

CHAPTER 6
EXPERIMENTAL

Melting points in degree Celsius were determined in sulphuric acid bath and are uncorrected. Optical rotations were determined in chloroform unless otherwise mentioned. IR spectra were recorded in KBr disc with nujol mulling. NMR spectra were recorded in CDCl_3 solution with TMS as an internal standard. All samples for analysis were dried in vacuo for 36 hours. Thin layer chromatography (TLC) experiments were performed, if not stated otherwise, on micro plates prepared by dipping the plate in a slurry of silica gel G (Merck) in CHCl_3 ; spots were developed by exposing to iodine vapour. Column chromatography was carried out with BDH silica gel (50-120 mesh). Each column was developed with petroleum ether. Petroleum ether used had boiling point $60-80^\circ$ Celsius. Extracts of products in organic solvent were generally washed with water and dried over anhydrous sodium sulphate. All evaporations were carried out under reduced pressure on a water bath. All acetylations (acetic anhydride) and oxidations (chromic oxide) were performed in anhydrous pyridine. After the reactions, the products were diluted with water and extracted with diethyl ether or chloroform. The organic

solvent layer was washed with 2N HCl and then water repeatedly to remove pyridine. Finally it was dried over anhydrous sodium sulphate and then evaporated to yield the desired material.

Extraction of *Gynocardia odorata* (R Br)

Air dried and powdered bark (10 kg) of *Gynocardia odorata* (R Br) was extracted with benzene in Soxhlet apparatus for 36 hours. The extract was cooled at room temperature and benzene was evaporated under reduced pressure to give a gummy residue (50 g). The residue was extracted with solvent ether while another insoluble portion separated out (2 g).

The ethereal solution was washed with 10% aqueous sodium hydroxide solution (3 x 500 ml) and then with water till neutral. The neutral ethereal solution was dried and the ether was distilled off to yield gummy residue (35 g), which constituted the neutral part of the extract.

The alkali washed portion, after acidification with dilute hydrochloric acid (1N), was extracted with ether which on usual work-up furnished acid part (10 g) of the extract.

Purification of ether insoluble part of the extract : isolation of odolactone (37)

The above ether insoluble part was dissolved in chloroform and few milligram of activated charcoal was added to it. The mixture was boiled and filtered hot to remove charcoal ingredients. To the filtrate hot methanol was added. The mixture furnished a semi-amorphous solid.

The process of crystallization was repeated unless the product gave a single spot on TLC. The compound, named odolactone, had mp $> 320^{\circ}$, $[\alpha]_D^{25} - 47.06^{\circ}$. It was shown to be a new triterpenoid lactone.

Elemental analysis : Found : C 79.0, H 10.11%

Calculated for $C_{30}H_{46}O_3$: C 79.30, H 10.13%

Mass spectrum : Fig 1

IR spectrum : Fig 2

CD spectrum : Fig 3

1H NMR spectrum : Fig 4

^{13}C NMR spectrum : Fig 6

Reduction of odolactone (37) with sodium borohydride

Sodium borohydride (1 g) was added to a solution of odolactone (0.20 g) in methanol-dioxane (400 ml) and the mixture was kept at room temperature for 24 hours. The solution was then concentrated under reduced pressure, diluted with water, while a solid mass separated out. The solid was extracted with chloroform and washed several times with water. It was then dried and the solvent was distilled off. The solid thus obtained was chromatographed over silica gel (5 g) column and the following fractions were collected (Table 9).

Examination of fractions 12-14 (Table 9)

The constituents of the fractions 12-14 (Table 9) were found to be identical (examined by TLC). They were mixed and crystallized from chloroform-methanol mixture for two times to yield a solid, mp $> 320^{\circ}$. This was identical with epi-odollactone (44) isolated from neutral part of G odorata (co-TLC and co-IR).

