb}(\text{OAc})_4$ reaction on lupanone hydrazone 15, was 198°.

Bamford Stevens reaction on lupanone tosylhydrazone 29 of lupanone 14 in aprotic condition:

The compound lupanone tosylhydrazone 29 (500 mg) which was obtained by the same way described previously, was taken in a mixture of sodium methoxide (prepared freshly from sodium (1 gm) and dry methanol (10 gm) and then excess methanol removed by distillation) in diglyme (10 ml) and refluxed for 3 hrs.²¹ Then the mixture was poured into water, filtered and dried. After chromatography of the product on silica gel (15 gm), the compound 27 (320 mg) m.p. 187° was obtained in petroleum ether fractions. Mixed m.p. with lup-2-ene 27 obtained by two ways (1) POCl_3

product of lupanol 13 and (2) HgO product of lupanone hydrazone 15 found identical (m.p. 188°).

Bamford Stevens reaction on friedelin tosylhydrazone 30 of friedelin 20 in protic condition:

Friedelin tosylhydrazone 30 (500 mg) which was prepared by the reaction of friedelin 20 with p-toluene sulphonyl hydrazide described previously for the case of lupanone, was dissolved in sodium (1 gm) in ethylene glycol (10 ml) and refluxed for 3 hours.²¹ Work up as usual was described previously. Then the residue was dissolved in minimum amount of benzene (15 ml) and chromatographed on a column of silica gel (20 gm) furnished the crystals (200 mg) of compound 23, m.p. 265° . Mixed m.p. with Δ^3 friedelene showed that the compound 23 was identical with Δ^3 friedelene 23 (obtained from $\text{Pb}(\text{OAc})_4$ oxidation of friedelin 20).

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