CHAPTER V

EXPERIMENTAL

Melting points are uncorrected. The petroleum ether used during the investigation had b.p. 60° - 80°C. All optical rotations were determined in chloroform solution unless stated otherwise. The I.R. spectra were recorded in Beckmann I.R. - 20 Spectrophotometer. U.V. absorption spectra were taken in Beckmann DU-2 Spectrophotometer. NMR spectra were determined on Varian FT-80A and XL-100 Spectrometer using chloroform-d solution containing tetramethylsilane as reference.

Isolation of the neutral benzene soluble portion of *Sapium baccatum* Roxb:

Dried and powdered stem bark of *Sapium baccatum* Roxb (2 Kg) was extracted with benzene for about twenty hours in a soxhlet apparatus. On cooling the benzene extract, a yellow solid separated out which was separated by filtration and was kept aside. The clear filtrate was concentrated when a residual gummy solid was obtained. This was taken up in ether (2 lit.). A cloudy precipitate that remained insoluble in the ether extract was separated out by filtration. The clear ether solution was

washed with 10% caustic soda solution (4 x 200 ml) to separate the acidic constituents. The ether layer was washed with water until the washings were found neutral, dried over anhydrous sodium sulphate. Filtered. The ether solution was then concentrated to remove the last trace of solvent when the neutral material (10.7 gm) was obtained as a yellow gummy solid.

Chromatography of the above gummy solid:

The above gummy solid (10.7 gm) was dissolved in minimum amount of benzene and the benzene solution was placed on a column of alumina (660 gm) deactivated by means of 40 ml of 10% aqueous acetic acid. The chromatogram was developed with petroleum ether and was eluted with the following solvents.

Table 1

Eluent	Fractions 250 ml each	Residue on evaporation	Melting point in °C
Petroleum ether	1-4	Oil (1.5 gm)	-
Petroleum ether	5-13	Solid (4.1 gm)	220°-222°

Contd...

Table 1 (Contd..)

Eluent	Fractions 250 ml each	Residue on evaporation	Melting point in °C
Petroleum ether: Benzene (4:1)	14-17	Solid with petroleum ether (1.1 gm)	65°-68°
Petroleum ether: Benzene (3:2)	18-20	Oil (0.2 gm)	-
Petroleum ether: Benzene (3:2)	21-23	Solid (0.3 gm)	265-270°
Petroleum ether: Benzene (2:3)	24-28	Solid (0.6 gm)	130-132°
Petroleum ether: Benzene (1:4)	29-32	Oil (0.3 gm)	-
Benzene	33-38	Oil (0.4 gm)	-
Benzene: Ether (4:1)	39-44	Solid (0.3 gm)	210°-220°

Examination of the fractions 5-13 (Table 1):

The fraction on repeated crystallisation from chloroform-methanol mixture gave taraxerone, mp 238-240°C $(\alpha)_D$ 10.8°, as already reported[3].

Examination of the fractions 14-17 (Table 1):

It has also been established[3] that this fraction on rechromatography and crystallisation gives 1-Hexacosanol, mp 78-79°C.

Examination of the fractions 21-23 (Table 1):

It has already been reported[3] that this fraction on crystallisation gives taraxerol mp 278-280°, $(\alpha)_D$ 75.7°.

Examination of the fractions 24-28 (Table 1):

It has been established[3] that this fraction contains β-sitosterol mp 136-137°, $(\alpha)_D$ -32°.

Examination of the fractions 39-44 (Table 1):

It has already been reported[9] that this fraction contains a nor-triterpene Baccatin mp 228-229°, $(\alpha)_D$-9.09°.

Examination of the Benzene-insoluble part of Sapium baccatum Roxb:

It has already been reported[7] that the benzene insoluble part of Sapium baccatum Roxb contains 3,3'-di-O-methyl ellagic acid.