Table 9

Eluent	Fractions collected (100 ml each)	Residue after removal of solvent	Melting point
Petroleum ether	1- 2	nil	-
Pet ether:benzene (4:1)	3- 4	nil	-
Pet ether:benzene (3:2)	5- 6	nil	-
Pet ether:benzene (2:3)	7- 8	nil	-
Pet ether:benzene (1:4)	9-10	nil	-
Benzene	10-11	nil	-
Benzene:solvent ether (19:1)	12-14	solid (0.1g)	>320°
Benzene:solvent ether (9:1)	15-17	solid (0.05g)	>320°

Further elution with more polar solvent did not furnished any material

Elemental analysis : Found : C 78.90, H 10.52%

Calculated for $C_{30}H_{48}O_3$: C 78.95, H 10.53%

Examination of fraction 15-17 (Table 9)

The constituents of fractions 15-17 (Table 9) were found to be identical (examined by TLC). They were mixed and crystallized from chloroform-methanol (two times) to yield a pure compound, mp > 320°. This was found to be identical with odollactone (41) isolated from G odorata (co-TLC and co-IR).

Elemental analysis : Found : C 78.92, H 10.50%

Calculated for $C_{30}H_{48}O_3$: C 78.95, H 10.53%

Chromatography of the neutral part of *G odorata*

The neutral part (35 g) of the extract of *G odorata* was dissolved in a minimum volume of benzene and poured into 100 g silica gel which was dried over water bath in an open can. It was then poured over a column of silica gel (775 g) and the column was eluted with solvents as shown in Table 10.

Isolation of β -sitosterol

The material under column B (Table 10) of fraction 4 was crystallized from chloroform-methanol mixture to afford white flakes, mp 136-137°, $[\alpha]_D^{25} - 34^\circ$. It showed no depression in melting point when mixed with authentic sample of β -sitosterol.

Elemental analysis : Found : C 83.34, H 11.62%

Calculated for $C_{29}H_{50}O$: C 83.98, H 12.15%

Preparation of β -sitosterol acetate

The above solid (0.2 g) was dissolved in 2 ml pyridine and 2 ml acetic anhydride was added to it. The mixture was kept overnight at room temperature. After usual work-up, the solid on crystallization from chloroform-methanol furnished crystals, mp 130-131°, $[\alpha]_D^{25} - 40^\circ$. It was found to be identical with authentic sample of β -sitosterol acetate (mixed mp, co-TLC and co-IR).

Elemental analysis : Found : C 78.50, H 11.05%

Calculated for $C_{31}H_{52}O_3$: C 78.81, H 11.01%

Table 10
Chromatography results of the neutral part of *Gynocardia odorata*

Fraction number	Eluent	Nature of residue with different amount of eluents			Melting point of the materials under Column B
		Column A	Column B ^X	Column C	
1	Petroleum ether	5 x 500 ml ^Y Oil (6 g) ^Z	-	1 x 500 ml ^Y Nil ^Z	-
2	Pet ether:benzene (4:1)	5 x 500 ml ^Y Oil (6 g) ^Z	-	1 x 500 ml ^Y Nil ^Z	-
3	Pet ether:benzene (3:2)	5 x 500 ml ^Y Oil (6 g) ^Z	-	1 x 500 ml ^Y Nil ^Z	-
4	Pet ether:benzene (2:3)	4 x 500 ml ^Y Oil (3 g) ^Z	5 x 500 ml ^Y Solid (5 g) ^Z	1 x 500 ml ^Y Nil ^Z	128-132°
5	Pet ether:benzene (4:1)	2 x 500 ml ^Y Oil (1 g) ^Z	2 x 500 ml ^Y Solid (0.5 g) ^Z	1 x 500 ml Nil ^Z	320°
6	Benzene	2 x 500 ml ^Y Oil (1 g) ^Z	2 x 500 ml ^Y Solid (2 g) ^Z	1 x 500 ml Nil ^Z	320°
7	Benzene:solvent ether (19:1)	2 x 500 ml ^Y Oil (1 g) ^Z	2 x 500 ml Solid (0.3 g) ^Z	1 x 500 ml ^Y Nil ^Z	320°
8	Benzene:solvent ether (9:1)	2 x 500 ml ^Y Oil (1 g) ^Z	2 x 500 ml ^Y Solid (0.5 g) ^Z	1 x 500 ml ^Y Nil ^Z	320°
9	Benzene:solvent ether (4:1)	2 x 500 ml ^Y Oil (1 g) ^Z	2 x 500 ml Solid (0.5 g) ^Z	1 x 500 ml ^Y Nil ^Z	285-290°

Further elution with more polar solvent did not yield any solid materials

X Only materials under column B were examined

Y Amount of eluents

Z Nature and amount of residue after evaporation of solvents

Isolation of O-acetylodollactone (40)

Compound from fraction 5 under column B (Table 10) was repeatedly crystallized from chloroform-methanol to yield O-acetylodollactone (40), mp $> 320^{\circ}$, $[\alpha]_D^{25} - 19^{\circ}$ (MeOH).

