

CHAPTER - III

EXPERIMENTAL

Melting points are uncorrected. Petroleum ether used throughout the experiments had b.p. 60-80°. All optical rotations were determined in chloroform solution unless otherwise stated. NMR spectra were determined on Varian-60 spectrometers using chloroform-d solution containing tetramethyl silane as reference. UV absorption were taken in a Zeiss VSU 1 spectrophotometer in 95% ethanol solution. TLC was done on chromatoplate of silica Gel (E.Merck) and the spots were developed with sulphuric acid-acetic anhydride (9:1) mixture.

Oxidation of taraxeryl acetate 67 with N-Bromosuccinimide: Isolation of 15-bromo $\beta$ -amyrenonyl acetate 68, 16-oxo taraxeryl acetate 69, 15-bromo-9(11), 12-olean diene 70 :

To a solution of taraxeryl acetate 67 (200 mg) in dioxan (400 ml) containing water (20 ml) and calcium carbonate (1.0 gm) was added NBS (1.2 gm) and the mixture was stirred for 5.5 hr. at room temperature in presence of visible light (100 watt bulb). A few drops of triethanol amine was added to discharge the yellow color. The reaction mixture was then diluted with water (200 ml) and extracted with ether. The ethereal layer was then washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Removal of ether gave a solid (180 mg).

TLC of the latter showed three distinct spots (using benzene as solvent,  $R_f$  0.93, 0.62, 0.46) indicating a mixture of at least three compounds. The residue (180 mg) was dissolved in benzene (2 ml) and poured on a column of alumina (12 gm deactivated with 0.5 ml of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution.

Table I

Eluent	Fractions 50 ml each	Residue on evaporation	Melting point
Petroleum ether	1-5	Solid (150 mg)	236-7°
Petroleum ether: benzene (4:1)	6-10	Solid (20 mg)	279-80°
Petroleum ether: benzene (4:1)	11-13	Solid (10 mg)	175-6°

Elution with more polar solvents did not give any solid material.

Examination of fractions 1-5: Isolation of 15-bromo- $\beta$  amyrenonyl acetate 68 :

The fractions 1-5 (Table I) were combined (150 mg) and crystallised from a mixture of chloroform and methanol. After three crystallisation<sup>S</sup> it gave crystals 68, (130 mg), m.p. 238-40° ( $\alpha$ )<sub>D</sub> 88.8°. Compound 68 showed positive copper-wire test for bromine. TLC

showed a single round spot ( $R_f = 0.93$  in benzene).

Found: C, 68.14; H, 8.68%

Calculated for  $C_{32}H_{49}O_3Br$ : C, 68.44; H, 8.73%

UV :  $\lambda_{max}$  249.5 m ( $\epsilon$ , 11,000)

IR :  $\nu_{max}^{nujol}$  1750, 1650, 1250  $cm^{-1}$

Examination of fractions 6-10: Isolation of 16-oxo taraxeryl acetate 69 :

The fractions 6-10 (Table I) were combined (20 mg) and crystallised from a mixture of chloroform and methanol to give crystals 69, (15 mg) m.p. 280-82°, ( $\alpha$ )<sub>D</sub> -38.71°, negative copper-wire test for bromine. TLC showed a single spot ( $R_f$  0.62 in benzene).

Found: C, 79.62; H, 10.44%

Calculated for  $C_{32}H_{50}O_3$  : C, 79.29; H, 10.81%

UV :  $\lambda_{max}$  245 m $\mu$  ( $\epsilon$ , 10,500)

IR :  $\nu_{max}^{nujol}$  1730, 1680, 1250  $cm^{-1}$  (Fig. 8)

NMR spectrum (60 Mc): Peaks at 5.85 (vinyl proton), 2.10 (-O-CO-CH<sub>3</sub>), 4.5 (-CH - O-CO-CH<sub>3</sub>) ppm (Fig. 9)

Mass spectrum: m/e 358 (base peak), 298, 249 and 482 (M<sup>+</sup>)  
(Fig. 10)

Examination of fractions 11-13: Isolation of 15-bromo-9(11), 12-olean diene 70 :

Fractions 11-13 (Table I) were combined (10 mg) and crystallised from methanol to furnish crystals of 70 (8 mg), m.p. 176-8°,

$(\alpha)_D$  249.12°. The compound showed a single round spot on a chromatoplate ( $R_f = 0.45$  in benzene) and gave a positive copper wire test for bromine.

