

## CHAPTER - III

### EXPERIMENTAL

Melting points are uncorrected. Petroleum ether used throughout the investigation had b.p. in the range of 60-80°. The infrared spectra were recorded in Beckmann IR-20 Spectrophotometer. Mass spectra were recorded by electron impact method. Silica gel used for column chromatography was of 60-120 mesh (BDH). TLC were performed in chromatoplates prepared on glass strips with silica gel G (BDH).

#### Isolation of Friedelin from bark Cork.

3 kgs of finely powdered cork was extracted with petroleum ether in a Soxhlet apparatus for 18 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 column developed with petroleum ether. Elution of the column with petroleum ether gave shining crystals of friedelin<sup>53</sup>, m.p. 262-3°,  $[\alpha]_D -48.7^\circ$ .

#### Autoxidation of friedelin:

Friedelin (2 gm) isolated from bark cork suspended in Potassium tertiary butoxide (prepared from 6 gm of potassium and 60 ml of tertiary butanol) was shaken in a stream of oxygen for three hours. The reaction mixture was then diluted with water and then 6N hydrochloric acid was added till the solution was acidic. It was then extracted with chloroform (150 ml) and the combined extract was dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent was removed

under reduced pressure. A yellowish gummy residue (1.9 gm) was obtained. It gave positive ferric chloride test for phenol. TLC of the crude product showed more than three spots on chromatoplate (using benzene as eluent), indicating the presence of at least three compounds. The product could not be purified by crystallisation, hence was subjected to chromatographic separation on silica gel column developed with petroleum ether. The following solvents were used for elution.

Table 1

Chromatography of the above gummy material (19 gm)

Eluent	Fractions 100 ml each	Residue on evaporation	Melting point °C
Petroleum ether	1-10	Solid (600 mg)	210-214°
Petroleum ether : benzene (4:1)	11-13	Nil	-
Petroleum ether : benzene (3:2)	14-17	Solid (50 mg)	261-64°
Petroleum ether : benzene (2:3)	18-20	Nil	-
Petroleum ether : benzene (1:4)	21-23	Nil	-
Benzene	22-23	Oil (100 mg)	-
Benzene: Ether (9:1)	24-27	Oil incorporated with solid (750 mg)	-
Benzene : Ether (4:1)	28-30	White solid (250 mg)	237-40°
Benzene : Ether (3:2)	31-33	Gummy solid	248-51°
Further elution with more polar solvents did not afford any solid material.			

Examination of fractions 1-10 (Table 1): Isolation of 3-nor-

$\Delta^{2(4)}$ -tertiary butyl friedelinate (A) 46

The solid fractions 1-10 (Table 1) were combined (600 mg), m.p. 210-14<sup>o</sup>, which after crystallisation from a mixture of chloroform and methanol afforded needle shaped crystals m.p. 218<sup>o</sup>,  $[\alpha]_D^{30}$  -8.4<sup>o</sup>. It showed a single round spot on a chromatoplate and responded TNM test.

Analysis report:

	%C	%H
Found	82.21	11.07
Calculated for C <sub>34</sub> H <sub>56</sub> O <sub>2</sub>	82.25	11.08

IR :  $\int_{\text{max}}^{\text{Nujol}}$  1705, 1635, 1250, 870, 790 cm<sup>-1</sup>.

(Fig. 1)

UV :  $\lambda_{\text{max}}$  (spectroscopic methanol) 235 nm

(Fig. 2)

Mass : m/z 496 (M<sup>+</sup>), 440 (M<sup>+</sup> - CH<sub>3</sub>-C(CH<sub>3</sub>)=CH<sub>2</sub>)  
425 (440 - CH<sub>3</sub>), 219, 205.