Elemental analysis : Found : C 76.98, H 10.15%

Calculated for $C_{32}H_{50}O_4$: C 77.11, H 10.04%

Mass spectrum : Fig 11

IR spectrum : Fig 12

1H NMR spectrum : Fig 13

Alkali hydrolysis of O-acetylodollactone (40)

A mixture of O-acetylodollactone 40 (0.05 g) and 5% methanolic potassium hydroxide (10 ml) was refluxed for 3 hr, water was added, acidified with 2 N hydrochloric acid and the resulting mixture was extracted with chloroform. The extract was washed with water, dried and then evaporated. The residue was chromatographed over silica gel, benzene-solvent ether (9:1) eluates of which gave odollactone 41 (0.03 g), crystallized from chloroform-methanol, mp $> 320^{\circ}$.

Elemental analysis : Found : C 79.00, H 10.41%

Calculated for $C_{30}H_{48}O_3$: C 78.95, H 10.53%

Isolation of epi-odollactone (44)

Compound from fraction 7 under column B (Table 10) was repeatedly crystallized from chloroform-methanol to yield pure epi-odollactone (44), mp > 320 , $[\alpha]_D^{25} - 2.48^{\circ}$.

Elemental analysis : Found : C 78.92, H 10.50%

Calculated for $C_{30}H_{48}O_3$: C 78.95, H 10.53%

Mass spectrum : Fig 14
 IR spectrum : Fig 15
¹H NMR spectrum : Fig 16

Acetylation of epi-odollactone (44)

To a solution of epi-odollactone 44 (0.05 g) in pyridine (1.5 ml), acetic anhydride (1.5 ml) was added and the reaction mixture was kept overnight at room temperature. After usual work-up, the product was purified by crystallization from chloroform-methanol to furnish O-acetyl-epi-odollactone (45), mp > 320°.

Elemental analysis : Found : C 77.15, H 10.20%
 Calculated for C₃₂H₅₀O₄ : C 77.11, H 10.04%
 IR spectrum : Fig 17
¹H NMR spectrum : Fig 18

Oxidation of epi-odollactone (44)

Anhydrous chromic oxide (0.1 g) was added to cold pyridine (1.5 ml). It was slowly added to a solution of epi-odollactone 44 (0.1 g) in pyridine (1.5 ml) and the reaction mixture was kept overnight at room temperature. It was then poured in water and the mass was extracted with chloroform. The chloroform layer was washed with 2N hydrochloric acid, then with water, dried and evaporated to yield gummy residue. It showed a single spot on TLC. It was chromatographed over silica gel to make it gum free and the substance obtained was crystallized from chloroform-methanol to furnish semi-amorphous solid, mp > 320°. It was found to be identical with odollactone 37 (co-TLC and co-IR).

Elemental analysis : Found : C 79.50, H 10.01%
 Calculated for C₃₀H₄₆O₃ : C 79.30, H 10.13%

Isolation of odollactone (41)

Compound of fraction 8 under column B (Table 10) was repeatedly crystallized from chloroform-methanol to afford crystalline solid, mp $> 320^{\circ}$, $[\alpha]_D^{25} - 12.14^{\circ}$. It was found to be 3 α -hydroxyfriedelan-27 \rightarrow 15 α -olide (41), named odollactone.

Elemental analysis : Found : C 78.92, H 10.50%

Calculated for $C_{30}H_{48}O_3$: C 78.95, H 10.53%

IR spectrum : Fig 19

1H NMR spectrum : Fig 20

Acetylation of odollactone (41)

To a solution of odollactone 41 (0.05 g) in pyridine (1.5 ml), acetic anhydride (1.5 ml) was added and the reaction mixture was kept overnight at room temperature. After usual work-up, the product was crystallized from chloroform-methanol to furnish crystalline solid, mp $> 320^{\circ}$. It was found to be identical with O-acetylodollactone 40 (co-TLC and co-IR).