Found: C, 70.47; H, 8.84%

Calculated for  $C_{32}H_{49}O_2Br$ : C, 70.46; H, 8.99%

UV :  $\lambda_{max}$  276 m $\mu$  ( $\epsilon$ , 6000)

NMR spectrum (60 Mc): Peaks at 5.34, 5.85 (two vinyl proton), 2.08 (singlet,  $-O-CO-CH_3$ ), 4.65 (multiplet,  $\underline{HC}-O-CO-CH_3$ ), 4.18 ppm (multiplet,  $\underline{H}-C-Br$ ), (Fig. 12)

Mass. spectrum : 465, 546 ( $M^+$ ) (Fig. 13).

Zinc dust-acetic acid treatment of 68 : Formation of  $\beta$ -amyrenonyl acetate 71 :

To a solution of 15-bromo  $\beta$ -amyrenonyl acetate 68 (200 mg) in acetic acid (26 ml), was added zinc dust (12 mg) and the mixture refluxed for 3 hours. The reaction mixture was filtered, diluted with water and extracted with ether. The ether layer was washed with water till neutral and then dried ( $Na_2SO_4$ ). Removal of ether gave a solid residue (175 mg) which on crystallisation from chloroform-methanol furnished solid 71, m.p. 265-70°,  $(\alpha)_D$  48.08. This was found to be identical with an authentic sample of  $\beta$ -amyrenonyl acetate (m.m.p. and IR comparison).

Found: C, 79.60; H, 10.32%

Calculated for  $C_{32}H_{50}O_3$  : C, 79.62; H, 10.44%

UV :  $\lambda_{max}$  252.5 m $\mu$  ( $\epsilon$ , 11,000).

Preparation of 15-bromo- $\beta$ -amyrin acetate 72 : NBS - DMSO treatment of taraxeryl acetate 67 :

To a solution of taraxeryl acetate 67 (700 mg) dissolved in chloroform (46.5 ml) and dimethyl sulfoxide (23.25 ml) was added NBS (700 mg) in portions and kept overnight. Next day, the reaction mixture was filtered. The filtrate was extracted with chloroform (150 ml), washed with water and dried ( $\text{Na}_2\text{SO}_4$ ). On removal of the solvent under reduced pressure, a yellowish solid (500 mg) was obtained. The solid was dissolved in benzene (5 ml) and poured on a column of alumina (25 gm deactivated with 1.0 ml of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution.

Table II

Eluent	Fractions 50 ml each	Residue on evaporation	Melting point
Petroleum ether	1-5	Solid (475 mg)	178-80°

Elution with more polar solvents did not give any solid.

Fractions 1-5 (Table II) were collected and on crystallisation from a mixture of chloroform-methanol afforded crystals of 15-bromo  $\beta$ -amyrin acetate 72, m.p. 180-2°,  $(\alpha)_D$  47.37°. It gave a single spot

on a chromatoplate ( $R_f = 0.8$ ) in petroleum ether: benzene (3:2) and also showed positive copper-wire test for bromine.