(Fig. 4)

<sup>1</sup>H NMR ( $\delta_{\text{CDCl}_3}$ ) : 0.805, 0.9375, 0.940, 0.965, 0.990,  
1.015, 1.18 (7s, 21H, 7 t-CH<sub>3</sub>),  
1.4825 (s, 9H, O-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>3</sub>)  
1.94 (s, 3H, =C-CH<sub>3</sub>)

(Fig. 3)

$^{13}\text{C}$  NMR : 166.73, 163.64, 127.92, 79.55, 50.29, 40.45,  
 38.22, 36.48, 29.99, 28.15 ( $10_{\underline{s}}$ ,  $10 > \overset{|}{\text{C}}-$ ),  
 39.31, 38.22, 36.49, 35.07, 35.98, 35.30, 32.77,  
 32.29, 30.2, 18.6 ( $10_{\underline{t}}$ ,  $10 - \overset{|}{\text{C}}\text{H}_2$ ), 35.05, 32.19,  
 31.79, 28.36, 28.36, 28.36, 19.86, 18.61, 18.2,  
 17.88, 11.32 ( $11_{\underline{q}}$ ,  $11 - \overset{|}{\text{C}}\text{H}_3$ ), 62.44, 53.66,  
 42.87 ( $3_{\underline{d}}$ ,  $3 - \overset{|}{\text{C}}-\text{H}$ )ppm

(Fig. 5)

Examination of fractions 14-17 (Table 1) : Isolation of diosphenol form of friedelan-dione.

The fractions 14-17 (Table 1) were combined (50 mg) and crystallised from a mixture of chloroform and methanol which afforded crystals (30 mg), m.p.  $265-6^{\circ}$ ,  $[\alpha]_{\text{D}} 18.6^{\circ}$ , TLC of the compound showed double spots on a chromatoplate. Ethanolic solution of it gave green colouration with neutral ferric chloride solution. It gave yellow colouration with TNM.

Analysis report:

	%C	%H
Found	81.78	10.85
Calculated for $\text{C}_{30}\text{H}_{48}\text{O}_2$	81.81	10.9

IR :  $\begin{cases} \text{Nujol} \\ \text{max} \end{cases}$  3600, 3200 (-OH), 1685 (conjugated - C = O),  
 1665, 1610, 840 (-C = C-)  $\text{cm}^{-1}$

(Fig. 6)

UV (methanol) :  $\lambda_{\text{max}}$  269 nm,  $\log \epsilon$  4.07

(Fig. 7)

Examination of fractions 24-27 (Table 1):

The fractions 24-27 (Table 1) were combined (750 mg). TLC experiment of the compound showed three distinct but close spots, hence, this was set aside for further purification.

Examination of fractions 28-30 (Table 1) : Isolation of 2 $\beta$ -hydroxy-2-carboxy-3-nor-Friedelane, 48 (C).

The fractions 28-30 (Table 1) were combined (250 mg) and crystallised from chloroform and methanol to afford white amorphous powder m.p. 242-4<sup>o</sup>. It showed negative test with TNM. It also showed single spot on TLC plate.

Analysis report :

	%C	%H
Found	78.21	10.83
Calculated for C <sub>30</sub> H <sub>50</sub> O <sub>3</sub>	78.42	10.91

IR :  $\int_{\text{max}}^{\text{Nujol}}$  3600-2800 (hump) (-OH), 1730-1695 (-COOH)

(Fig. 8)



UV : No absorption between 220-300 nm.

IR :  $\int_{\text{max}}^{\text{Nujol}}$  3520 (-OH), 1730 (C = O)  $\text{cm}^{-1}$ .

(Fig. 11)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ) : Peaks at 0.88-1.19 (s, 15H, 5-C- $\text{CH}_3$ ),

1.2 (m, 3H,  $\begin{array}{c} \text{-C-CH}_3 \\ | \\ \text{H} \end{array}$ ),

1.26 (m, 3H, C -  $\text{CH}_3$ ),

1.35 (s, 3H, C -  $\text{CH}_3$ ),

2.66-2.7 (d, H, -O-CH.OH-C)ppm

(Fig. 12)

Mass (m/z) relative intensity : 458 ( $\text{M}^+$ ), 440( $\text{M}^+ - \text{H}_2\text{O}$ , 8.33)

412 ( $\text{M}^+ - \text{CO}$ , 6.38), 381 (11.36)

and 95 (base peak)

(Fig. 13)

Examination of fractions 24-27 (Table 1) : Acetylation of the oily solid : Isolation of A-nor-friedelene 49, 3-nor-Friedelin

$\Delta^{2(4)}$  acetate 51, and 3-nor-  $\Delta^{2(4)}$  - friedelin-2-carboxylic acid 47a.

To a solution of oily solid mass fractions 24-27 (Table 1) (750 mg) dissolved in pyridine (7.5 ml) was added acetic anhydride (7.5 ml) and the mixture kept over water bath for 12 hours. The mixture was poured into ice cold water and the solid was collected by filtration. A crude acetylated product (700 mg) was obtained.