Elemental analysis : Found : C 77.10, H 10.00%

Calculated for $C_{32}H_{50}O_4$: C 77.11, H 10.04%

Oxidation of odollactone (41)

Odollactone 41 (0.05 g) in pyridine (1 ml) was oxidized with CrO_3 -pyridine (0.05 g CrO_3 in 2 ml pyridine) complex which gave gummy residue after usual work-up. The product was made gum free by silica gel column chromatography and then crystallized from chloroform-methanol to furnish semi amorphous solid, mp $> 320^{\circ}$. It was found to be identical with odollactone 37 (co-TLC and co-IR).

Elemental analysis : Found : C 79.15, H 10.10%
 Calculated for $C_{30}H_{46}O_3$: C 79.30, H 10.13%

Isolation of trichadenic acid A (43)

Compound from fraction 9 under column B (Table 10) was purified by repeated crystallization from chloroform-methanol to afford crystalline solid, mp 292-293°, $[\alpha]_D^{25} + 25^\circ$. It was shown to be identical with trichadenic acid A from its physical and chemical properties.

Elemental analysis : Found : C 78.48, H 10.80%
 Calculated for $C_{30}H_{50}O_3$: C 78.60, H 10.92%
 Mass spectrum : Fig 21
 IR spectrum : Fig 22

Esterification of trichadenic acid A (43) with diazomethane

Trichadenic acid A 43 (0.1 g) was dissolved in ether (20 ml) and cooled at 0°. To this solution, a solution of diazomethane in ether at 0°, prepared from nitrosomethyl urea (0.1 g) by decomposition with potassium hydroxide, was added. The mixture was kept for 12 hr maintaining the temperature below 5° and then kept at room temperature. The excess of diazomethane was destroyed with acetic acid. The ether solution was then washed with water, 10% sodium bicarbonate solution and again with water till neutral and dried. Evaporation of ether yielded the solid (0.1 g) which gave a single spot on TLC. Repeated crystallization of the solid from chloroform-methanol furnished crystalline solid of methyltrichadenate A (46), mp 200-201°, $[\alpha]_D^{25} + 95.5$.

Elemental analysis : Found : C 78.69, H 10.98%
 Calculated for $C_{31}H_{52}O_3$: C 78.81, H 11.01%

Acetylation of trichadenic acid A (43)

To a solution of trichadenic acid A 43 (0.05 g) in pyridene (1.5 ml), acetic anhydride (1.5 ml) was added and the reaction mixture was kept overnight at room temperature. After usual work-up, the product was crystallized from chloroform-methanol to afford crystalline solid of O-acetyl-trichadenic acid A (43a) mp 250-251°, $[\alpha]_D^{25} + 28.34^\circ$.

Elemental analysis : Found : C 76.59, H 10.50%

Calculated for $C_{32}H_{52}O_4$: C 76.80, H 10.40%

Oxidation of trichadenic acid A (43)

Trichadenic acid A 43 (0.2 g) in pyridine (3 ml) was treated with CrO_3 -pyridine complex (0.2 g CrO_3 in 3 ml pyridine) and the reaction mixture was kept overnight at room temperature. After usual work-up, the product was made gum free by silica gel column chromatography and crystallized from chloroform-methanol to afford crystalline solid of trichadonic acid (47), mp 243-244°, $[\alpha]_D^{25} + 2.69^\circ$.

Elemental analysis : Found : C 78.88, H 10.50%

Calculated for $C_{30}H_{48}O_3$: C 78.95, H 10.53%

Esterification of trichadonic acid (47) with diazomethane

Trichadonic acid 47 (0.1 g) in ether (20 ml) was treated with an excess of diazomethane at 0° and left overnight maintaining the temperature below 5°. The product, after usual work-up, was crystallized from chloroform-methanol to furnish crystalline solid of methyltrichadonate (48), mp 180-181°, $[\alpha]_D^{25} + 5.0^\circ$.

