CHAPTER VI

Experimental

The petroleum ether used throughout the investigation had boiling point 60-80°. All rotations were measured in chloroform solution. UV was recorded in Carl Zeiss Zena VSU-1 in 95% ethanol solution. Infrared were recorded in Perkin-Elmer spectrophotometer 337.

Extraction: Isolation of the neutral fraction

Dried and powdered trunk bark and stem of Aleurites montana (2 Kg.) was extracted with benzene in a soxhlet apparatus for twenty hours. Benzene was distilled off and the gummy residue (9 gm) was taken up in ether (1 litre). The ether solution was washed with 10% aqueous sodium hydroxide solution (3 x 300 ml) and with water till neutral ether solution was dried over anhydrous sodium sulphate and the ether evaporated, when a gummy material (4.6 gm) was obtained.

Chromatography of the above gummy material

The above gummy material (4.6 gm) dissolved in benzene (6 ml) and was placed on a column of alumina (200 gm) deactivated with 8 ml of 10% aqueous acetic acid. The chromatogram was developed with petroleum ether and was eluted with the following solvents (Table IX).

Table IX

Chromatography of the above gummy material (4.6 gm).

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether (400 ml)	1-8	Solid contaminated with oil m.p. 244-48° (2.16 gm)
Petroleum ether: benzene (4:1) (100 ml)	9-10	Oily material (210 mg)
Petroleum ether: benzene (3:2) (400 ml)	11-18	Solid m.p. 128-32° on digestion with methanol (1.23 gm)

Further elution with more polar solvent did not afford any crystalline material.

Isolation of friedelin 68

Fractions 1-8 (table IX) were combined (2.16 gm), dissolved in 5 ml of benzene and was rechromatographed over a column of active alumina (80 gm). The chromatogram was developed with petroleum ether (Table X).

Table X

Chromatography of the residue of fractions 1-8 of table X

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether (150 ml)	1-3	Oil (0.8 gm)
Petroleum ether (400 ml)	4-11	Oily solid (850 mg) crystalline solid m.p. 250-52° on digestion with methanol

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

The above solids (fractions 4-11, table X) were digested with 10 ml of petroleum ether and allowed to stand at room temperature for a few days when fine needle shaped colorless crystals m.p. 254-56° separated out. The crystals were collected by filtration which after repeated crystallisation from a mixture of chloroform and methanol gave crystals of m.p. 258-9°, $(\alpha)_D$ - 36°. Its melting point was not depressed when mixed with an authentic specimen of friedelin. IR of the compound was also superimposable with the IR of an authentic sample of friedelin.

Found: C, 84.18; H, 11.76%

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

Lithium aluminium hydride reduction of friedelin

To friedelin (800 mg) taken in dry ether (80 ml) was added lithium aluminium hydride (200 mg) and the reaction mixture was refluxed on a water bath for four hours. Excess of lithium aluminium hydride was decomposed carefully with moist ether and then a saturated solution of sodium sulphate was added to the reaction mixture. The ethereal solution was washed with water and dried (Na_2SO_4). After removal of the solvent a solid residue (710 mg.) was obtained, which showed two spots on the chromatoplate. The residue was then chromatographed over alumina (50 gm) deactivated with 2 ml of 10% aqueous acetic acid.

Table XI

Chromatography of the above residue (710 mg)

Eluent	Fractions (50 ml each)	Residue on evaporation
Petroleum ether (100 ml)	1-2	Nil
Petroleum ether:benzene (4:1) (200 ml)	3-6	Solid (80 mg) m.p. 272-5°
Petroleum ether:benzene (3:2) (300 ml)	7-12	Solid (580 mg) m.p. 292-4°

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

Isolation of epi-friedelanol 69

The fractions 3-6 (80 mg) (table XI) were collected and after repeated crystallisations from a mixture of chloroform and methanol fine needle shaped crystals, m.p. 275-7°, $(\alpha)_D$ + 9° were obtained. The latter was found to be identical with an authentic specimen of epi-friedelanol 69 (m.m.p. and IR comparison). (lit.[65] m.p. 278-80°, $(\alpha)_D$ + 8.1, + 9.2°). Found: C, 84.32; H, 12.06. Calc. for $C_{30}H_{52}O$, C, 84.11; H, 12.14%.