Examination of the acid part of Sapium baccatum Roxb:

The ether solution of Sapium baccatum Roxb was washed with 10% sodium hydroxide solution to free it from acidic constituents. The alkaline layer was acidified with cold and dilute 10% hydrochloric acid when some insoluble solid separated out. The acidified portion was extracted with ether and the ether solution was washed with water until neutral. Dried over anhydrous sodium sulphate, ether was removed when a gummy residue was obtained. A portion of this gummy residue (1.5 gm) was left aside for direct chromatography on a silicagel column. The rest of the acid was then esterified with diazomethane in ether solution. On the following day, excess of diazomethane was decomposed with acetic acid. The ether solution was washed with water, 10% sodium bicarbonate solution, water to make the ether solution neutral. The ether solution of the ester was then dried over anhydrous sodium sulphate. Removal of ether left a gummy residue (625 mg).

Chromatography of the ester:

The above crude ester was dissolved in minimum amount of benzene and it was placed on a column of alumina (40 gms deactivated with 2.4 ml of 10% aqueous acetic acid). The chromatogram was developed with petroleum ether and was eluted with the following solvents:

Table 2

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether	1-10	Solid mp 64°C
Petroleum ether: Benzene (4:1)	11-28	Solid mp 232-236°C

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

Fractions 11-28 (Table 2) were combined and the residue was crystallised from a mixture of chloroform and methanol. Fine needle shaped crystals having mp 241-242°, $(\alpha)_D$ 23.08° were

obtained. The compound was found to be identical with an authentic sample of acetyl methyl aleuritolate[10] (mmp and I.R. comparison).

Chromatography of the Crude acid obtained from Sapium baccatum: Isolation of Acetyl Aleuritolic Acid:

1.5 gm of the crude acid was dissolved in minimum amount of benzene and the benzene solution was poured on a column of 30 gms BDH silicagel. The chromatogram was developed with petroleum ether and was eluted with the following solvents:

Table 3

Eluent	Fractions 100 ml each	Residue on evaporation
Petroleum ether	1-6	Trace oil
Petroleum ether: Benzene (4:1)	7-10	Trace oil
Petroleum ether: Benzene (3:2)	11-19	Oily solid with methanol

Contd..

Table 3 (Contd..)

Eluent	Fractions 100 ml each	Residue on evaporation
Petroleum ether: Benzene (2:3)	20-26	Trace oil
Petroleum ether: Benzene (1:4)	27-36	Solid

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

Fractions 27-36 (Table 3) were combined and the mass was crystallised from a mixture of chloroform and methanol when crystals of Acetyl aleuritolic acid mp 278-281° were obtained.

Analysis Report:

Found:	C, 79.32;	H, 10.11%
Calc. for $C_{32}H_{50}O_4$	C, 79.66;	H, 10.37%

The acid on esterification with diazomethane produced a sample identical with acetyl methyl aleuritolate (mmp and I.R. comparison).

Conversion of Taraxerone to Taraxerol:

The ketone (200 mg) was dissolved in 50 ml dry tetrahydrofuran and to it 50 mg of lithium aluminium hydride was added. The mixture was refluxed for about six hours. The reaction mixture was then cooled and to this 30 ml of moist ether was added followed by a saturated solution of sodium sulphate. The mixture was extracted with ether, washed with water to make it neutral. The solution was dried by means of anhydrous sodium sulphate. Removal of ether gave a solid mass (190 mg) which was chromatographed over alumina. A column of alumina (10 gm deactivated with 0.6 ml of 10% aqueous acetic acid) was developed with petroleum ether and the above residue dissolved in minimum amount of benzene was poured on it. The following solvents were used for elution.

Table 4

Eluent	Fraction 50 ml each	Residue on evaporation
Petroleum ether	1-3	Nil
Petroleum ether:Benzene (4:1)	4-5	Nil
Petroleum ether:Benzene (3:2)	6-12	Solid mp 268-271°

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

Fractions 6-12 (Table 4) were combined and the solid was crystallised from chloroform and methanol when crystals of mp 278-280° were obtained. Its melting point was not depressed when mixed with an authentic sample of taraxerol.