Elemental analysis : Found : C 79.00, H 10.65%
 Calculated for $C_{31}H_{50}O_3$: C 79.15, H 10.64%

Chromatography of the acid part of *G odorata*

The acid part of the extract of *G odorata* was dissolved in minimum volume of benzene and poured over a column of silica gel (250 g). The column was eluted with solvents as shown in Table 11.

Table 11

Chromatography results of the acid part of *G odorata*

Eluent	Fractions collected (250 ml each)	Nature of residue after removal of solvents	Melting point
Petroleum ether	1- 4	oil (1 g)	-
Pet ether:benzene (4:1)	5- 8	oil (1 g)	-
Pet ether:benzene (3:2)	9-12	oil (1 g)	-
Pet ether:benzene (2:3)	13-16	oil (1 g)	-
Pet ether:benzene (1:4)	17-20	oil (1 g)	-
Benzene	21-24	oil (1.5 g)	-
Benzene:solvent ether (9:1)	25-28	oil (0.5 g)	-
Benzene:solvent ether (4:1)	29-32	solid (0.5 g)	285-290°

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

Isolation of trichadenic acid A (43) from acid part

The constituents of the fractions 29-32 (Table 11) were found to be identical (examined by TLC). They were mixed and crystallized from chloroform-methanol to yield

crystalline solid having constant melting point 292-293° and $[\alpha]_D^{25} + 25^\circ$. The compound is found to be identical with trichadenic acid A isolated from neutral part of G odorata (mixed mp, co-TLC and co-IR).

Elemental analysis : Found : C 78.50, H 10.80%

Calculated for $C_{30}H_{50}O_3$: C 78.60, H 10.92%

Modified Wolff-Kishner reduction of odolactone (37) :
preparation of deoxyodolactone (49) and iso-deoxyodolactone
(50)

Odolactone (1 g) in diethylene glycol (150 ml) was refluxed with hydrazine hydrate (11.5 ml) for 30 minutes. After addition of KOH (1 g) the mixture was further refluxed for one hour. The condenser was then removed and the mixture was heated to 190°. After refluxing for another 2.5 hr the reaction mixture was cooled, diluted with water when a solid material separated out. It was extracted with ether while a portion of the solid remained insoluble. The ether was evaporated to furnish solid A. The ether insoluble portion was separated by filtration to furnish solid B.
Purification of solid A to obtain deoxyodolactone (49)

The solid A (0.5 g) was dissolved in a minimum volume of benzene and chromatographed over silica gel (12.5 g). Elution of the column with petroleum ether : benzene (4:1) furnished a solid that was crystallized from chloroform-methanol to afford crystals of deoxyodolactone 49 (friedelan-27→15 α -olide), mp 314-315°, $[\alpha]_D^{25} -14.25^\circ$.

Elemental analysis : Found : C 81.85, H 10.88%

Calculated for $C_{30}H_{48}O_2$: C 81.82, H 10.91%

Mass spectrum : Fig 24

IR spectrum : Fig 25

1H NMR spectrum : Fig 26

^{13}C NMR spectrum : Fig 28

Purification of solid B to obtain iso-deoxydolactone (50)

The solid B (0.4 g) was chromatographed over silica gel (10 g) and elution of the column with petroleum ether : benzene (3:1) afforded solid that was crystallized from chloroform-methanol to yield crystalline iso-deoxydolactone 50 (friedelan-27→16 α -olide), mp > 320°, $\angle^{-\alpha} \int_D + 23^\circ$.

Elemental analysis : Found : C 81.88, H 10.90%

Calculated for C₃₀H₄₈O₂ : C 81.82, H 10.91%

Mass spectrum : Fig 29

IR spectrum : Fig 30

¹H NMR spectrum : Fig 31

¹³C NMR spectrum : Fig 32

Conversion of deoxydolactone (49) to friedelan-27→16 α -olide (50) with KOH-diethylene glycol

A mixture of deoxydolactone 50 (0.2 g) and KOH (0.2 g) in diethylene glycol (15 ml) was heated in a round bottom flask in an heating mantel initially without condenser till all the moisture escaped from the mixture. The condenser was then fitted and the mixture was refluxed for another four hours. The mixture was then cooled, acidified with dil HCl and extracted with chloroform. The chloroform extract was washed with water, dried and then evaporated. The residue was chromatographed over silica gel (5 g). Elution of the column with pet ether : benzene (4:1) gave deoxydolactone 49 (0.04 g) as crystals (CHCl₃-MeOH), mp 314-315°, $\angle^{-\alpha} \int_D - 14.25^\circ$. Further elution with pet ether : benzene (3:1) gave iso-deoxydolactone 50 (friedelan-27→16 α -olide) (0.15 g) as white crystals (CHCl₃-MeOH), mp > 320°, $\angle^{-\alpha} \int_D + 23^\circ$.