Found: C, 70.09; H, 8.9%

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

UV : No absorption in the region 220-300  $m\mu$

IR : 2) <sup>nujol</sup> max 1720 and 1250  $cm^{-1}$  (Fig. 1)

NMR spectrum (60 Mc) : Peaks at 5.3 (multiplet, vinyl proton), 4.30 (multiplet,  $H_{CBr}$ ), 2.09 ( $-O-CO-CH_3$ ) and 4.53 ( $H-C-O-CO-CH_3$ ) ppm. (Fig. 2)

Mass spectrum: Peaks at  $m/e$  189, 216, 217, 249, 297, 466 ( $M^+ - HBr$ ), 547 ( $M^+$ ). (Fig. 3)

Zinc-acetic<sup>acid</sup> treatment of 72: Isolation of  $\beta$ -amyrin acetate 73:

To 15-bromo- $\beta$ -amyrin acetate 72 (100 mg) in acetic acid was added zinc-dust (10 mg) and the mixture was refluxed for 5 hours. The reaction mixture was filtered and then diluted with water. The product which precipitated out was filtered and washed thoroughly with water. The crude product (75 mg) was dissolved in benzene (3 ml) and poured on a column of alumina (12 gm deactivated with 0.5 ml of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution.

Table III

Eluent	Fractions 50 ml each	Residue on evaporation	Melting point
Petroleum ether	1-4	Solid (60 mg)	226-28°

Elution with more polar solvents did not give any solid material.

Fractions 1-4 (Table III) were combined (60 mg) and after repeated crystallisation from acetone afforded crystals of  $\beta$ -amyrin acetate 73, m.p. 227-30°,  $(\alpha)_D^{25}$  85.1°. The solid was found to be identical with an authentic sample of  $\beta$ -amyrin acetate (m.m.p and I.R. comparison, Fig. 4).

Found: C, 81.89; H, 11.08%

Calculated for  $C_{32}H_{52}O_2$  : C, 81.99; H, 11.18%

Chromium trioxide-acetic acid oxidation of 15-bromo- $\beta$ -amyrin acetate 72 : Preparation of 15-bromo  $\beta$ -amyrenonyl acetate 68 :

Chromium trioxide (300 mg) dissolved in acetic acid (7 ml) was added to a solution of 15-bromo  $\beta$ -amyrin acetate 72 (400 mg) in acetic acid (26.6 ml). The mixture was refluxed for one hour at 130-32°. The reaction mixture was then cooled, diluted with water and extracted with ether. The ethereal layer after being washed with

water till neutral was dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed and a solid residue (300 mg) was obtained. The solid was dissolved in benzene (2 ml) and poured on a column of alumina (25 gm deactivated with 1 ml of 10% aqueous acetic acid) developed with petroleum ether. The chromatogram was eluted with the following solvents.

Table IV

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether	1-7	Solid (275 mg) m.p. 236-38°

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

Fractions 1-7 (Table IV) were collected and combined, which on crystallisation from methanol gave crystals of 68, m.p. 238-40°,  $(\alpha)_D$  88.08°. This was found to be identical with 15-bromo  $\beta$ -amyrenonyl acetate obtained during aq. dioxan- NBS treatment of taraxeryl acetate (from fraction 1-5, Table I) m.m.p. and IR comparison, Fig.5.

Found: C, 68.24; H, 8.63%

Calculated for  $\text{C}_{32}\text{H}_{49}\text{O}_3\text{Br}$  : C, 68.44; H, 8.73%

UV :  $\lambda_{\text{max}}$  249 m $\mu$  ( $\epsilon$ , 11,000).

Solvolysis of 15-bromo $\beta$ -amyrenonyl acetate 72: Formation of Olean-12, 15-dien-3 $\beta$ -yl acetate 74 :

To the acetate 72 (200 mg) dissolved in acetic acid (27 ml) was added anhydrous potassium acetate (500 mg) and the mixture was refluxed for 5 hr. It was then cooled, diluted with water and extracted with ether. The ether solution after being washed with water till neutral, was dried ( $\text{Na}_2\text{SO}_4$ ). On removal of the solvent, a solid residue (150 mg) was obtained. The solid was dissolved in benzene (2 ml) and poured on a column of alumina (12 gm deactivated with 0.5 ml of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution.

