CHAPTER-III

EXPERIMENTAL

Melting points are uncorrected. Petroleum ether used had b.p.60-80°. All optical rotations were determined in chloroform solution unless stated otherwise. The mass spectra were determined with an MS-9 mass spectrometer, using direct sample introduction into the ion source. NMR spectra were obtained on Varian A-60 and HA-100 spectrometers, using chloroform-d solutions containing tetramethylsilane as reference. The IR spectra were recorded in Perkin-Elmer 337 and 221 spectrophotometer. UV absorption spectra were taken in Zeiss VSU-1 spectrophotometer.

Examination of the neutral portion B (Part-I, Chapter-IV, p.19) of the trunk bark and stem of *Sapium sebiferum* Roxb.

Extraction: The details of the extraction and the separation of the neutral portion has already been described in Part-I, Chapter-IV, p.19.

Chromatography of the neutral portion A

The gummy material (16.0 g.) dissolved in benzene (30.0 ml.) was placed on a column of alumina (640.0 g., deactivated with 25.5 ml. of 10% aqueous acetic acid). The chromatogram was developed with petroleum ether and eluted with the following solvents (Table-I).

TABLE-I

Chromatography of the above gummy material (16.0 g.)

Eluent	Fractions 100 ml.each	Residue on evaporation (gm.)	Melting point °C
Petroleum ether	1 - 6	Oil (3 g.)	-
Petroleum ether	7 - 18	Solid (2.5 g.)	180-90°
Petroleum ether:benzene(9:1)	19 - 26	Solid (1.0 g.)	200-215°
Petroleum ether:benzene(4:1)	27 - 32	Solid (1.0 g.)	85-6°
Petroleum ether:benzene(3:2)	35 - 40	Solid (0.6 g.)	200-220°
Petroleum ether:benzene(1:1)	42 - 53	Solid (1.5 g.)	128-32°
Petroleum ether:benzene(2:3)	56 - 59	Oil (0.5 g.)	-
Petroleum ether:benzene(1:4)	60 - 64	Oil (0.7 g.)	-
Benzene (1)	66 - 70	Oil (0.2 g.)	-
Benzene:ether (4:1)	71 - 75	Oil (0.8 g.)	-
Benzene:ether (3:2)	77 - 84	Solid (0.5 g.)	210-15°

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

Examination of Fractions 7-18 (Table-I) : Isolation of moretenone 114

The solid fractions 7-18 (Table-I) were combined (2.5 g.), m.p. 180-90° and was rechromatographed over active alumina (120 gm.). The solid dissolved in benzene (5 ml.) was placed on a column of alumina. The chromatogram was developed in petroleum ether and was eluted with the following solvents (Table-II).

TABLE-II

Chromatography of the above material (3.0 g.)

Eluent	Fractions 50 ml.each	Residue on evaporation	m.p.
Petroleum ether	1 - 3	Trace oil, soluble in petroleum ether	-
Petroleum ether:benzene(4:1)	4 - 7	Trace low melting solid, soluble in pet.ether	50-60°
Petroleum ether:benzene(3:2)	8 - 15	Crystalline solid	185-95°

Further elution with more polar solvents did not afford any material

The fractions 8-15 (Table-II) were combined (2.2 g.) and crystallised from a mixture of chloroform and methanol to afford pure sample of moretenone 114, m.p. 198-99°, $[\alpha]_D$ +50°. It showed no depression in melting point when mixed with an authentic sample of moretenone, IR spectra of which were superimposable.

Found	:	C,84.44; H,11.33%. Mol.wt. 407 (Rast).
Calculated for $C_{30}H_{48}O$	:	C,84.84; H,11.39%. Mol.wt. 424.
UV (95% Ethanol)	:	λ_{max} 287 mμ (ϵ, 71.5).
IR (KBr disc)	:	ν_{max} 1705, 1640, 875 cm^{-1}.
Mass spectra	:	m/e 189, 205, 381, 424 (Fig. 4).
NMR	:	Signals at 0.70, 0.94, 0.95, 1.02(6-H), 1.08(6-Methyl groups); 1.68 (-C=C-CH_3); 2.33, 2.43 (-CO-CH_2-, protons); 4.68 (C=CH_2) ppm (Fig.5).
ORD curve	:	$[\alpha]_{585}$ +42, $[\alpha]_{342.5}$ +490(peak), $[\alpha]_{330}$ +486(peak), $[\alpha]_{312}$ +268(shoulder), $[\alpha]_{280}$ +14(trough) (Fig.3).

Deuteration of moretenone 114 in methanol-O-D was performed and the mass and NMR of the product were taken :

Mass spectra(of deuterated moretenone) : m/e 189, 207, 383, 426.

NMR spectra(" " "): signals at 0.70, 0.94, 0.95, 1.02-(6-H), 1.08(6-$C\underline{H}_3$ groups); 1.68 (=C-$C\underline{H}_3$) and 4.68 (=CH_2) ppm.

Colour reaction tests:

a) Tetranitromethane developed a yellow colour.

b) Leibermann-Burchard reaction : The compound developed a violet colouration with a mixture of acetic anhydride and conc. sulphuric acid.

c) Zimmermann colour test was positive.

Preparation of 2,4-Dinitrophenylhydrazone derivative of moretenone

2,4-Dinitrophenylhydrazine (0.3 g.) dissolved in rectified spirit (5 ml.) and a few drops of conc. H_2SO_4 was added to the solution of moretenone (0.2 g.) in $CHCl_3$ (1 ml.). The reaction mixture was concentrated when orange red crystals commenced to separate out. The crude DNP product m.p. 267-8° on crystallisation from chloroform and methanol yielded pure 2,4-DNP derivative of moretenone, m.p. 271-3°.

Found : C,71.32; H,8.27; N,9.43%.

Calculated for $C_{36}H_{52}O_4N_2$: C,71.52; H,8.61; N,9.27%.

Lithium Aluminium Hydride reduction : Preparation of Moretenol 108b

Moretenone (0.5 g.) in dry ether (150 ml.) was refluxed with $LiAlH_4$ (0.2 g.) for four hrs. Excess of $LiAlH_4$ was decomposed with a saturated solution of sodium sulphate in cold. The reaction mixture was transferred to a separating funnel

and then extracted with ether, the ether extract was washed with water and then dried (Na_2SO_4). Ether was distilled off and the residue (0.5 g.), m.p. 210-200° was chromatographed over alumina. A column of alumina (20 g., deactivated with 0.8 ml. of 10% of aqueous acetic acid) was developed with petroleum ether and the above residue dissolved in benzene (10 ml.) was added to it. The following solvents were used for elution (Table-III).