Conversion of odollactone (41) to 3 α -hydroxyfriedelan-27
 →16 α -olide (51) with KOH-diethylene glycol

A mixture of odollactone 41 (0.1 g) and KOH (0.1 g) in diethylene glycol (10 ml) was refluxed for 4 hr as described before. The solid obtained after usual work-up was chromatographed over silica gel (3 g). Elution of the column with benzene : solvent ether (4:1) gave 3 α -hydroxyfriedelan-27 →16 α -olide 51 (0.08 g) as white crystals (from CHCl_3 -MeOH), mp > 320°.

Elemental analysis : Found : C 78.90, H 10.50%

Calculated for $\text{C}_{30}\text{H}_{48}\text{O}_3$: C 78.95, H 10.53%

IR spectrum : Fig 33

^1H NMR spectrum : Fig 34

Treatment of odolactone (37) with KOH-diethylene glycol :
 preparation of 3 α -hydroxyfriedelan-27 →16 α -olide (51)
 from odolactone

A mixture of odolactone 37 (0.1 g) and KOH (0.1 g) in diethylene glycol was refluxed for 4 hr. The residue obtained after usual work-up was chromatographed over silica gel (3 g). Elution of the column with benzene : solvent ether (9:1) yielded small amount solid and it was found to be a mixture of several compounds (from TLC). A second solid (0.08 g) was obtained after elution the column with benzene : solvent ether (4:1) which afforded white crystals, mp > 320° from CHCl_3 -MeOH. It was found to be identical with 3 α -hydroxyfriedelan-27 →16 α -olide 51 (co-TLC & co-IR).

Treatment of odollactone (41) with lithium-ethylenediamine :
 preparation of 3 α -hydroxyfriedelan-27-oic acid (43)

0.1 g odollactone (41) was dissolved in 40 ml dry

ethylenediamine. To the solution 0.1 g lithium was added in small portions with stirring in an atmosphere of nitrogen gas. After the addition of lithium, the reaction mixture was cooled and solid NH_4Cl was added to destroy the excess lithium. Then the mixture was acidified with 6 N HCl and extracted with solvent ether. The ether layer was then washed with water, dried and evaporated to yield solid material. The solid was chromatographed over silica gel (3 g). The elution of the column with benzene : solvent ether (4:1) afforded a solid (0.08 g) that was crystallized from CHCl_3 -MeOH to furnish crystals, mp $292-293^\circ$, $[\alpha]_D^{25} + 25^\circ$, IR; 3300(OH) & 1685(COOH) cm^{-1} . It gave methyl ester with diazomethane which had mp $200-201^\circ$, $[\alpha]_D^{25} + 95.5^\circ$, identical with methyl-3 α -hydroxyfriedelan-27-oate 46 (methyltrichadenate A) (mmp, co-TLC & co-IR).

Treatment of O-acetyldollactone (40) with lithium-ethylenediamine : isolation of friedelan-27-oic acid (52) and trichadenic acid A (43)