Table V

---

Eluent	Fraction 50 ml each	Residue on evaporation
Petroleum ether	1-2	Oil (trace)
Petroleum ether	3-7	Solid (120 mg) m.p. 195-7°

---

Elution with more polar solvents did not give any solid.

---

Fractions 3-7 (Table V) were combined and on crystallisation from methanol afforded crystals of 74, m.p. 199-200°, ( $\alpha$ )<sub>D</sub> 41.86°. It showed a single spot on a chromatoplate ( $R_f$  = 0.43 in benzene) and negative copper wire test for bromine.

Found : C, 81.96; H, 10.81%

Calculated for C<sub>32</sub>H<sub>50</sub>O<sub>2</sub> : C, 82.35; H, 10.80%

UV : No absorption in the region 220-300 m $\mu$ .

NMR spectrum (60 Mc): Peaks at 5.2 to 5.6 (three vinyl Protons), 2.08 (-O-CO-CH<sub>3</sub>), 4.50 (H-C-O-CO-CH<sub>3</sub>) ppm (Fig. 6)

Dimethyl aniline treatment of 15-bromo- $\beta$ -amyrin acetate 72 :

Isolation of olean-12, 15-dien-3 $\beta$ -yl acetate 74 :

15-bromo  $\beta$ -amyrin acetate 72 (200 mg) was refluxed with dimethyl aniline (30 ml) for 6 hours. The reaction mixture was diluted with water, acidified with 6N hydrochloric acid (20 ml) and extracted with ether. The ethereal layer was washed with water till neutral and dried (Na<sub>2</sub>SO<sub>4</sub>). On removal of the solvent, a solid (175 mg) was obtained. The latter was dissolved in benzene (3 ml) and poured on a column of alumina (15 gm, deactivated with 6 ml of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution.

Table VI

---

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether	1-6	Solid (150 mg) m.p. 196-7°

---

Elution with more polar solvents did not give any solid material.

---

Fractions 1-6 (Table VI) were combined and crystallised from chloroform-methanol to give crystals of 74, m.p. 199-200°, ( $\alpha$ )<sub>D</sub> 41.86°. The solid was found to be identical (m.m.p. and IR, Fig. 7) with a sample of olean-12, 15-dien-3 $\beta$ -yl acetate 74 obtained from solvolysis of 15-bromo- $\beta$ -amyrin acetate with anhydrous potassium acetate and acetic acid.

Found : C, 82.57; H, 10.82%

Calculated for C<sub>32</sub>H<sub>50</sub>O<sub>2</sub> : C, 82.35; H, 10.80%

Preparation of  $\beta$ -amyrenonyl acetate 71 from  $\beta$ -amyrin acetate 73 :

$\beta$ -amyrin acetate (200 mg) dissolved in acetic acid (25 ml) was added to a solution of chromium trioxide (330 mg) in acetic acid (7 ml, 80%). The mixture was refluxed for one hour. On cooling

it was diluted with water, filtered and washed with water till neutral. The solid was dissolved in benzene (3 ml) and poured on a column of alumina (12 gm deactivated with 0.5 ml of 10% aqueous acetic acid). Following solvents were used for elution.

Table VII

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether	1-2	Oil (trace)
Petroleum ether	3-8	Solid (150 mg) m.p. 265-67 <sup>o</sup>

Elution with more polar solvents did not give any solid material.

Fractions 3-8 (Table VII) were combined and on crystallisation from methanol gave 71, m.p. 268-70<sup>o</sup>, ( $\alpha$ )<sub>D</sub> 48.8<sup>o</sup>.

Found: C, 79.55; H, 10.30%

Calculated for C<sub>32</sub>H<sub>50</sub>O<sub>3</sub>: C, 79.62; H, 10.40%

UV:  $\chi_{\max}$  252.5 m $\mu$  ( $\epsilon$ , 11,000).