Preparation of epi-friedelanol acetate

To the above epi-friedelanol (200 mg) dissolved in pyridine (2 ml) was added acetic anhydride (2 ml) and the solution was heated on a water bath for five hours. The solution was then poured in ice cold water when a crystalline solid separated out. The solid was collected, washed with water, till the washings were neutral and dried. The crude acetate (190 mg), on crystallisation from methanol chloroform mixture afforded pure epi-friedelanol acetate (160 mg), m.p. 290-92°, $(\alpha)_D$ + 40°. Its melting point was not depressed when mixed with an authentic specimen of epi-friedelanol acetate (m.m.p.) lit.[66] m.p. 290-4°, $(\alpha)_D$ + 45°).

Found: C, 81.58; H, 11.32%

Calc. for $C_{32}H_{54}O_2$: C, 81.70, H, 11.49%.

Isolation of friedelanol 70

The solids (580 mg) from fractions 7-12 (table XI) were collected and crystallised from a mixture of methanol and chloroform.

After three crystallisations it gave fine crystals (460mg), m.p. 297-9°, $(\alpha)_D$ + 15.6°. The melting point could not be raised by further crystallisation. The solid was found to be identical with an authentic sample of friedelanol (m.m.p. and IR comparison).

Found: C, 84.31; H, 12.53%

Calc. for $C_{30}H_{52}O$, C, 84.11; H, 12.14%.

Preparation of friedelanol acetate

To the above friedelanol (300 mg.) dissolved in pyridine (5 ml) was added acetic anhydride (5 ml) and the solution was heated on a water bath for five hours. The solution was then poured in ice cooled water when a crystalline solid separated out. The solid was collected, washed with water and then dried. The crude acetate (290 mg) on crystallisation from a mixture of chloroform and methanol gave crystals m.p. 263-5°. Its melting point could not be raised by further crystallisation and was not depressed when mixed with an authentic specimen of friedelanol acetate.

Found; C, 81.49; H, 11.23%

Calc. for $C_{32}H_{54}O_2$: C, 81.70; H, 11.49%.

Preparation of friedelin oxime

The oxime of friedelin was prepared by the method of Drake and Jacobsen. The solid after pouring in water was collected by filtration. After drying it was crystallised from a mixture of chloroform and methanol, when the pure oxime m.p. 294-6° was obtained.

Isolation of β-sitosterol 71

Fractions 11-18 (table IX) were combined (1.23 gm) dissolved in 5 ml of benzene and was rechromatographed over a column of alumina (50 gm) deactivated with 2 ml of 10% aqueous acetic acid. The chromatogram on eluting with benzene afforded shining flakes m.p. 134-6° which after two crystallisation from acetone gave fine needle shaped crystals of m.p. 135-7°, $(\alpha)_D$ - 40°. Its melting point was not depressed when mixed with an authentic specimen of β-sitosterol.

Preparation of β-sitosterol acetate 72

To the sterol (180 mg) dissolved in pyridine (2 ml) and the solution was allowed to stand at room temperature for eighteen hours. The solution was then poured into ice cold water when a crystalline solid separated out. The solid was collected, washed with water till the washings were neutral and dried. The crude acetate (180 mg) m.p. 124-5°, on crystallisation from methyl alcohol afforded pure β-sitosterol acetate (80 mg), m.p. 128-29° $(\alpha)_D$ - 38°. Its melting point was not depressed when mixed with an authentic specimen of β-sitosterol acetate.

Found: C, 81.47; H, 11.46%

Calc. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48%.

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