It showed three spots on a chromatoplate (developed with benzene-ethyl acetate, 9:1).

It was then chromatographed over a column of silica gel (15 gm) developed with petroleum ether. The above residue (700 mg) dissolved in benzene (10 ml) was added to the column. The following solvents were used for elution (Table 2).

Table 2

Chromatography of the acetylated product (700 mg)

Eluent	Fractions 100 ml each	Residue	M.P.
Petroleum ether	1-4	Solid (150 mg)	218-22°
Petroleum ether : benzene (4:1)	5-10	Solid (220 mg)	229-33°
Petroleum ether: benzene (3:2)	11-13	Nil	-
Petroleum ether: benzene (1:4)	14-15	Nil	-
Benzene	16-17	Oil (100 mg)	-
Benzene : ether (9:1)	18-24	Solid ( 200 mg)	280-5°

Further elution with more polar solvent did not yield any solid material.



Examination of fractions 1-4 (Table 2): Isolation of A-nor-friedelene, 49 (B<sub>1</sub>)

The above fractions 1-4 (Table 2) were combined (150 mg) and crystallised from a mixture of chloroform and methanol, when a crystalline solid m.p. 227-8°  $[\alpha]_D^{30} + 40^\circ$  was obtained. It showed a single spot on a chromatoplate and gave yellow colouration with TNM.

Analysis report:

	%C	%H
Found	88.02	12.29
Calculated for C <sub>29</sub> H <sub>48</sub>	87.87	12.12

IR :  $\int_{\text{max}}^{\text{Nujol}}$  1650, 810 cm<sup>-1</sup>

(Fig. 14)

<sup>1</sup>H NMR (360 MHz) : 0.84, 0.94, 0.97, 1.00, 1.01, 1.02, (S CDCl<sub>3</sub>)  
1.18 (2H, seven tertiary methyl group),  
1.57 (3H, tertiary methyl group on double bond, =C - CH<sub>3</sub>), 5.30 (s, 1H, C = CH) ppm

(Fig. 15)

Mass (m/z), rel. inst. : 396 (M<sup>+</sup> 20.7), 381 (M<sup>+</sup> - CH<sub>3</sub>, 100),  
257, 243 (5.00), 205 (20), 191(15),  
177, 163, 149.

(Fig. 16)

Examination of fractions 5-10 (Table 2): Isolation of 3-nor-  
friedelin-  $\Delta^{2(4)}$ -2-acetate 51 (B<sub>2</sub>)

The fractions 5-10 (Table 2) were combined (220 mg), m.p. 229-33° and crystallised from a mixture of chloroform and methanol to afford needle shaped crystals, m.p. 235-7°.

It showed a single round spot on TLC plate and showed positive TNM test.

Analysis report:

	%C	%H
Found	81.65	11.21
Calculated for C <sub>31</sub> H <sub>50</sub> O <sub>2</sub>	81.93	11.01

IR :  $\int_{\text{max}}^{\text{Nujol}}$  1740, 1220 (-OCC<sub>3</sub>H<sub>7</sub>), 890 (C = CH) cm<sup>-1</sup>

(Fig. 17)

<sup>1</sup>H NMR (360 MHz) : Peaks at 0.94, 0.94, 0.98, 0.99, 1.01, (δ CDCl<sub>3</sub>) 1.01, 1.17 (7s, 2H, 7 t -CH<sub>3</sub>), 1.55 (s, 3H, methyl group on double bond, = C-CH<sub>3</sub>) 2.13 (s, 3H, -O-C(=O)-CH<sub>3</sub>) ppm

(Fig. 18)

Mass (m/z) : 454 (M<sup>+</sup>), 439 (M<sup>+</sup>-15), 412, 397, 381, 205, and 191.

(Fig. 19)

Examination of fractions 18-24 (Table 2) : Isolation of 3-nor- $\Delta^{2(4)}$ -friedelin-2-carboxylic acid, 47a ( $B_3$ ).

The fractions 18-24 (Table 2) were combined (.2 gm) and crystallised from chloroform-methanol mixture to afford white amorphous solid, m.p.  $290-2^{\circ}$ . It responded positive TNM test.