Analysis Report:

Found:	C, 84.13; H, 11.39%
Calc. for $C_{30}H_{50}O$	C, 84.50; H, 11.73%

Conversion of Taraxerol to Taraxeryl Acetate 32:

Taraxerol (200 mg) was dissolved in 5 ml pyridine. 5 ml of acetic anhydride was added and the mixture was heated on a waterbath for about six hours. The solution was cooled and was then poured into ice-cold water when a crystalline solid separated out. The solid was collected by filtration, washed with water till the washings were found neutral. The crude acetate was crystallised from chloroform-methanol mixture when pure taraxeryl acetate (150 mg), mp 295-296° was obtained.

Analysis Report:

Found:	C, 81.82; H, 11.32%
Calc. for $C_{32}H_{52}O_2$:	C, 82.05; H, 11.11%

I.R. spectra (Fig. 1) showed peaks at 1720 cm^{-1} and 1250 cm^{-1} indicating the presence of acetate group.

Preparation of 15-Bromo β-amyrin acetate 36: NBS-DMSO treatment on Taraxeryl acetate:

N-Bromo succinimide (1 gm) was added in portions to a solution of taraxeryl acetate (1 gm) dissolved in chloroform (50 ml) and dimethyl sulfoxide (25 ml) and the mixture was kept

overnight. On the following day, the reaction mixture was filtered. The filtrate was extracted with chloroform (200 ml), washed with water and was dried over anhydrous sodium sulphate. The solvent was removed when a yellowish solid was obtained. The solid was dissolved in benzene (10 ml) and was poured on a column of alumina (60 gm deactivated with 3.6 ml of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution.

Table 5

Eluent	Fractions 100 ml each	Residue on evaporation
Petroleum ether	1-10	Solid (900 mg) mg 178-180°

Elution with more polar solvents did not give any solid.

Fractions 1-10 (Table 5) were combined and the mixture was crystallised from a mixture of chloroform and methanol when crystals of 15-Bromo β-amyrin acetate 36 mp 180-182°, $(\alpha)_D$ 47.37°

were obtained. It gave a single spot on a chromatoplate (R_f = 0.8) and also showed positive copper-wire test for bromine.

Analysis Report:

Found: C, 70.09; H, 8.9%

Calc. for $C_{32}H_{51}O_2Br$: C, 70.20; H, 9.3%

U.V. : No U.V. absorption in the region 220-300 nm

I.R. : ν_{max} 1720 and 1250 cm^{-1} (Fig. 2)

NMR spectrum: Peaks at 5.3 (multiplet, vinyl proton), 4.30 (multiplet, HCBr), 2.09 ($-OCOCH_3$) and 4.53 (H-C-$OCOCH_3$) ppm (Fig. 3)

Mass spectrum: Peaks at m/e 189, 216, 217, 249, 297, 466 (M -HBr), 547 (M^+) (Fig. 4)

Preparation of 15-Bromo β-amyrenonyl acetate 44 : Oxidation of 15-Bromo β-amyrin acetate 36 :

15-Bromo β-amyrin acetate (1 gm) was dissolved in 40 ml benzene and the solution was refluxed with stirring. A solution of sodium dichromate (1 gm) in glacial acetic acid (30 ml) maintained at about 70°C was added slowly. When the addition was complete, stirring was continued for about twenty four hours,

the temperature of the mixture being maintained at about 80° - 85°C.

Then added 4 ml rectified spirit and the mixture was concentrated to 1/3rd volume. Then it was poured into ice-cold water when an insoluble solid separated which was collected by filtration. It was taken up in ether and washed with water, dried with sodium sulphate. The solvent was removed when a solid was obtained. This was crystallised from chloroform-methanol mixture when crystals (0.75 g) having mp 240-241° were obtained.