TABLE-III

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 2	Nil
Petroleum ether:benzene (4:1)	3 - 4	Nil
Petroleum ether:benzene (3:2)	5 -10	Crystalline solid (0.45 g.), m.p. 222-4°

Further elution with more polar solvents did not yield any material

Fractions 5-10 (Table-III) were combined and the solid (0.45 g.) was crystallised from chloroform and methanol mixture when a constant melting solid, m.p. 231-33°, $[\alpha]_D$ +17° was obtained.

Found	:	C,84.38; H,11.89%.
Calculated for $C_{30}H_{50}O$	:	C,84.44; H,11.81%.
Mass spectra	:	m/e 189, 207, 383, 426.
NMR spectra	:	signals at 0.69, 0.77, 0.83, 0.94, 0.99(6-H), (6-CH_3); 1.67 (=C-CH_3); 3.22 (HC-OH); 4.68 (=CH_2) ppm.

Preparation of moretenyl benzoate

To moretenol (0.1 g.) dissolved in pyridine (1 ml.) benzoyl chloride (1 ml.) was added and the mixture kept over water bath for 4 hours. The mixture was poured into cold water and the solid formed was collected by filtration. The crude benzoate m.p. 237° on crystallisation from chloroform and methanol furnished pure moretenyl benzoate, m.p. 248-9°, $[\alpha]_D$ +37°.

Found	:	C,83.83; H,10.18%.
Calculated for $C_{37}H_{54}O_2$	:	C,83.72; H,10.25%.

Preparation of moretenyl acetate 108c

To a solution of moretenol (0.5 g.) dissolved in pyridine (5 ml.) was added acetic anhydride (5 ml.) and the mixture kept over water bath for four hours. Fine needle shaped crystals separated out which was collected (0.4 g.), m.p. 271-2°. The crystals were crystallised several times when moretenyl acetate, m.p. 278-9°, $[\alpha]_D$ +23° was obtained.

Found	:	C,81.56; H,11.00%.
Calculated for $C_{32}H_{52}O_2$	:	C,81.99; H,11.18%.
IR (KBr disc)	:	ν_{max} 3070, 1725, 1640, 1250, 883 cm^{-1}.
Mass spectra	:	signals at 0.68, 0.86 (3-CH_3), 0.95, 0.98 (6-CH_3); 1.68 (=C-CH_3); 2.05 (-O.COCH_3); 4.73 (=CH_2) ppm.

Perbenzoic acid titration on moretenyl acetate : Estimation of double bond and isolation of moretenyl acetate oxide

Moretenyl acetate (0.1001 g.) was dissolved in chloroform in a 50 ml. volumetric flask and a solution of perbenzoic acid in chloroform (5 ml.) was

added and the volume made up to 50 ml. with chloroform. A similar blank solution with perbenzoic acid (5 ml.) was prepared. Titration values showed that it consumed exactly one mole equivalent of perbenzoic acid within an hour. There was no further uptake even after 24 hours. Hence the presence of only one double bond was confirmed in moretenyl acetate. The whole reaction mixture was treated with sodium thiosulphate solution and the chloroform solution was washed with aqueous NaOH solution followed by water, dried (Na_2SO_4) and chloroform was evaporated. Crystallisation of the solid from chloroform and methanol mixture afforded moretenyl acetate oxide, m.p. 271°, $[\alpha]_D$ +20.45°.

Found	:	C,79.00; H,10.28%.
Calculated for $C_{32}H_{52}O_3$	:	C,79.33; H,10.74%.

Retropinacoline transformation of moretenol

To a suspension of PCl_5 (0.32 g.) in dry petroleum ether (10 ml.), moretenol (0.5 g.) was added and the mixture shaken for 30 minutes. The reaction mixture became clear within 20 minutes. The petroleum ether solution was washed with warm water, dried (Na_2SO_4). Evaporation of the solvent furnished a solid, m.p. 175-80°. The solid (0.4 g.) was chromatographed over alumina (16 g.). The chromatogram was developed with petroleum ether and eluted with the following solvents (Table-V).

TABLE-V

Eluent	Fractions, 50 ml.each	Residue on evaporation
Petroleum ether	1 - 3	Solid (0.4 g.), m.p. 185-6°

Elution with more polar solvents did not furnish any material

Fractions 1-3 (Table-V) were combined and the solid crystallised from chloroform and methanol when a diene was obtained, m.p. 189-90°, $[\alpha]_D$ +14.54°.

Found	:	C,88.30; H,11.54%.
Calculated for $C_{30}H_{48}$	:	C,88.16; H,11.84%.
UV (Ethanol)	:	No absorption within the range 220-300 mμ.
Mass spectra	:	m/e 189, 339, 365, 408.

Hydrogenation of moretenol : Preparation of moretenol 109b

Moretenol (0.5 g.) dissolved in ethyl acetate (30 ml.) was hydrogenated in presence of palladium-on-charcoal at room temperature and ordinary pressure. One mole of hydrogen was consumed within 30 minutes. The catalyst was removed by filtration and the filtrate evaporated to dryness. The solid residue was crystallised from chloroform and methanol mixture when crystals of moretenol 109b, separated out, m.p. 224-6°, $[\alpha]_D$ +11°.

Found	:	C,84.00; H,11.92%.
Calculated for $C_{30}H_{50}O$	:	C,84.11; H,12.19%.

Retropinacoline rearrangement of moretanol : Preparation of hydrocarbon 110

To a suspension of PCl_5 (0.30 g.) in dry petroleum ether (10 ml.) moretanol (0.5 g.) was added and shaken for 30 minutes. On working up the reaction mixture as in the previous case, a solid of m.p. 139-40° was obtained. The solid was crystallised from chloroform and methanol to afford the hydrocarbon 110, m.p. 142-3°, $[\alpha]_D$ +7°.

Found	:	C,87.61; H,12.35%.
Calculated for $C_{30}H_{50}$	:	C,87.73; H,12.27%.

Ozonisation of the hydrocarbon 110 : Preparation of tris-nor-ketone 111

The hydrocarbon 110 (0.2 g.) in ethyl acetate (100 ml.) was ozonised at 0° and excess of ozone removed by a stream of nitrogen and the ozonide decomposed with 10% acetic acid (100 ml.) and zinc dust (1 g.). Ethyl acetate removed under reduced pressure and the residue extracted with ether, washed with water, dried (Na_2SO_4) and ether distilled off. The residue (0.15 g.) was crystallised from chloroform and methanol mixture to afford a ketone 111, m.p. 195-6°, $[\alpha]_D$ +110°.