Analysis report:

	%C	%H
Found	81.97	10.94
Calculated for $C_{30}H_{48}O_2$	81.818	10.909

IR :  $\int$  Nujol 3400-2600 (hump), 1670, 1620  $cm^{-1}$   
max

(Fig. 20)

Mass (m/z) : 440 ( $M^+$ , 34.8), 425 ( $M^+ - CH_3$ , 20.3),  
382 (3.4), 316 (7), 205 (40), 191, 40 (base).

(Fig. 21)

Esterification of 3-nor- $\Delta^{2(4)}$ -friedelin-2-carboxylic acid  
47a to 3-nor- $\Delta^{2(4)}$ -methyl friedelinate 47b.

3-nor- $\Delta^{2(4)}$ -friedelin-2-carboxylic acid 47a (100 mg) was dissolved in ether and cooled to  $0^{\circ}$  by keeping the conical flask in a freezing mixture bath. To this ethereal solution was added well cooled ether solution of diazomethane prepared from 500 mg of nitrosomethyl urea and was kept overnight. On the following day excess of diazomethane was destroyed with acetic acid. The ether solution was washed with water, 10% sodium

bicarbonate solution and again with water till neutral and then dried over anhydrous sodium sulphate. Evaporation of ether yielded a solid residue (90 mg). This after crystallization from acetone-methanol mixture yielded needle shaped crystals (75 mg) m.p.  $206-7^{\circ}$ . It showed positive test with TNM and showed a single round spot on a chromatoplate. It was analysed for 3-nor-  $\Delta^{2(4)}$ -methyl friedelinate 47b.

Analysis report:

	%C	%H
Found	81.79	11.07
Calculated for $C_{31}H_{50}O_2$	81.93	11.01

IR :  $\int_{\text{max}}^{\text{Nujol}}$  1710, 1225 ( $COOCH_3$ ), 1635, 850, 810 ( $C=C$ )  $cm^{-1}$

(Fig. 22)

$^1H$  NMR (360 MHz) : 0.887, 0.942, 0.976, 0.998 (2 Me),  
( $SCDCl_3$ ) 1.019, 1.18 (7s, 2H, 7 t  $-CH_3$ ),  
1.96 (s, 3H, tertiary methyl group  
on double bond)  
3.70 (s, 3H,  $-COOCH_3$ ), 2.26 (m, 2H,  
 $H_2C-COOCH_3$ ) ppm.

(Fig. 23)

Mass (m/z) rel. inst. 454 ( $M^+$ , 34.5), 439 ( $M^+-CH_3$ , 31.4),  
330, 205, 191, 177, 149.

(Fig. 24)

Hydrogenation of 3-nor- $\Delta^{2(4)}$ -methyl friedelinate 47b to  
2  $\alpha$ -carbomethoxy A-nor-friedelin 49.

50 mg of 3-nor- $\Delta^{2(4)}$ -methyl friedelinate 47b in glacial acetic acid (1.5 ml) and ethyl acetate (1.5 ml) was reduced with hydrogen at atmospheric pressure in presence of Adam's catalyst (1 mg). The catalyst was filtered off, the solvent evaporated in vacuum and the residue on crystallisation from a mixture of chloroform-methanol afforded crystals (35 mg), m.p.  $263-5^{\circ}$ , identical with sample of 2  $\alpha$ -carbomethoxy-A-nor-friedelene 49 (m.m.p., CO-IR, CO-TLC).

Lithium ethylene diamine (Li-EDA) reduction of 3-nor- $\Delta^{2(4)}$ -  
tertiary butyl friedelinate (A), 46 :

200 mg of A, 46 was dissolved in dry ethylenediamine (60 ml) and to this solution was added lithium metal (200 mg) in small pieces at intervals. The mixture was refluxed for 2 hours under nitrogen blanket. The reaction mixture was cooled and treated with solid ammonium chloride to destroy excess of lithium metal. It was acidified with dil. HCl, extracted with ether and treated with dil. NaOH to separate the neutral and acid parts.

Treatment of alkali layer (acid part)

The alkali layer was treated with dil. HCl till the whole solution was acidic. White solid was precipitated. It was extracted with ether, washed several times with water till

neutral. The ether solution was dried over anhydrous sodium sulphate. After recovery of ether, a yellowish gummy solid was obtained. The crude product showed a single spot on a TLC plate. Hence it was subjected to crystallisation. On repeated crystallisation from chloroform-methanol mixture it afforded white amorphous solid m.p.  $246-7^{\circ}$ . The compound showed negative TNM test. It was analysed for  $C_{30}H_{50}O_2$ .

