[Jour. Indian Chem. Soc., Vol. 44, No. 8, 1967]

# Terpenoids and Related Compounds. Part V[1]. Chemical Investigation of *Baccaurea sapida* Muell

Debranjan Misra and Hari Narayan Khastgir

*Baccaurea sapida* Muell[2,3] (fam: Euphorbiaceae) Beng. Latka is a large evergreen tree which grows usually in the base of Eastern Himalayas, Assam, Sylhet, Burma, Malay Peninsula and Andaman Islands. Bark of the tree is used by Lepchas as a mordant in dyeing with manjit or lac[2]. The fruits are sweet when ripe and are edible. The stembark and leaves are stated to be toxic[2].

The present investigation was undertaken with the bark of *B. sapida* since it was not chemically examined before. The dried and powdered bark was extracted with benzene. The benzene extract was separated into ether soluble and ether insoluble portions. The latter fraction after acetylation, chromatography and crystallisation from acetone gave a solid m.p. 162-64° in very poor yield, which was not investigated further. The ether soluble fraction was separated into acidic and neutral fractions. The acidic fraction was esterified with diazomethane. Chromatography of the crude ester over deactivated alumina afforded with petroleum a solid ester, m.p. 138-39°, $[\alpha]_D$-40°. On further elution with more polar solvents (petroleum: benzene 4:1) furnished a second ester, m.p. 220-22° $[\alpha]_D$+5° which has been identified as methyl betulinate.

The neutral fraction on chromatography over alumina first provided a substance which after rechromatography and crystallisation gave a solid, m.p. 256-58°, identified as friedlin. The second solid which followed the former in the chromatography was *epi*-friedelanol, m.p. 274-76°, $[\alpha]_D$+9°. The last crystalline solid from the chromatogram was identified as $\beta$-sitosterol. The homogeniety of the compounds were confirmed by thin-layer chromatography.

## EXPERIMENTAL

All melting points are uncorrected. The petroleum used throughout the investigation had b.p. 60-80°.

*Extraction of the Bark of* B. sapida :—Dried and powdered bark of *B. Sapida* (1 Kg) was extracted with benzene for 18 hr. Benzene was distilled and the dark resinous residue obtained was taken up in ether. A solid insoluble in ether separated out. This was collected by filtration. The solid was acetylated by heating with acetic anhydride and pyridine, chromatographed and crystallised from acetone, m.p. 162-64°. The clear ether solution

1. Part IV.—H. N. Khastgir and B. P. Pradhan, *J. Ind. Chem. Soc.*, 1967, 44, 159.
2. Hooker, "Flora of British India" Vol. V, 371, Reprint 1954.
3. Cowan and Cowan, "The Trees of North Bengal", page 115, 1929.

was washed with cold 10% NaOH solution and then with water. The alkali washed portion was collected and kept aside. The neutral ether solution was dried (anhydrous $Na_2SO_4$) and evaporated to furnish a gummy material (8 gms).

The above gummy neutral residue was chromatographed over a column of alumina (350 gms. deactivated with 14 ml of 10% aqueous acetic acid). On elution with petroleum a crystalline solid A (0.8 gm), m.p. 242-48° was obtained. Immediately after this another solid B (0.2 gm), m.p. 261-68° was obtained. Further elution with a mixture of petroleum and benzene (3:2) furnished a third crystalline solid C (1.0 gm), m.p. 134-36°.

*Friedelin*:—The first crystalline solid (A) (0.8gm) was rechromatographed over active alumina (25 gms). On elution with a mixture of petroleum and benzene (4:1), a crystalline solid (0.6 gm), m.p. 248-50° was obtained, which on repeated crystallization from a mixture of chloroform and methanol gave a crystalline solid, m.p. 256-58°, $(\alpha)_D$ $CHCl_3$-36°, (lit[4] m.p. 260-62°; $[\alpha]_D$-29°) which showed a negative test with tetranitromethane and was found to be identical with an authentic specimen of Friedelin (mixed m.p). (Found: C, 84.18; H, 11.76. Calc. for $C_{30}H_{50}O$: C, 84.44; H, 11.81%).