Found	:	C,84.25; H,11.32%.
Calculated for $C_{27}H_{44}$	:	C,84.37; H,11.46%.
IR (KBr disc)	:	ν_{max} 1745 cm^{-1}.

Modified Wolff-Kishner reduction of moretenone : Preparation of moretene 108a

Moretenone (1 g.) in diethylene glycol (150 ml.) was refluxed with hydrazine hydrate (11.2 ml.) for 30 minutes. After addition of KOH (1.0 g.) the mixture was further refluxed for one hour. The condenser was removed and the mixture was heated to 190°. After refluxing for another 2½ hours the reaction mixture was cooled, diluted with water when a solid separated out. The solid (0.92 g.) was chromatographed over a column of active alumina (60 g.). The chromatogram was developed in petroleum ether. The solid (0.92 g.)dissolved in petroleum ether (5 ml.) was placed over the column and it was eluted with the following solvents (Table-VI).

TABLE-VI

Eluent	Fractions, 50 ml,each	Residue
Petroleum ether	1 - 5	Solid (0.9 g.), m.p. 190-5°
Further elution with more polar solvents did not furnish any material		

Fractions 1-5 (Table-VI) were combined and the solid on crystallisation from chloroform and methanol afforded a hydrocarbon 108a, m.p. 203-5°, $[\alpha]_D$ +22°.

Found	:	C,87.58; H,12.05%.
Calculated for $C_{30}H_{50}$	:	C,87.73; H,12.27%.
Mass spectra	:	m/e 189, 191, 367, 410.
NMR spectra	:	signals at 0.70, 0.94, 0.95, 1.02(2-CH_3), 1.08(6-CH_3); 1.68(-C=C-CH_3); 4.68 (=CH_2) ppm.

Ozonolysis of moretene 108a : Preparation of isoadiantone 112

Moretene (0.5 g.) in ethyl acetate (50 ml.) was ozonised at 0° for 3 hours. The ozonide was decomposed with zinc and acetic acid and ethyl acetate removed by distillation under reduced pressure. The residue was extracted with ether, and the extract was washed with water, dried (Na_2SO_4) and ether was evaporated off. The residue (0.45 g.), m.p. 225-6° was chromatographed on a column of silica gel (20 g.). The chromatogram was developed with petroleum ether and the solid (0.45 g.) dissolved in benzene (2 ml.) was placed on the column. It was eluted with the following solvents (Table-XV).

TABLE-XV

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 10	Solid (0.4 g.), m.p. 228-30°
Further elution with more polar solvents did not yield any material		

Fractions 1-10 (Table-XV) were combined (0.4 g.) and on crystallisation from chloroform and methanol afforded crystalline solid, m.p. 230°, $[\alpha]_D$ +5°

was obtained which was identical with isoadiantone (m.m.p. and IR comparison) kindly supplied by Prof. Berti.

Found	:	C,84.50; H,11.29%.
Calculated for $C_{29}H_{48}O$	:	C,84.46; H,11.40%.

Hydrogenation of moretene 108a : Preparation of moretane 109a

Moretene (0.2 g.) dissolved in ethanol (50 ml.) was hydrogenated in presence of palladium-on-charcoal catalyst at room temperature and ordinary pressure. Within 30 minutes the uptake of hydrogen stopped, the reaction mixture filtered and the filtrate on concentration and crystallisation of the solid from chloroform and methanol furnished moretane 109a, m.p. 176 and 196° (double melting), $[\alpha]_D$ +20°.

Found	:	C,87.50; H,12.52%.
Calculated for $C_{30}H_{52}$	:	C,87.38; H,12.68%.
Mass spectra	:	m/e 191, 369, 412.

ACID ISOMERISATION OF MORETENONE

i) Preparation of Hopenone-I

To a solution of moretenone (0.5 g.) in glacial acetic acid (50 ml.) a mixture of glacial acetic acid (9 ml.) and conc.H_2SO_4 (3.5 ml.) was added. Crystalline solids started to separate within 10 minutes. The reaction mixture diluted with water and the solid was collected and crystallised from chloroform and methanol to furnish hopenone-I 42a, (0.3 g.), m.p. 195-7°, $[\alpha]_D$ +91.43°.

Found	:	C,84.79; H,11.25%.
Calculated for $C_{30}H_{48}O$	:	C,84.84; H,11.39%.

ii) Preparation of Hopenone-II

Hopenone-I (0.3 g.) prepared above was dissolved in glacial acetic acid (65 ml.) and benzene (25 ml.) and was treated with conc.H_2SO_4 (12.8 ml.) in acetic acid (20 ml.). After keeping at room temperature for 20 hours the solution was diluted with water and the product isolated with ether. The ether extract was washed with water, dried (Na_2SO_4) and the ether removed. The solid (0.25 g.) was chromatographed over alumina (15 g.). The chromatogram was developed in petroleum ether and the solid dissolved in benzene (4 ml.) was placed on the column. The following solvents were used for elution (Table-VII).

TABLE-VII

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 2	Nil
Petroleum ether:benzene (4:1)	3 - 4	Nil
Petroleum ether:benzene (7:3)	5 - 7	Solid (0.2 g.), m.p. 145-6°
Further elution with more polar solvents afforded no material		

Fractions 5-7 (Table-VII) were combined (0.2 g.) and crystallisation of the solid from chloroform and methanol furnished hopenone-II 113, m.p. 150-3°, $[\alpha]_D$ +52°.

Found	:	C,84.80; H,11.10%.
Calculated for $C_{30}H_{48}O$	:	C,84.84; H,11.39%.

Examination of Fractions 19-26 (Table-I) : Isolation of 3-epi-moretenol 115

The fractions 19-26 (Table-I) were combined (1.0 g.), m.p. 200-215° and the solid boiled with methanol when most of the solids went into solution. It was filtered hot to separate some of the insoluble solids (m.p. 50-60°, vide infra). The filtrate on concentration gave a crystalline solid (0.7 g.), m.p. 215-18°. The latter was rechromatographed over active alumina (25 g.). The chromatogram was developed with petroleum ether and the solid dissolved in benzene (10 ml.) was placed over the column and was eluted with the following solvents (Table-VIII).