Analysis Report:

Found:	C, 68.24; H, 8.63%
Calc. for $C_{32}H_{49}O_3Br$:	C, 68.42; H, 8.69%

U.V. : λ_{max} 249 nm (ϵ 11,000)

Attempted dehydrobromination of 15-Bromo β-amyrenonyl acetate 44:

(a) 500 mg compound was refluxed with dimethyl aniline for six hours. Cooled, acidified with 6 N HCl. The mass was extracted with ether, washed the ether solution to make it acid free. The solution was dried with anhydrous sodium sulphate. Solvent was then removed. The residue was then chromatographed in a column of 30 gm alumina deactivated by means of 1.8 ml 10%

aqueous acetic acid. The column was developed with petroleum ether and the following fractions were collected.

Table 6

Eluent	Fractions 100 ml each	Residue on evaporation
Petroleum ether	1-12	Solid mp 229-230°

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

Fractions 1-12 (Table 6) were combined. The mass was crystallised from chloroform-methanol mixture when crystals having mp 240° were obtained. The compound showed positive test for bromine. Mixed melting point with the starting material was also undepressed.

(b) 200 mg of the bromo compound was refluxed with 15 ml s-collidine in an oil bath maintained at 180°. The mixture was refluxed for 18 hours. The mass was then acidified with 5% H_2SO_4, extracted with ethyl acetate. The organic layer was washed with

5% H_2SO_4 to remove last traces of collidine, washed with water to make organic layer neutral. Dried with anhydrous sodium sulphate. The solvent was then removed. The residue (190 mg) was then dissolved in minimum amount of benzene and was then chromatographed in a column of alumina developed with petroleum ether and the following fractions were collected.

Table 7

Eluent	Fractions 100 ml each	Residue on evaporation
Petroleum ether	1-4	Trace oil
Petroleum ether: Benzene (4:1)	5-14	Solid mp 228-230°

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

Fractions 5-14 (Table 7) were combined. The mass was crystallised from chloroform and methanol when needle shaped crystals of mp 240-241° were obtained. Mmp with the parent compound and Beilstein test indicated that dehydrobromination did not occur.

(c) 0.5 gm of metallic potassium was dissolved in about 10 ml dry tert. butanol using a guard tube and a condenser. Occasional heating was also required. When all the metal was dissolved, excess tert. butanol was removed by suction in pump. A solid residue was left.

0.4 gm potassium tert. butoxide was taken in 10 ml dry dimethyl sulfoxide and 0.1 gm bromo compound was added. The mixture was refluxed in an oil bath for a period of about six hours. The mass was diluted with water. 5% HCl was added to acidify the mass when a brown precipitate appeared. The mass was extracted with ether. The ether solution was washed to make it neutral, dried with anhydrous sodium sulphate. A dark coloured oily residue (0.1 gm) was left. This was dissolved in minimum amount of benzene and was then chromatographed in a column of 10 gm alumina deactivated with 0.6 ml 10% aqueous acetic acid. The chromatogram was developed with petroleum ether and the following fractions were collected.

Table 8

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether	1-4	Nil
Petroleum ether: Benzene (4:1)	5-14	Solid mp 228-230°

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

Fractions 5-14 (Table 8) were combined. The mass was crystallised from a mixture of chloroform and methanol when crystals having mp 240° were obtained. Mmp with the parent compound showed that dehydrobromination reaction did not occur.

Dimethyl aniline treatment of 15-Bromo β-amyrin acetate 36: Preparation of olean-12, 15-dien-3 β-yl acetate 45:

15-Bromo β-amyrin acetate 36 (300 mg) was refluxed with distilled dimethyl aniline (30 ml) for six hours. The reaction mixture was diluted with water, acidified with 6N hydrochloric acid and was extracted with ether. The ether extract was washed with water till neutral and was dried with sodium sulphate. The solvent was removed when a solid (170 mg) was obtained. The solid was dissolved in minimum amount of benzene and the solution was poured on a column of alumina (15 gm deactivated with 0.9 ml of 10% aqueous acetic acid) developed with petroleum ether. The following fractions were collected.

Table 9

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether	1-5	Solid (155 mg) mp 195-197°

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

Fractions 1-6 (Table 9) were combined and the mixture was crystallised from chloroform-methanol mixture when crystals of **45**, mp 199-200°, $(\alpha)_D$ 41.86° were obtained.