Attempted sodium borohydride reduction of 16-oxo-taraxeryl acetate 69 in tetrahydrofuran (THF):

To a solution of 16-oxo-taraxeryl acetate 69 (200 mg) in dry tetrahydro furan (50 ml) was added sodium-borohydride (200 mg) and

the mixture was stirred for 6 hours at room temperature. A portion of the solvent was removed by distillation, cooled and acidified with dilute hydrochloric acid and then extracted with ether. The ethereal layer was washed with water till neutral and then dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the <sup>ether</sup> gave a solid which on crystallisation from methanol gave crystals m.p.  $280-82^\circ$ . The solid was found to be identical with the starting material 16-oxo-taraxeryl acetate (m.m.p.).

Attempted reduction of 16-oxo-taraxeryl acetate 69 with sodium borohydride in methanol:

To compound 69 (200 mg) dissolved in methanol (50 ml) was added sodium borohydride (200 mg) and the reaction mixture was stirred for 4 hours at room temperature. After working up in the usual way it gave a solid, m.p.  $279-81^\circ$ , identified as the original 16-oxo-taraxeryl acetate by m.m.p.

Meerwein-Ponndorff reduction of 16-oxo-taraxeryl acetate 69:

A mixture of 16-oxo-taraxeryl acetate 69 (250 mg), aluminium isopropoxide (325 mg) in dry isopropanol (6 ml) was distilled slowly with the addition of isopropanol to maintain constant volume. After 6 hours, the distillate no longer contained acetone. The solution was concentrated to a small volume. The reaction mixture was then diluted with water followed by 10% sulphuric acid (20 ml) and then extracted with ether. The solid product obtained after removal of ether was dissolved in benzene (2 ml) and poured on a column of

alumina (12 gm deactivated with 0.5 ml of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used as eluent.

Table VIII

Eluent	Fractions 50 ml each	Residue
Petroleum ether	1-2	trace of oil
Petroleum ether: benzene (4:1)	3-7	Solid m.p. 290-2° 200 mg

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

The solid from fraction 3-7 (Table VIII) were combined which after crystallisation from methanol afforded 16-oxo-taraxerol 78 m.p. 292-3°.

Found: C, 81.20; H, 11.08%

Calculated for  $C_{30}H_{50}O_2$  : C, 81.39; H, 11.38%

IR :  $\nu_{\text{max}}^{\text{KBr}}$  3360, 1680  $\text{cm}^{-1}$ .

Lithium aluminium hydride reduction of 16-oxo-taraxeryl acetate 69:

Formation of 16-oxo-taraxerol 78 :

To the ketone 69 (200 mg) dissolved in dry tetrahydro furan

was added lithium aluminium hydride (25 mg) and the mixture was refluxed for 10 hours on water bath. The reaction mixture was then cooled and to this was added dropwise a cold saturated solution of sodium sulphate (15 ml). After this addition the mixture was extracted with ether, washed to neutral with water and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of ether gave a solid (190 mg) which was chromatographed over alumina. A column of alumina (10 gm deactivated with 0.4 ml of 10% aqueous acetic acid) was developed with petroleum ether and the above residue dissolved in benzene (4 ml) was added to it. The following solvents were used for elution (Table IX).

Table IX

---

Eluent	Fractions 50 ml each	Residue
Petroleum ether	1-2	Nil
Petroleum ether: benzene (4:1)	3-6	Crystalline solid 180 mg m.p. $290-2^\circ$ .

---

Elution with more polar solvents did not yield any material.

---

Fractions 3-6 (Table IX) were combined and the solid (180 mg) was crystallised from chloroform and methanol mixture when pure crystals of 78 m.p.  $292-3^\circ$ , was obtained. This was found to be identical with

16-oxo-taraxerol obtained by Meerwein-Ponndorff reduction of 69 (m.m.p. and I.R. comparison).