TABLE-VIII

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 3	Small amount of solid, m.p. 50-60°
Petroleum ether:benzene (4:1)	4 - 6	Nil
Petroleum ether:benzene (3:2)	7 - 11	Solid (0.6 g.), m.p. 220-22°

More polar solvents did not elute any further material

Fractions 7-11 (Table-VIII) were combined and crystallised from methanol to afford fine needle shaped crystals of 3-epi-moretenol 115, m.p. 223-4°, $[\alpha]_D$ -2.53°.

Found	:	C,84.59; H,11.93%.
Calculated for $C_{30}H_{50}O$	:	C,84.44; H,11.81%.
UV (Ethanol)	:	No absorption within the range 220-300 mμ.
Mass spectra	:	m/e 189, 207, 383 (very small), 426 (Fig.7).
NMR spectra	:	signals at 0.68 (3H), 0.83(6H), 0.95-0.98(9H), 1.68(=C-CH_3), 3.40 ($\frac{W}{2}$, 7Hz, -OH), 4.68(=CH_2) ppm (Fig.6).

Preparation of 3-epi-moretenyl acetate 115a

3-epi-moretenyl (0.5 g.) was acetylated with pyridine (5 ml.) and acetic anhydride (5 ml.) by the usual method. The acetate, m.p. 226-8°, was crystallised from chloroform and methanol to afford a pure sample of 3-epi-moretenyl acetate 115a, m.p. 233-4°, $[\alpha]_D$ -19.35°.

Found	:	C,81.66; H,11.33%.
Calculated for $C_{32}H_{52}O_2$	:	C,81.99; H,11.18%.
Mass spectra	:	m/e 189, 202, 402, 425, 468.
NMR spectra	:	signals at 0.70(3-H), 0.84-0.88(9-H), 0.98(6-H)(6-CH_3); 1.68 (=C-CH_3); 2.07 (-O.COCH_3); 4.64 (H-C-O.$COCH_3$); 4.68 (=CH_2) ppm

Preparation of moretenone 114

3-epi-moretenol (0.2 g.) was oxidised with CrO_3-Py complex prepared from pyridine (2 ml.) and CrO_3 (0.2 g.) and was kept at room temperature for 14 hours. The crude product (0.1 g.) obtained by working up in the usual way was chromatographed over a column of active alumina (5 g.). The chromatogram was prepared with petroleum ether and the product dissolved in benzene (5 ml.) was poured on the column. It was eluted with the following solvents (Table-IX).

TABLE-IX

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 2	Nil
Petroleum ether:benzene (4:1)	3 - 4	Nil
Petroleum ether:benzene (7:3)	5 - 6	Solid, m.p. 196-8°

Further elution with more polar solvent did not yield any material

Fractions 5-6 (Table-IX) (0.1 g.) on recrystallisation from chloroform and methanol furnished needle shaped crystals, m.p. 199-200°, $[\alpha]_D$ +50°, which was found to be identical with authentic sample of moretenone (m.m.p. and comparison IR).

Found	:	C,84.69; H,11.08%.
Calculated for $C_{30}H_{48}O$	:	C,84.84; H,11.23%.

ACID ISOMERISATION OF 3-EPI-MORETENYL ACETATE

i) Preparation of 3-epi-hop-17(21)-enyl acetate 116

3-epi-moretenyl acetate (0.3 g.) was dissolved in glacial acetic acid (30 ml.) and heated on water bath to dissolve the substance. It was cooled to room temperature and a mixture of conc.H_2SO_4 (2.1 ml.) in glacial acetic acid (5.5 ml.) was added. Some solid separated within a few minutes. After two hours the reaction mixture diluted with water when a solid precipitated out. The latter (0.25 g.) was dissolved in benzene and placed on a column of alumina (10 g., deactivated with 0.4 ml. of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution (Table-X).

TABLE-X

Eluent	Fractions, 50 ml. each	Residue
Petroleum ether	1 - 3	Solid (0.25 g.), m.p. 218°
More polar solvents did not yield any further material		

Fractions 1-3 (Table-X) (0.25 g.) on crystallisation from chloroform and methanol furnished fine needle shaped crystals, m.p. 222-3°, $[\alpha]_D$ +11.11°.

Found : C,80.80; H,10.82%.

Calculated for $C_{32}H_{52}O_2, \frac{1}{2}CH_3OH$: C,80.57; H,11.15%.

Preparation of 3-epi-hop-17(21)-en-ol 116a

3-epi-hop-17(21)-enyl acetate 116 (0.2 g.) was hydrolysed with 10% methanolic KOH (5 ml.) in benzene (4 ml.) by refluxing for 4 hours. The solvent was evaporated and the residue was extracted with ether. The ether extract was washed with water till neutral, dried (Na_2SO_4) and ether evaporated off. The solid (0.15 g.) was dissolved in benzene and was placed on a column of alumina (0.1 g., deactivated with 0.4 ml. of 10% aqueous acetic acid). The following eluents were used (Table-XI).

TABLE-XI

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 2	Nil
Petroleum ether:benzene (4:1)	3 - 5	Solid (0.15 g.), m.p.170-5°
Further elution with more polar solvents did not yield any material		

Fractions 3-5 (Table-XI) (0.14 g.) on crystallisation from methanol yielded fine needle shaped crystals of 3-epi-hop-17(21)-en-ol 116a, m.p. 185-6°, $[\alpha]_D$ +47.06°.

Found : C,84.72; H,11.68%.

Calculated for $C_{30}H_{50}O$: C,84.44; H,11.81%.

Preparation of Hopenone-I from 3-epi-hop-17(21)-en-ol 116a

3-epi-hop-17(21)-en-ol (0.2 g.) was oxidised with CrO_3-Py complex prepared from pyridine (2 ml.) and CrO_3 (0.2 g.) in the usual manner. The crude ketone obtained after working up in the usual manner was dissolved in benzene (3 ml.) and placed on a column of active alumina (10 g.). The chromatogram was developed on petroleum ether and was eluted with the following solvents (Table-XII).

TABLE-XII

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 2	Nil
Petroleum ether:benzene (4:1)	3 - 4	Nil
Petroleum ether:benzene (7:3)	5 - 8	Solid(0.1 g.), m.p.190-2°
Further elution with more polar solvents did not yield any material		

Fractions 5-8 (Table-XII) (0.1 g.) on crystallisation from chloroform and methanol yielded crystals of hopenone-I, m.p. 192-4°, $[\alpha]_D$ +88° identified with an authentic specimen (m.m.p. and comparison IR) of hopenone-I.

ii) Preparation of 3-epi-hop-13(18)-enyl acetate 117

3-epi-hop-17(21)-enyl acetate 116 (0.3 g.) dissolved in glacial acetic acid (65 ml.) and benzene (25 ml.) was treated with a mixture of conc.H_2SO_4 (12.8 ml.) and acetic acid (20 ml.). The reaction mixture was kept for 18 hours at room temperature, diluted with water and extracted with ether and the ether solution dried (Na_2SO_4). Ether was evaporated and a solution of the residue (0.25 g.) in

benzene (3 ml.) was placed on a column of alumina (10 g., deactivated with 0.4 ml. of 10% aqueous acetic acid). The following solvents were used for elution (Table-XIII).