Analysis Report:

Found : C, 82.57; H, 10.83%

Calc. for $C_{32}H_{50}O_2$: C, 82.35; H, 10.80%

U.V. : No absorption in the region 220-300 mm

I.R. : ν_{max} 1730, 1240 cm^{-1} (Acetate)

875 cm^{-1} (-CH = CH-) (Fig. 5)

820 cm^{-1} (trisubstituted double bond)

NMR: 5.2 to 5.6 ppm for three vinyl (Fig. 6)

protons accounting for one trisubstituted

and one disubstituted double bond 2.08

($O.COCH_3$), 4.5 ($HC-OCOCH_3$)

<u>Oxidation of olean-12,15-dien-3β-yl acetate **45**: Preparation of 3β-acetoxy olean-12, 15-dien-11-one **46**:</u>

The solution of sodium dichromate (4 gm) in glacial acetic acid (100 ml) maintained at 70°C was added slowly during a period of one hour to the vigorously stirred solution of olean-12, 15-dien-3β-yl acetate (4 gms) in refluxing benzene (50 ml).

Then continued refluxing for 24 hours. Added 50 ml rectified spirit, concentrated to 1/3rd volume, poured the contents into ice-cold water when a solid separated. The solid was extracted with ether. The ether solution was washed with water to make it neutral, dried with anhydrous sodium sulphate. The solvent was removed. The residue (4 gms) was dissolved in minimum amount of benzene and was poured on a column of alumina (240 gm deactivated with 15 ml of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution.

Table 10

Eluent	Fractions 100 ml each	Residue on evaporation
Petroleum ether	1-5	Nil
Petroleum ether: Benzene (4 : 1)	6-10	Nil
Petroleum ether: Benzene (3:2)	11-18	Solid mp 238-240°

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

Fractions 11-18 (Table 10) were combined and the mixture was crystallised from chloroform-methanol mixture when needle-shaped crystals of 3β-acetoxy olean-12, 15-dien-11-one **46** mp 243-245°, $(\alpha)_D$ 23.57° were obtained.

Analysis Report:

Found:	C, 79.36; H, 9.95%
Calc. for $C_{32}H_{48}O_3$	C, 79.95; H, 10.06%

U.V. : λ_{max} 244 nm (ϵ 11,376)

I.R. : ν_{max} 1730, 1240 cm^{-1} (Acetate) (Fig. 7)
1660 cm^{-1} (6-membered ring α,β unsat. ketone),
890 cm^{-1} (-CH = CH-)

NMR : 0.8 to 1.5 ppm (vinyl groups) (Fig. 8)
2.04 ppm ($-OCOCH_3$)
5.5 to 5.7 (three vinyl protons)
4.5 ppm ($-CH-OCOCH_3$)

Lithium aluminium hydride reduction of 3β-acetoxy olean-12, 15-dien-11-one 46: Preparation of olean-12,15-dien-3,11-diol 39:

A solution of the 11-keto acetate (2.5 gm) in 30 ml dry benzene and 70 ml dry ether was added with stirring to a mixture of 5.0 gm LAH and 300 ml refluxing ether (stirred previously for 2 hours under reflux) during a period of two hours.

After stirring for 6 hours at reflux, the solution was stirred for 12 hours at room temperature. To destroy excess hydride a minimum volume of water was added dropwise at room temperature. The precipitate was separated by decantation and was washed with ether. The combined ethereal solution was washed with 10% aqueous sodium hydroxide solution and then with water. The ether solution was dried over anhydrous sodium sulphate and was then evaporated when 1.9 gm of olean-12, 15-dien-3, 11-diol 32 mp 198-200° was obtained.