A mixture of 0.1 g O-acetyldollactone (40) and 0.1 g lithium in 40 ml ethylenediamine was refluxed for 2 hr under N_2 atmosphere as described above. The residue obtained after usual work-up was chromatographed over silica gel (3 g). Elution with benzene gave friedelan-27-oic acid 52 (0.04 g) as white crystals (from CHCl_3 -MeOH), mp $290-291^\circ$, $[\alpha]_D^{25} + 28.57^\circ$, IR 1680 cm^{-1} (COOH). Methyl ester (with diazomethane), white crystals (from CHCl_3 -MeOH), mp $180-181^\circ$, $[\alpha]_D^{25} - 24^\circ$, IR 1735 cm^{-1} (COOMe); $^1\text{H NMR } \delta$ 0.73 (3H, d, $J = 6 \text{ Hz}$), 0.78, 0.88, 0.96, 1.02, 1.14, 1.23 (18H, s each, 6 Me groups), 3.72 (3H, s, COOCH_3); $^{13}\text{C NMR } \delta$ 177.17 (s), 60.66 (d), 54.98 (s), 53.20 (d), 50.53 (q), 45.85 (d), 43.06 (d), 41.14 (t), 39.31 (s), 38.19 (t), 37.89 (t), 37.58 (s), 37.19 (s), 36.20 (t), 35.64 (t), 35.5 (q), 33.18 (t), 32.36

(t), 31.03 (q), 30.87 (t), 30.51 (s), 30.33 (q), 28.31 (s), 27.78 (t), 27.30 (t), 22.72 (q), 20.58 (t), 18.59 (q), 18.40 (t), 15.09 (q), 13.56 (q). Further elution of the column with benzene : solvent ether (4:1) gave trichadenic acid A 43 (0.04 g) (mmp, co-IR & co-TLC).

Conversion of odolactone (37) to 3 α -hydroxyfriedelan-27-oic acid (43) with lithium-ethylenediamine

A mixture of 0.1 g odolactone (37) and 0.1 g lithium in 40 ml ethylenediamine was refluxed for 2 hr under nitrogen atmosphere. The residue obtained after usual work-up was chromatographed over silica gel (3 g). Elution of the column with benzene : solvent ether (4:1) gave trichadenic acid A 43 (0.08 g) (mmp & co-TLC) as white crystals (from CHCl_3 -MeOH), mp 292-293 $^\circ$, $\angle^- \alpha \int_D + 28.57^\circ$.

Conversion of deoxyodolactone (49) to friedelan-27-oic acid (52) with lithium-ethylenediamine

A mixture of 0.1 g deoxyodolactone (49) and 0.1 g lithium in 40 ml ethylenediamine was refluxed for 2h under N_2 atmosphere. The residue obtained after usual work-up was chromatographed over silica gel (3 g). Elution of the column with benzene gave deoxytrichadonic acid 52 (0.08 g) as white crystals (from CHCl_3 -MeOH), mp 291-292 $^\circ$, $\angle^- \alpha \int_D + 28.57^\circ$.

Treatment of friedelan-27→16 α -olide (50) with lithium
-ethylenediamine : isolation of deoxytrichadonic acid (52)
and friedelan-16 α ,27-diol (54)

A mixture of 0.1 g iso-deoxydolactone (50) and 0.1 g lithium in 40 ml ethylenediamine was refluxed for 2 hr under N_2 atmosphere. The product obtained after usual work-up was chromatographed over silica gel (3 g). Elution of the column with benzene gave deoxytrichadonic acid 52 (0.02 g) as white crystals ($CHCl_3$ -MeOH), mp 290-291 $^\circ$, $[\alpha]_D^{25} + 28.57^\circ$. Further elution with benzene : solvent ether (9:1) gave friedelan-16 α , 27-diol 54 (0.06 g) as white crystals (MeOH), mp 240-241 $^\circ$, $[\alpha]_D^{25} + 6.85^\circ$, IR 3275 cm^{-1} (broad, OH), 1H NMR δ 0.72 (3H, d, J = 7 Hz), 0.80, 0.90, 0.97, 0.98, 1.00, 1.24 (18 H, s each, 6 Me groups), 3.88 (1 H, m, HO-C16-H), 4.00 (2 H, AB q, HO-C27-H₂). (Found C 81.05, H 11.75%. $C_{30}H_{52}O_2$ require C 81.02, H 11.79%).