TABLE-XIII

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 2	Solid (0.2 g.), m.p.175°
Further elution did not furnish any solid		

Fractions 1-2 (Table-XIII) crystallised several times from methanol to give crystals of 3-epi-hop-13(18)-enyl acetate 117, m.p. 179-81°, $[\alpha]_D$ -32.14°.

Found : C,82.42; H,11.02%.

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

Separation of 3-epi-hop-13(18)-en-ol 117a

3-epi-hop-13(18)-enyl acetate 116 (0.3 g.) was refluxed with 10% methanolic KOH (5 ml.) in benzene (5 ml.) for 4 hours. The solvent was evaporated and the residue extracted with ether, the ether solution washed with water, dried (Na_2SO_4) and the solvent evaporated off. The residue (0.35 g.) dissolved in benzene (5 ml.) was placed on a column of alumina (10 g., deactivated with 0.4 ml. of 10% aqueous AcOH) developed with petroleum ether. The following solvents were used for the chromatographic separation (Table-XIV).

TABLE-XIV

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 2	Nil
Petroleum ether:benzene (4:1)	3 - 4	Nil
Petroleum ether:benzene (7:3)	5 - 6	Oil,solid with methanol, m.p. 210°

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

Fractions 5-6 (Table-XIV) were combined (0.25 g.) and the solid on crystallisation from methanol furnished fine needle shaped crystals of 3-epi-hop-13(18)-en-ol 117a, m.p. 218-20°, $[\alpha]_D$ -14.8°.

Found : C,84.02; H,11.73%.

Calculated for $C_{30}H_{50}O$: C,84.44; H,11.81%.

Preparation of Hopenone-II from 3-epi-hop-13(18)-en-ol

A cold solution of 3-epi-hop-13(18)-en-ol (0.2 g.) was added to a complex prepared from CrO_3 (0.2 g.) and pyridine (2 ml.) and kept overnight. Next day it was worked up in the usual way and afforded a solid which on crystallisation from chloroform and methanol furnished crystals, m.p. 148-50°, $[\alpha]_D$ +49°, identical with an authentic specimen of Hopenone-II (m .m.p. and IR comparison).

Found : C,84.45; H,11.55%.

Calculated for $C_{30}H_{48}O$: C,84.84; H,11.39%.

Meerwein-Pondorff reduction of Moretenone : Preparation of 3-epi-moretenol 115

A mixture of moretenone (1.0 g.) and Al-isopropoxide (1.3 g.) in absolute isopropanol (12.5 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 evaporated to dryness. The product isolated in the usual way with ether was dissolved in benzene (10 ml.) and poured on a column of alumina (60 g., deactivated with 2.2 ml. of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution (Table-XIX).

TABLE-XIX

Eluent	Fractions, 50 ml.each	Residue on evaporation
Petroleum ether	1 - 4	Nil
Petroleum ether:benzene (9:1)	5 - 8	Nil
Petroleum ether:benzene (4:1)	9 -16	Solid (0.3 g.), m.p.218-20°
Petroleum ether:benzene (3:2)	20 -29	Solid (0.6 g.), m.p.228-9°

Further elution with more polar solvents did not yield any material

Fractions 9-16 (Table-XIX) were combined and crystallised from methanol to give crystals of 3-epi-moretenol, m.p. 222-3° which did not depress the melting point when mixed with an authentic sample of 3-epi-moretenol. The acetate prepared in the usual manner had melting point 233-4°, identical with 3-epi-moretenyl acetate (m.m.p.).

Fractions 20-29 (Table-XIX) were combined and crystallised from chloroform and methanol to give crystals m.p. 230-1° acetylation of which afforded an acetate m.p.278-88°, identical (m.m.p.) with an authentic specimen of moretenyl acetate.

EXAMINATION OF FRACTIONS 27-32 (TABLE-I) : ISOLATION OF THE PARAFFIN ALCOHOL $C_{28}H_{58}O$

Fractions 27-32 (Table-I) (1.0 g.) was dissolved in benzene and placed on a column of alumina (50 g., deactivated with 2 ml. of 10% aqueous acetic acid) developed with petroleum ether. The following solvents were used for elution (Table-XVI).

TABLE-XVI

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 4	Nil
Petroleum ether:benzene (9:1)	5 - 7	Nil
Petroleum ether:benzene (4:1)	8 - 15	Low melting solid (0.8 g.), m.p. 85°

Further elution with more polar solvents did not afford any material

Fractions 8-15 (Table-XVI) were recrystallised from chloroform and methanol when flaky crystals, m.p. 86-9°, $[\alpha]_D$ -13.18° were obtained.

Found : C,82.15; H,14.13%.

Calculated for $C_{28}H_{58}O$: C,81.95; H,14.14%.

UV absorption : no absorption within the range 220-310 mμ.

Preparation of the acetate of the paraffin alcohol $C_{28}H_{58}O$

The paraffin alcohol (0.2 g.), m.p. 86-9° was acetylated with pyridine (2 ml.) and acetic anhydride (2 ml.) in the usual manner. The crude acetate (0.2 g.) dissolved in benzene (2 ml.) was placed in a column of alumina (10 g., deactivated with 0.4 ml. 10% aqueous acetic acid) developed with petroleum ether. The chromatogram was eluted with the following solvents (Table-XVII).

TABLE-XVII

Eluent	Fractions, 50 ml. each	Residue
Petroleum ether	1 - 3	Oil, solid with methanol
Further elution with more polar solvents did not yield any material		

Fractions 1-3 (Table-XVII) were combined (0.15 g.) and the solid crystallised from chloroform and methanol to afford acetate m.p. 85-6°, $[\alpha]_D$ -20.4°. It showed depression in melting point when mixed with the original alcohol (m.m.p. 75°).

Found	:	C,79.42; H,13.09%.
Calculated for $C_{30}H_{60}O_2$	:	C,79.62; H,13.27%.