Acetylation of 16-oxo-taraxerol 78 : Preparation of 16-oxo-taraxeryl acetate 69 :

The compound 78 (200 mg) was acetylated with pyridine (2 ml) and acetic anhydride (2 ml) in the usual way. The solid obtained, after crystallisation from methanol gave crystals of 69 m.p. 280-2°, found to be identical with 16-oxo-taraxeryl acetate 3 (m.m.p.).

Treatment of taraxeryl acetate 67 with NBS (2 moles) in carbon tetrachloride: Isolation of 16-bromo-olean-9,12,15-trien-3<sup>(11)</sup>β-yl acetate 75 :

To a solution of taraxeryl acetate (1 gm) dissolved in dry carbon-tetrachloride (185 ml), was added NBS (700 mg) and the reaction mixture was refluxed for 3 hours in presence of visible light (100 watt bulb). As the reaction proceeded, insoluble succinimide, which was at the bottom, floated on the surface. The reaction mixture was then cooled and filtered. The filtrate was extracted with chloroform (200 ml), washed with water and then dried (Na<sub>2</sub>SO<sub>4</sub>). On removal of the solvent under reduced pressure a solid (800 mg) was obtained which was chromatographed on a column of alumina (25 gm deactivated with 1 ml of 10% aqueous acetic acid). The chromatogram was developed with petroleum ether and the solid (800 mg) dissolved in benzene (4 ml) was placed on the column. It was eluted with the following solvents (Table X).

Table X

Eluent	Fractions 50 ml each	Residue
Petroleum ether	1-9	Solid m.p. 238-39° (775 mg)

Elution with more polar solvents did not give any material.

Fractions 1-9 (Table X) were combined (775 mg) and after several crystallisation<sup>55</sup> from methanol furnished 75, m.p. 240°, ( $\alpha$ )<sub>D</sub> 267.53°. It showed a single spot on a chromatoplate ( $R_f$  0.84) in petroleum ether: benzene (3:2) and showed positive copper wire test for bromine.

Found: C, 70.40; H, 8.37%

Calculated for  $C_{32}H_{47}O_2Br$ : C, 70.70; H, 8.67%

UV:  $\lambda_{max}$  279 m $\mu$  ( $\epsilon$ , 6000)

IR:  $\nu_{max}^{nujol}$  1725, 1250, 840  $cm^{-1}$  (Fig. 14)

NMR spectrum (60 Mc): Peaks between 5.68 to 5.88  
(three vinyl protons), 2.10 (-O-CO-CH<sub>3</sub>) and 4.5  
(-CHOCOCH<sub>3</sub>) ppm (Fig. 15)

Mass spectrum: m/e, 544 (isotope), 543, 542 (M<sup>+</sup>) (Fig. 16)

In another experiment this product showed a very weak peak between 620-25 (it was not possible to count Fig. 17) due to a small contaminant<sup>of</sup> a dibromide, other peaks were similar to as shown in Fig. 16.

Attempted zinc-acetic acid treatment of 16-bromo-olean-9,12,15-trien-3 $\beta$ -yl acetate 75:

To a solution of 75 (200 mg) in glacial acetic acid (40 c.c) was added zinc-dust (40 mg) and the reaction mixture was refluxed for 8 hours. After working up in the usual way it afforded a solid which on crystallisation from methanol gave crystals m.p. 239-40°. This solid was found to be identical with the starting material 75 (m.m.p.).

Attempted dehalogenation of 75 with palladium-on-charcoal catalyst :

To the 16-bromo-oleana-9,12,15-trien-3  $\beta$ -yl-acetate 75 (200 mg) dissolved in ethyl acetate (40 ml) was added 10% palladium-on-charcoal catalyst (100 mg) and the mixture was stirred at room temperature in an atmosphere of hydrogen. No absorption of hydrogen took place even after eight hours. It was then filtered and the filtrate was evaporated to dryness. The residue m.p. 238-39° (190 mg), on crystallisation from methanol gave crystals, m.p. 240° and was found to be unchanged 75 (m.m.p.).