Conversion of 3 β -acetoxyoleanan-18 α -H-28→13 β -olide (56)
to oleanan-18 α -H-28-oic acid (59) and 3 β -hydroxyoleanan
-18 α -H-28-oic acid (57) with Li-ethylenediamine

A mixture of 0.1 g 3 β -acetoxyoleanan-18 α -H-28→13 β -olide (56) and 0.1 g lithium in 40 ml ethylenediamine was refluxed for 2 hr under N_2 atmosphere. The residue obtained after usual work-up was chromatographed over silica gel (3 g). Elution with benzene gave oleanan-18 α -H-28-oic acid 57 (0.04 g) as white crystals ($CHCl_3$ -MeOH), mp 270-271 $^\circ$, IR 1695 cm^{-1} (COOH), 1H NMR δ 70-0.94 (18H, 7 Me groups). (Found C 81.45, H 11.40%. $C_{30}H_{50}O_2$ requires C 81.39, H 11.38%). Further elution of the column with benzene : solvent ether (4:1) gave 3 β -hydroxyoleanan-18 α -H-28-oic acid 57 (0.04 g) as white crystals ($CHCl_3$ -MeOH), mp 295-296 $^\circ$,

IR 3460 cm^{-1} (OH), 1690 cm^{-1} (COOH). (Found C 78.48, H 10.98%. $\text{C}_{30}\text{H}_{50}\text{O}_3$ requires C 78.55, H 10.99%). Methyl ester (with diazomethane), white crystals (CHCl_3 -MeOH), mp 198° $\left[\alpha \right]_D^{20} + 17^\circ$; IR 3250 cm^{-1} (OH), 1725 cm^{-1} (COOCH_3); $^1\text{H NMR } \delta$ 0.74, 0.80, 0.82, 0.85, 0.88, 0.90, 0.93 (21 H, s each, 7 Me groups), 3.20 (1H, m, HO-C₃-Ha), 3.65 (3H, COOCH_3).

Conversion of 3-oxooleanan-18 α -H-28 \rightarrow 13 β -olide (55) to 3 β -hydroxyoleanan-28-oic acid (57) with Li-ethylenediamine

A mixture of 0.1 g 3-oxooleanan-18 α -H-28 \rightarrow 13 β -olide (55) and 0.1 g lithium in 40 ml ethylenediamine was refluxed for 2 hr under N_2 atmosphere. The product obtained was chromatographed over silica gel (3 g). Elution with benzene : solvent ether (4:1) gave 3 β -hydroxyoleanan-28-oic acid 57 (0.08 g) as white crystals (CHCl_3 -MeOH), mp 270 - 271° (identified from mmp, co-TLC & co-IR).

Treatment of 3 β -acetoxyoleanan-18 α -H-28 \rightarrow 19 β -olide (60) with Li-ethylenediamine : isolation of oleanan-18 α -H-28-oic acid (59), 3 β -hydroxyoleanan-18 α -H-28-oic acid (57) and oleanan-18 α -H-3 β , 19 β , 28-triol (61)

A mixture of 0.2 g 3 β -acetoxyoleanan-18 α -H-28 \rightarrow 19 β -olide (60) and 0.2 g lithium in 80 ml ethylenediamine was refluxed for 2 hr under nitrogen atmosphere. The residue obtained after usual work-up was chromatographed over silica gel (6 g). Elution of the column with benzene gave oleanan-18 α -H-28-oic acid 59 (0.06 g) as white crystals (CHCl_3 -MeOH), mp 270 - 271° (mmp & co-TLC). Elution with benzene : solvent ether (4:1) gave 3 β -hydroxyoleanan-18 α -H-28-oic acid 57 (0.06 g) as white crystals, mp 295 - 296°

(mmp & co-TLC). Further elution with benzene : solvent ether (3:2) gave oleanan-18 α -H-3 β , 19 β , 28-triol 61 (0.03 g) as white crystals (CHCl₃-MeOH), mp 290-292 $^{\circ}$, $[\alpha]_D^{23} + 23^{\circ}$ (lit mp 296-298 $^{\circ}$, $[\alpha]_D^{24} + 24^{\circ}$), IR 3475 cm⁻¹ (broad, OH), ¹H NMR δ 0.74-1.30 (21H, 7 Me groups), 3.50 (2H, b, HO-C 28-H₂); 4.13 (1H, m, HO-C3-H_a), 4.26 (1H, m, C 19-H). It gave triacetate by Ac₂O-py method, mp 211-212 $^{\circ}$ (lit mp 213-216 $^{\circ}$), IR 1725 cm⁻¹ (b), 1745 cm⁻¹ (b), no band in hydroxy region.

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