*epi-Friedelanol*: The solid (B) (0.2 gm) in the above chromatogram was rechromatographed over active alumina (10 gm) which after repeated crystallisation from a mixture of chloroform and methanol provided *epi*-friedelanol, m.p. 274-76° $[\alpha]_D CHCl_3$+9° (lit.[5,6] 278-80°; $[\alpha]_D$+ 8.7, +9.2) and was found to be identical with an authentic specimen of *epi*-friedelanol (mixed m.p.). (Found C, 80.56; H, 12.00; Calc. for $C_{30}H_{52}O$, $CH_3OH$ C, 80.85; H, 12.17%). The acetate melting point 290-92°, $[\alpha]_D CHCl_3$+40°, prepared in the usual manner was found to be identical in all respects with an authentic specimen of *epi*-friedelanyl acetate (Mixed m.p. and I.R.) (lit.[7] m.p. 290-94°, $[\alpha]_D$ +45°).

*β-Sitosterol*: The solid (C) (1 gm) obtained in the above chromatogram after several crystallisations from a mixture of chloroform and methanol yielded β-sitosterol, m.p. 135-36°, $[\alpha]_D$ $CHCl_3$-40° identical with an authentic sample of β-sitosterol. (Found C, 84.03; H, 12.38; Calc. for $C_{29}H_{50}O$; C, 83.99; H, 12.15%). The acetate, m.p., 125-26°, $[\alpha]_D$ $CHCl_3$-38° prepared in the usual manner was found to be identical with an authentic specimen of β-sitosterol acetate. (Found C, 81.68; H, 11.33; Calc. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48%).

*Isolation of ester m.p.* 138-39° *and methyl betulinate*: The alkali washed portion of the ether solution was acidified with dil. HCl. The precipitated solid acid was extracted with ether. The ethereal solution after washing and drying was concentrated to a small volume. The ethereal solution of the acid was esterified with an ethereal solution of diazomethane (from 1 gm. of Nitrosomethylurea) and after usual working up, the crude ester was chromatographed over deactivated alumina (30 gm. deactivated with 1 ml. of 10% aqueous acetic acid). Elution with petroleum furnished a solid, m.p. 130-34° which on crystallisation from methanol gave a crystalline solid, m.p. 138-39° $[\alpha]_D$ $CHCl_3$-40°, (Found C, 81.89; H, 11.54; $C_{31}H_{48}O_2$ requires C, 81.93; H, 11.26%). Further elution with petroleum: benzene (4:1) furnished a solid (0.5 gm), m.p. 210-220° which on crystallisation from methanol furnished

4. Drake, Jacobsen, *J. Amer. Chem. Soc.*, 1935, 57, 1570, 1954.
5. Susumu Nomomura, *J. Pharm. Soc., Japan*, 1955, 75, 80-3.
6. T. Takemotu and Nodoka Yahagi, *J. Pharm. Soc., Japan*, 1955, 75, 1164-66.
7. Jefferies, *J. Chem. Soc.*, 1954, 473.

needle shaped crystals of methyl betulinate, m.p. 220-22° $[\alpha]_D$ $CHCl_3$ + 5° (lit.[8] m.p. 224-25° $[\alpha]_D$ +5°) identical with an authentic sample of methyl betulinate (Found: C, 78.76; H, 10.58; Calc. for $C_{31}H_{50}O_3$: C, 79.10; H, 10.71%).

*Acetyl methyl betulinate*: The above methyl betulinate (0.2 gm) was acetylated in the usual manner. On working up in the usual manner and after chromatography it furnished a solid, m.p. 190-96° in the petroleum fraction. This solid after repeated crystallisation from a mixture of methanol and chloroform gave pure acetyl methyl betulinate, m.p. 200-2° identical with an authentic sample of acetyl methyl betulinate. (Found: C, 77.37; H, 10.13; Calc. for $C_{33}H_{52}O_4$: C, 77.34; H, 10.15%).

The authors express their sincere thanks to Prof. (Mrs.) A. Chatterjee of the University College of Science, Calcutta and to Dr. P. Sengupta of Kalyani University, Kalyani for authentic specimens of Friedelin and *epi*-friedelanol respectively. The authors are grateful to Dr. S. K. Sengupta of East India Pharmaceutical Works Ltd., Calcutta for optical rotations. The authors are also indebted to East India Pharmaceutical Works Ltd., Calcutta for the award of a fellowship to one of them (D.R.M.)

Chemistry Department,
University of North Bengal,
P.O. North Bengal University,
Dist. Darjeeling (West Bengal)

*Received, February* 28, 1967.

8, Simonsen and Ross, "The Terpenes", Vol V, The University Press, Cambridge 1957, p. 317.