EXAMINATION OF FRACTIONS 35-40 (TABLE-I) : ISOLATION OF MORETENOL

Fractions 35-40 (Table-I) (0.6 g.) were combined and crystallised from a mixture of chloroform and methanol when fine crystals of moretenol 114 separated out, m.p. 228-30°, $[\alpha]_D$ +25°.

Found : C,84.34; H,11.75%.

Calculated for $C_{30}H_{50}O$: C,84.44; H,11.81%.

Preparation of Moretenyl acetate

Moretenol (0.2 g.) isolated above was acetylated with pyridine (2 ml.) and acetic anhydride (2 ml.) in the usual way. The solid obtained (0.2 g.) was crystallised from chloroform and methanol to afford crystals, m.p. 277-8°, $[\alpha]_D$ +28° which did not show depression in melting point when mixed with an authentic specimen of moretenyl acetate and the IR of which were identical.

Found : C,81.90; H,11.71%.

Calculated for $C_{32}H_{52}O_2$: C,81.99; H,11.81%.

Preparation of Moretenone

Moretenol (0.2 g.) isolated above was oxidised with CrO_3-Pyridine complex in the usual way. The solid (0.2 g.) produced was dissolved in benzene (2 ml.) and placed in a column of alumina (20 g.) developed in petroleum ether. The following solvents were used for elution (Table-XVIII).

TABLE-XVIII

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 2	Nil
Petroleum ether:benzene (4:1)	3 - 4	Nil
Petroleum ether:benzene (3:2)	5 - 7	Solid (0.15 g.), m.p.185-90°

Further elution did not elute any material

Fractions 5-7 (Table-XVIII) were combined and on crystallisation from chloroform and methanol gave crystals, m.p. 198-200°. It was identical (m.m.p., IR comparison) with an authentic sample of moretenone.

EXAMINATION OF FRACTIONS 42-53 (TABLE-I) : ISOLATION OF β -SITOSTEROL

Fractions 42-53 (Table-I) were combined (1.5 g.) and the solid crystallised from chloroform and methanol mixture when fine needle shaped crystals of β-sitosterol was obtained, m.p. 136-7°, $[\alpha]_D$ -32°.

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

β-sitosterol (0.5 g.) was acetylated with pyridine (5 ml.) and acetic anhydride (5 ml.) in the usual manner. The product isolated in the usual way with ether was crystallised with chloroform and methanol when crystals of acetate, m.p. 126-7°, $[\alpha]_D$ -40° were obtained which was identified as β-sitosterol acetate by comparing with an authentic specimen of β-sitosterol acetate (m.m.p. and IR comparison).

Found	:	C,81.15; H,11.35%.
Calculated for $C_{31}H_{52}O_2$	:	C,81.52; H,11.48%.

EXAMINATION OF FRACTIONS 77-84 (TABLE-I) : ISOLATION OF A NEW NOR-TRITERPENE ALCOHOL

Fractions 77-84 (Table-I) were combined (0.5 g.) and its solution in benzene (5 ml.) was placed on a column of alumina (30 g., deactivated with

1.2 ml. of 10% aqueous acetic acid). The chromatogram was developed with petroleum ether and eluted with the following solvents (Table-XX).

TABLE-XX

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether:benzene (1:1)	1 - 4	Nil
Petroleum ether:benzene (1:3)	5 - 7	Nil
Benzene	8 - 13	Oil
Benzene:ether (4:1)	14 - 16	Oil
Benzene:ether (3:2)	18 - 22	Solid (0.4 g.), m.p.220-2°

Further elution with polar solvents did not yield any material

Fractions 18-22 (Table-XX) were combined and on crystallisation several times with chloroform yielded fine needle shaped crystals, m.p. 228-9°, $[\alpha]_D$ -9.09°.

Found	:	C,75.92; H,10.14%.
Calculated for $C_{29}H_{46}O_4$	:	C,75.98; H,10.05%.
UV spectra (Ethanol)	:	no absorption in the range 220-300 mμ.
IR spectra[80] (KBr disc)	:	ν_{max} 3360 (-OH, broad), 2070 ($-CH_2-$ broad), 1467, 1453 (-CH=CH-, doublet); 1398, 1369 (gem dimethyl-, sharp) 890, 875 (-CH=CH-) cm^{-1}.
Mass spectra[80]	:	m/e 426, 440, 458 (Fig.11).
NMR spectra	:	signals at 0.88,0.91,0.95,1.04,1.06,1.14,1.18 (21H,7 tert-CH_3),2.16,2.2,2.28,2.32(quartet of doublets, 2 C-OH groups);3.22,3.3(2H,

2 H-COH); 4.00 (quartet of doublets, $-CH_2-$); and 6.42, 6.52, 6.72, 6.80 (AB quartet, CH=CH) ppm. (Fig.9).

Preparation of the acetate of nor-triterpene $C_{29}H_{46}O_4$

The compound (0.2 g.) was acetylated with pyridine (2 ml.) and acetic anhydride (2 ml.) in the usual way. The solid obtained was dissolved in benzene (5 ml.) and was placed on a column of alumina (10 g., deactivated with 0.4 ml. of 10% aqueous acetic acid). The chromatogram was developed with petroleum ether and eluted with the following solvents (Table-XXI).

TABLE-XXI

Eluent	Fractions, 50 ml.each	Residue
Petroleum ether	1 - 3	Nil
Petroleum ether:benzene (9:1)	4 - 6	Nil
Petroleum ether:benzene (4:1)	7 - 12	Solid (0.18 g.), m.p.200-5°

Further elution with more polar solvents did not yield any material

Fractions 7-12 (Table-XXI) were combined which on crystallisation of the solid from chloroform and methanol mixture afforded fine needle shaped crystals, m.p. 213-5°, $[\alpha]_D$ +47.5°.

Found	:	C,72.79; H,9.07%.
Calculated for $C_{33}H_{50}O_6$	:	C,73.06; H,9.22%.
UV spectra (Ethanol)	:	no absorption in the range 220-300 mμ.

IR spectra ($CHCl_3$)[80] : ν_{max} 1737 ($-OCOCH_3$); 1467, 1453 (-CH=CH-, doublet); 1389, 1369 (gem dimethyl, sharp); 1245-50 ($-OCOCH_3$); 895-872 (-C=CH-)(Fig.8). No hydroxyl absorption.

Mass spectra[80] : peaks at 422, 482, 510, 524, 542 (Fig.12).