Analysis report:

	%C	%H
Found	81.37	11.29
Calculated for $C_{30}H_{50}O_2$	81.44	11.33

IR :  $\int_{\text{max}}^{\text{Nujol}}$  3400-2600 (hump), 1690-1700 ( $-\text{COOH}$ )  $\text{cm}^{-1}$

(Fig. 25)

Mass (m/z) rel. int. : 442 ( $M^+$ , 13.6), 427 ( $M^+ - \text{CH}_3$ , 12.8)  
413 (6.7), 318(20), 69 (base).

(Fig. 26)

Hydrolysis of 3-nor- $\Delta^{2(4)}$ -tertiary butyl friedelinate 46, (A)

with 20% methanolic KOH:

3-nor- $\Delta^{2(4)}$ -tertiary butyl friedelinate 46, A (150 mg)

dissolved in benzene (2 ml) was refluxed with 20% methanolic KOH (15 ml) for 4 hours. After 4 hours the mixture was then cooled and poured on ice-cold water when a white solid separated out. It was extracted with ether and the ether solution was

separated from the alkali layer. The ether solution was washed with little water to remove any acidic part. The alkali layer and water wash were mixed and kept aside for further treatment.

Treatment of neutral part.

The ethereal solution which now contained neutral part only, was washed with dil. HCl, then with water till neutral and finally dried over anhydrous sodium sulphate. The filtered ether solution on evaporation to dryness yielded white solid (80 mg). It showed a single roundspot on a chromatoplate and responded TNM test. On careful crystallisation from chloroform-methanol mixture it yielded needle shaped crystals of m.p.  $227-8^{\circ}$ . It was analysed for  $C_{29}H_{48}$  and was found identical with C<sub>1</sub> (m.m.p., IR, CO-TLC) the structure of which has been established as A-nor-friedelene 49.

Treatment of alkali layer (Acid part)

The alkali layer that remained after separation of neutral part was treated with 20% HCl till the whole solution was acidic. White precipitate that separated out was extracted with ether. The ether solution was washed with water and dried over anhydrous sodium sulphate. After recovery of ether, a yellowish white residue was left. It showed a single spot on

a chromatoplate. Hence it was crystallised from chloroform-methanol mixture to afford white amorphous powder, m.p. 290-2°. It was found identical with 47a, (B<sub>3</sub>)  $\angle$  m.m.p., CO-IR, CO-TLC  $\checkmark$  which has been characterised as 3-nor- $\Delta^{2(4)}$ -friedelin-2-carboxylic acid 47a.

Esterification of 2 $\beta$ -hydroxy-2-carboxy-3-nor-Friedelane,

48 (C): Isolation of C<sub>34</sub>H<sub>58</sub>O<sub>4</sub> (a'), C<sub>34</sub>H<sub>58</sub>O<sub>4</sub> (b'),

C<sub>34</sub>H<sub>58</sub>O<sub>3</sub> (c'), C<sub>32</sub>H<sub>54</sub>O<sub>4</sub> (d') and C<sub>31</sub>H<sub>52</sub>O<sub>3</sub> (e').

2  $\beta$ -hydroxy-2-carboxy-3-nor-Friedelane, 48 ( 200 mg) was dissolved in ether and cooled to 5°. To this was added well cooled ethereal solution of diazomethane prepared from 500 mg nitrosomethyl urea and was kept overnight. Next day, excess of diazomethane was destroyed with acetic acid. The ether solution was washed with water, 10% NaHCO<sub>3</sub> solution and again with water till neutral and was dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of ether yielded a solid residue. This after several crystallisations from acetone-methanol mixture gave needle shaped crystals. TLC gave single spot, but m.p. determination did not show fixed m.p. TNM gave negative test.

<sup>1</sup>H NMR (SCDC1<sub>3</sub>) : 2.15 and 2.21 (single proton at C-10)  
3.63, 3.68, 3.69, 3.71 and 3.77 (5 methyl  
of carboxylate) ppm

(Fig. 27)



Mass : mass peaks at  $m/z$  530, 514, 502 and 472 ( $M^+$ ),  
457, 454, 439, 429, 413.

(Fig. 28)

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