I.R. : ν_{max} 3460 (free OH group),
875 cm^{-1} (-OH = CH-) (Fig. 9)

Treatment of olean-12,15-dien-3,11-diol 32 with hydrogen peroxide in acid medium:

To 1.9 gm of olean-12, 15-dien-3, 11-diol 32 in 100 ml of methylene chloride was added 85 ml of oxidising solution which was prepared from 5 ml of 30% H_2O_2 in 80 ml of tertiary butyl alcohol containing 3.0 gm of p-toluene sulphonic acid at room temperature. The solution was stirred slowly for 24 hours and was then poured into water. The mixture was extracted with methylene chloride and the methylene chloride solution was washed with water, aqueous sodium bicarbonate solution and then again

with water. The organic layer was dried over anhydrous sodium sulphate and was then evaporated when a solid residue of 1.9 gm, mp 200-210° was obtained.

Chromatography of the product:

1.9 gm of the compound was dissolved in minimum amount of benzene and was then poured on a column of 40 gms silicagel.

Table 11

Eluent	Fractions 100 ml each	Residue on evaporation
Petroleum ether	1-7	Trace oil
Petroleum ether: Benzene (4:1)	8-12	Nil
Petroleum ether: Benzene (3:2)	13-23	Trace oil
Petroleum ether: Benzene (2:3)	24-31	Nil
Petroleum ether: Benzene (1:4)	32-39	Nil
Benzene	40-55	Solid .632 g, mp 232-35°

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

Fractions 40-55 (Table 11) were combined and the mixture was crystallised from methanol when crystals of $C_{30}H_{46}O_3$, mp 240-241° were obtained.

Analysis Report:

Found: C, 78.94; H, 9.89%

Calc. for $C_{30}H_{46}O_3$: C, 79.25; H, 10.20%

U.V. : No absorption in the region 220-300 nm

I.R. : ν_{max} 3520 cm^{-1} (free OH group) (Fig. 10)

875 cm^{-1} (-CH = CH-),

1775 cm^{-1} (lactone)

Acetylation of the oxidation product 50:

0.1 gm of the compound was dissolved in 1 ml dry pyridine and the solution was treated with 1 ml acetic anhydride. The mixture was left at room temperature for 48 hours. After usual work up, the acetylated product was crystallised from chloroform methanol mixture when crystals of 51 $C_{32}H_{48}O_4$ mp 215-216° were obtained.

Analysis Report:

Found: C, 77.25; H, 9.89%

Calc. for $C_{32}H_{48}O_4$: C, 77.33; H, 9.74%

U.V. : No absorption in the region 220-300 nm

I.R. : ν_{max} 1720 cm^{-1}, 1250 cm^{-1} (Fig. 11)

($OCOCH_3$), 1780 cm^{-1} (lactone)

Reduction of the acetate **51** by means of LAH:

700 mg of the acetate was taken in 150 ml dry ether, 1.5 gm LAH was added. The mixture was refluxed for a period of 8 hours. Saturated sodium sulphate solution was added. It was acidified with 10% hydrochloric acid when the hydroxides dissolved. The mass was extracted with ether and the ethereal solution was washed with water to make it acid-free. It was dried with anhydrous sodium sulphate. Solvent was removed. The mass obtained was crystallised from acetone when crystals of $C_{30}H_{52}O_3$ **52** mp 280-282°C separated. The compound showed a single spot on a chromatoplate.

Acetylation of the LAH reduction product $C_{30}H_{52}O_3$, **52**:

200 mg of the compound was dissolved in 10 ml pyridine. 10 ml acetic anhydride was then added. The mixture was kept at room temperature for 48 hours. The mass was poured into ice-water when a solid separated. It was filtered, washed with water. The mass was crystallised from chloroform methanol mixture when crystals of the triacetate $C_{36}H_{58}O_6$, **53**, mp 185-190°C were obtained.

Analysis Report:

Found: C, 72.96; H, 10.52%

Calc. for $C_{36}H_{58}O_6$: C, 73.68; H, 9.96%

U.V. : No U.V. absorption in the region 220-300 nm

I.R. : ν_{max} 1740 cm^{-1}, 1250 cm^{-1} (Acetate groups)

NMR : 0.5 to 1.5 ppm (tertiary methyl groups) (Fig. 17)

2.05 ppm ($-COOCH_3$); 5.25 (vinyl protons)

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