NMR spectra (100 Mc/s) : signals at 0.885, 0.930 (6-HO, 0.960, 0.980, 1.010, 1.024 (21-H, 7 tert-CH_3); 1.990 and 2.055 (6H, 2 $-OCOCH_3$); 4.700, 4.8 (2H, 2H-C-$OCOCH_3$); 6.400, 6.490, 6.675, 6.750 (AB quartet, -CH=CH-) ppm.(Fig.10).

Perbenzoic acid titration of the above acetate : Isolation of the reaction product

To the above acetate (0.150 g.) dissolved in chloroform in a 25 ml. volumetric flask, a solution of perbenzoic acid (5 ml.) was added and the volume made up to 25 ml. with chloroform. A blank solution of perbenzoic acid (5 ml.) was prepared in a 25 ml. volumetric flask. On titrating the above two solutions with a standard $\frac{N}{100}$ sodium thiosulphate solution there was no difference in the titer value even after 24 hours.

After the titration was over the reaction mixture was treated with KI solution in acetic acid and then with thiosulphate solution to destroy perbenzoic acid. The clear chloroform solution was washed with $NaHCO_3$ solution, and then with water, dried (Na_2SO_4). Chloroform was evaporated when an oily residue was obtained. The latter formed crystals after keeping for 15 days. The solid was insoluble in all the solvents but was soluble in water. The solid was crystallised from aqueous methanol when needle shaped crystals of m.p.$> 360^{o}$ was obtained. Further work on this product is in progress

KI-Acetic acid titration on the acetate, m.p. 213-5°

The acetate, m.p. 213-5° (0.0445 g.) was dissolved in glacial acetic acid in a 25 ml. volumetric flask and a saturated solution of KI in glacial acetic acid was added and then the volume made up to 25 ml. A similar blank solution of KI in glacial acetic acid was prepared in a 25 ml. volumetric flask. The above solutions were titrated against sodium thiosulphate solution (0.02969 N). The difference in the titer value was 2.4 ml. of thiosulphate solution for 10 ml. of each solution. Calculation revealed that two equivalent atoms of iodine were liberated by the compound, showing that one atom of iodine is liberated by one atom of oxygen, indicating a peroxide linkage of the type C-O-O-C in the molecule.

Hydrogenation of the acetate, m.p. 213-5°

The acetate, m.p. 213-5° (0.2 g.) dissolved in ethanol (30 ml.) was hydrogenated in presence of palladium-on-charcoal catalyst at ordinary temperature and pressure. Two mole equivalents of hydrogen were consumed within 1 hour. On working up the reaction mixture fine needle shaped crystals on m.p. 262-3° were obtained. Acetylation of this product furnished an acetate, m.p. 170°.

Further work on these products are in progress.

LAH reduction of the original alcohol, m.p. 228-9°

To a solution of the original alcohol, m.p. 228-9° (0.3 g.) in dioxan (15 ml.) was added LAH (0.2 g.) and the mixture refluxed on the water-bath for an hour. Excess of LAH was destroyed with ethyl acetate (100 ml.) and the organic layer was washed with water, and dried (Na_2SO_4). Evaporation

of the solvent furnished a crystalline solid which on crystallisation from methanol gave crystals, m.p. 302-3°. Acetylation of this compound by acetic anhydride-pyridine method furnished an acetate, m.p. 300°.

Further work is in progress.