Attempted dehalogenation of 75 with Adam's catalyst:

A solution of compound 75 (200 mg) in ethyl acetate (40 ml) was stirred in presence of Adams catalyst (20 mg) at room temperature and pressure. During a period of ten hours the mixture did not show any absorption of hydrogen. On working up the reaction mixture in the usual manner, a residue (200 mg) was obtained. The latter on crystallisation from methanol afforded crystals, m.p.  $240^{\circ}$ , and was found to be identical with the starting material 75 .

Attempted dehalogenation of 75 with lithium carbonate and lithium bromide:

A mixture of compound 75 (200 mg) in dimethyl formamide (30 ml), lithium carbonate (200 mg) and lithium bromide (270 mg) was stirred in an atmosphere of nitrogen at  $100^{\circ}$  for 3 hours. The product was then taken up in chloroform and the chloroform layer was washed with 40% acetic acid (50 ml), then with water till neutral and then dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvent gave a residue (175 mg), which on crystallisation from methanol furnished a solid, m.p.  $239-40^{\circ}$ , which did not depress the melting point when mixed with the starting material 75 .

Attempted solvolysis of 75 with anhydrous potassium acetate and acetic acid: (SN1)

16-bromo compound 75 (200 mg) was refluxed with anhydrous potassium acetate (150 mg) and acetic acid (20 ml) for 4 hours. The product was then diluted with water and the precipitate was filtered,

and washed thoroughly with water. The crude product (150 mg) on crystallisation from methanol furnished a solid, m.p.  $240^{\circ}$ , identical with the starting material (m.m.p.).

Attempted dehydrohalogenation of 75 with dimethyl aniline:

Compound 75 (200 mg) was refluxed for 10 hours with freshly distilled dimethyl aniline (50 ml). The solvent was removed by distillation under reduced pressure, and the residue was diluted with water and extracted with ether. The ethereal layer was washed with 6N hydrochloric acid (10 ml) followed by water till neutral and then dried ( $\text{Na}_2\text{SO}_4$ ). On removal of solvent a solid residue (175 mg) was obtained which on crystallisation afforded a solid, m.p.  $240^{\circ}$ , identical with 16-bromo-olean-9,<sup>(11)</sup>12,15-trien-3  $\beta$ -yl acetate 75 (m.m.p.).

Formation of olean-12,15-dien-3  $\beta$ -yl acetate 74: Treatment of taraxeryl acetate 67 with NBS (1 mole) in carbon tetrachloride :

To a solution of taraxeryl acetate 67 (300 mg), dissolved in dry carbon tetrachloride (100 ml), was added NBS (116 mg) and benzoyl peroxide (a few crystals) and the reaction mixture was refluxed for six hours in presence of visible light (600 watt bulb). The reaction mixture was cooled and filtered and the filtrate was extracted with chloroform. The chloroform layer was washed with water and dried ( $\text{Na}_2\text{SO}_4$ ). On evaporation of solvent, a yellow solid (250 mg) was obtained. The latter was taken up in ether, washed with 5% cold sodium

hydroxide solution, followed by water till neutral and dried over anhydrous sodium sulphate. On removal of ether, a solid residue was obtained which after several crystallisations gave solid 74 m.p. 196-9°, ( $\alpha$ )<sub>D</sub> 41.86°. It showed a single spot on a chromatoplate ( $R_f = 0.43$  in benzene) and showed negative copper wire test for bromine. This product 74 was found to be identical with the product obtained by solvolysis of 15-bromo- $\beta$ -amyrin acetate 72 (m.m.p. and I.R ).

Found: C, 82.00; H, 10.70%

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

UV : No absorption above 220 m $\mu$ .