REFERENCES

1. Paterno, Ber.dtsch.Chem.Ges., 1876, 346.
   Idem. Gazz., 1880, 157.
   Idem. ibid., 1882, 231.

2. Zopf, Annalen, 1895, 288, 50.
   Idem. ibid., 1909, 364, 273.

3. Hesse, J.Pr.Chem., 1898, ii, 58, 482.
   Idem. ibid., 1902, ii, 65, 554.
   Idem. ibid., 1906, ii, 73, 113.

4. Asahina and Akagi, Ber.dtsch.Chem.Ges., 1938, 980.

5. Asahina and Yosioka, Ber.dtsch.Chem.Ges., 1940, 742.

6. D.H.R.Barton and T.Brunn, J.Chem.Soc., 1952, 1683.

7. D.H.R.Barton, P. deMeyo and J.C.Orr, J.Chem.Soc., 1958, 2239.

8. S.Huneck and L.M.Lehn, Bull.Soc.Chim. France, 1963, 1702.

9. I.Yosioka and T.Nakanishi, Chem.Pharm.Bull.Japan, 1963, 1468.

10. I.Yosioka, T.Nakanishi and I.Kitagawa, Chem.Pharm.Bull. Japan, 1967, 353.

11. M.N.Galbraith, C.J.Miller, J.W.L.Rawson, E.Ritchie, J.S.Shannon, W.C.Taylor, Aust.J.Chem., 1965, 226.

12. I.Yosioka, T.Nakanishi and I.Kitagawa, Tetrahedron Letters, 1968, 1485.

13. T.Nakanishi, T.Fujiwara and K.Tomita, Tetrahedron Letters, 1968, 1491.

14. G.V.Baddeley, T.G.Halsall and E.R.H.Jones, J.Chem.Soc., 1961, 3891, and literature cited therein.

15. Asahina and Akagi, Ber.dtsch.Chem.Ges., 1938, 982.

16. S.Huneck, ibid., 1961, 614.

17. I.Yosioka, T.Nakanishi and E.Tsuda, Tetrahedron Letters, 1966, 607.

18. M.Shamma, R.E.Glick, R.O.Mumma, J.Org.Chem., 1962, 4512.

19. I.Yosioka, T.Nakanishi and I.Kitagawa, Tetrahedron Letters, 1966, 5182.

20. J.S.Mills and A.E.A.Werner, J.Chem.Soc., 1955, 3132.

21. K.Schaffner, L.Cagliote, D.Arigoni, O.Jeger, H.Fazakerley, T.G.Halsall and E.R.H.Jones, Proc.Chem.Soc., 1957, 353.

22. L.Ruzicka, in "Perspectives in Organic Chemistry" (Ed. A.R.Todd), Interscience, London, 1956, p.265.

23. A.Eschenmoser, L.Ruzicka, O.Jeger and D.Arigoni, Helv.Chem.Acta, 1955, 1890.

24. G.V.Baddeley, T.G.Halsall and E.R.H.Jones, J.Chem.Soc., 1960, 1715.

25. W.J.Dunstan, H.Fazakerley, T.G.Halsall, E.R.H.Jones, Croat.Chem.Acta, 1957, 173.

26. Y.Tsuda and K.Isoba, Tetrahedron Letters, 1965, 3337.

27. W.Nagata and H.Itazaki, Chem.& Ind., 1964, 1194.

28. H.R.Arthur, W.H.Hui, C.N.Lam and S.K.Szeto, Aust.J.Chem., 1964, 697.

29. G.N.Pandey and C.R.Mitra, Tetrahedron Letters, 1967, 1353.

30. I.Yosioka, A.Matsuda and I.Kitagawa, Tetrahedron Letters, 1966, 613.

31. H.N.Khastgir, B.P.Pradhan, A.M.Duffield and L.J.Durham, Chem.Comm., 1967, 1217.

32. G.Berti, F.Bottari, A.Marsili, J.-M.Lehn, P.Witz and G.Ourisson, Tetrahedron Letters, 1963, 1283.

33. H.Ageta, K.Iwata, Y.Arari, Y.Tsuda, K.Isoba and S.Fukushima, Tetrahedron Letters, 1966, 5679.

34. H.Ageta and K.I.Wata, Tetrahedron Letters, 1966, 6069.

35. H.Ageta, K.Iwata and K.Yonizawa, Chem.Pharm.Bull.(Japan), 1963, 408.

36. H.Ageta, K.Iwata and S.Natori, Tetrahedron Letters, 1963, 1447.

37. H.Vorbruggen, S.C.Pakrashi, C.Djerassi, Ann., 1963, 668.

38. K.Nakanishi, Y.Y. Linn, H.Kakisawa, H.Y.Hsu and H.C.Hsin, Tetrahedron Letters, 1963, 1451.

39. P.Sengupta and H.N.Khastgir, Tetrahedron, 1963, 123.

40. F.N.Lahey, M.V.Leeding, Proc.Chem.Soc., 1958, 342.

41. Axial and equatorial -COOMe absorb at 1155, and 1245 cm^{-1}.

42. H.Fazakerley, T.G.Halsall, E.R.H.Jones, J.Chem.Soc., 1959, 1877.

43. T.Kariyoni and H.Ageta, Yakugakuzasshi, 1959, 105.

44. H.Ageta, K.Iwata and K.Yonizawa, Chem.Pharm.Bull. (Japan), 1963, 407.

45. P.Crabbe, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry", Holden-Day, Amsterdam, 1965, p.120.

46. G.Berti, F.Bottari, A.Marsilli, Il. Farmaco (Pavia). Ed. Sci. 1963, 441.

47. G.Berti, F.Bottari and A.Marsilli, Tetrahedron Letters, 1964, 1.

48. G.Brownlie, F.S.Spring, R.Stevenson and W.S.Strachan, J.Chem.Soc., 1956, 2419.

49. A.C.Paton, F.S.Spring and R.Stevenson, J.Chem.Soc., 1958, 2640.

50. H.Ageta, K.Iwata and S.Natori, Tetrahedron Letters, 1964, 3413.

51. H.R.Arthur, S.W.Tam and V.Augsusingh, Aust.J.Chem., 1960, 506.

52. H.R.Arthur, W.H.Hui and R.T.Aplin, Tetrahedron Letters, 1965, 937.

53. T.Kariyone, Y.Hashimoto and S.Tobinaga, Chem.Pharm.Bull.Japan, 1957, 369.

54. S.Nakamura, T.Yamada, H.Wada, Y.Inoua, T.Coto and Y.Hirata, Tetrahedron Letters, 1965, 2017.

55. J.M.Beaton, F.S.Spring, R.Stevenson and L.J.Stewart, Tetrahedron, 1958, 246.

56. H.Budzikiewicz, J.M.Wilson and C.Djerassi, J.Amer.Chem.Soc., 1963, 3688.

57. T.Ohmoto, K.Nishimoto, M.Ito and S.Natori, Chem.Pharm.Bull.(Japan), 1965, 224.

58. G.Eglinton, R.J.Hamilton, M.Martin-Smith, S.J.Smith and G.Subramanian, Tetrahedron Letters, 1964, 2323.

59. S.K.Kundu, A.Chatterjee and A.S.Rao, Tetrahedron Letters, 1966, 1043.

60. H.Wada, G.Coto and T.Coto, Tetrahedron Letters, 1966, 3461.

61. K.Nishimoto, M.Ito, S.Natori and T.Ohmoto, Tetrahedron, 1968, 735.

62. S.C.Pakrashi and S.K.Ray, J.Sci.Ind.Res.(New Delhi) Section B, 20, 1961, 186.

63. M.C.Dawson, T.G.Halsall and R.E.H.Swayne, J.Chem.Soc., 1953, 590.

64. O.Kennard, L.Riva-di Sanseverino, H.Vobruggen and C.Djerassi, Tetrahedron Letters, 1965, 3433.

65. L. Ruzicka, Experimentia, 1953, 357.

66. L.Ruzicka, "Perspective in Organic Chemistry", Interscience, London, 1956, 265.

67. H.Vorbruggen, S.C.Pakrashi and C.Djerassi, Ann.Chem., 1963, 668.

68. L.Ruzicka, Proc.Chem.Soc., 1959, 341; J.H.Richards and J.B.Handrickson, "The biogenesis of steroids, terpenes and Acetogenins", Benzamin, New York, 1964; R.B.Clayton, Quart.Rev., 1965, 168.

69. E.J.Corey, W.E.Russey and P.R.O.de Montellano, J.Amer.Chem.Soc., 1966, 4750; E.E.von Tamelen, J.D.Willett, R.B.Clayton and K.E.Lord, J.Amer.Chem.Soc., 1966, 4752.

70. Zimmernann, Z.Physiol.Chem., 1935, 257; 1936, 247.

71. D.H.R.Barton and P.De Mayo, J.Chem.Soc., 1954, 887.

72. Huang-Minlon, J.Amer.Chem.Soc., 1949, 3301.

73. H.Budzikiewicz, C.Djerassi and D.H.Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day: San Francisco, 1964.

74. A.C.Paton, F.S.Spring and R.Stevenson, J.Chem.Soc., 1958, 2640.

75. Fieser and Fieser, "Steroids", Asia Publishing House, New York, 1960, p. 96.

76. E.Skan and W.Bergmann, J.Org.Chem., 1939, 166.

77. N.S.Bacca and D.H.Williams, "Application of NMR spectrometry in Organic Chemistry", Holden-Day: San Francisco, 1964.

78. H.T.Cheung and M.C.Fing, J.Chem.Soc., 1968, 1047.

79. P.Potier, B.C.Das, A.M.Bui, M.M.Janot, A.Pourrat and H.Purrat, Bull.Soc. Chim.,France, 1966, 3458.

80. Only the significant peaks of IR and Mass spectra are recorded.