

LIST OF THE PUBLISHED AND COMMUNICATED PAPERS

1. Terpenoids and Related Compounds : Part IV. Chemical Investigation on E. Pulcharimma Willd., J. Ind. Chem. Soc., Vol.44, No.2, p.159, 1967.
2. Identification of a New Triterpene, 3-epi-moretenol, from the Bark of Sapium sebiferum Roxb., Chem. Comm., p.1217, 1967.
3. Chemical Investigation of Croton Caudatus Geisel., Communicated to J. Ind. Chem. Soc.
4. Terpenoids and Related Compounds : Part VII. Chemical Investigation of Sapium Eugenifolium Ham., communicated to J. Ind. Chem. Soc.
5. Terpenoid and Related Compounds : Part-VIII. Chemical Investigation of Sapium Baccatum, Roxb., communicated to J. Ind. Chem. Soc.



Identification of a New Triterpene, 3-Epimoretenol, from the Bark of *Sapium sebiferum* Roxb.

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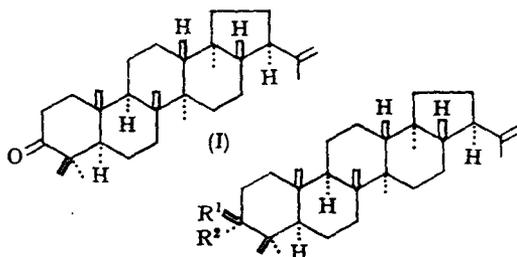
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THE isolation of moretenone (I), moretenol (II), and 3-epimoretenol (III) from the neutral ether-soluble portion of the bark extract of the bark of *Sapium sebiferum* (Euphorbiaceae) is believed to constitute the first report of the occurrence of triterpenes of the hopane series in the Euphorbiaceae species. Moretenone (I), the product of oxidation of moretenol (II),² was the triterpene present in greatest quantity. This is the first isolation of moretenone from natural sources.

The third triterpene, $C_{30}H_{50}O$, m.p. 223–224°, $[\alpha]_D - 2.5$, {acetate $C_{32}H_{52}O_2$, m.p. 233–234° $[\alpha]_D - 19.4$ } was obviously related to (I) and (II) from comparison of their respective mass (m/e 189, 207, 426) and n.m.r. spectra. Signals in the n.m.r. spectrum of this triterpene appeared at 0.68 (3H), 0.83 (6H), 0.95–0.98 (9H), and 1.68 p.p.m. (3H) corresponding to six methyl groups on saturated carbon and one on a doubly bonded carbon atom, respectively. A signal at 3.40 p.p.m. (width at half height of 7 Hz.) indicated that the proton attached to the carbon bearing the



(II) $R^1=OH, R^2=H$

(III) $R^1=H, R^2=OH$

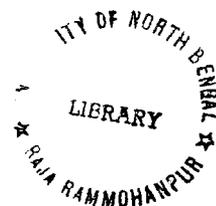
hydroxy-group was equatorial. The signal of the terminal methylene appeared at 4.68 p.p.m. Chromium trioxide-pyridine oxidation yielded moretenone (I) and established the unknown to be 3-epimoretenol (III).

The authors wish to thank Dr. E. Ritchie of the University of Sydney for samples of moretenone and moretenyl acetate.

(Received, October 10th, 1967; Com. 1086.)

¹ R. N. Chopra, S. L. Nayar, and I. C. Chopra, "Glossary of Indian Medicinal Plants", C.S.R.I., India, 1956, p. 221.

² M. N. Gabraith, (the late) C. J. Miller, J. W. L. Rowson, E. Ritchie, J. S. Shannon, and W. C. Taylor, *Austral. J. Chem.*, 1965, 18, 226.



Terpenoids and Related Compounds. Part IV¹. Chemical Investigation of *Euphorbia pulcherimma* Willd

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Euphorbia pulcherimma Willd², belonging to the *Euphorbiaceae* family is a shrub which is commonly called as Poinsettia. It is cultivated in the district of Darjeeling up to a height of 4,000 ft. for its showy scarlet bracts. We became interested to undertake a chemical investigation of the whole plant of *E. pulcherimma*, since no investigation on it was reported in the literature. The whole plant was dried and powdered and extracted with benzene. The neutral material from the benzene extract was chromatographed over alumina. The less polar fraction from the chromatogram was identified as the acetate of the triterpene alcohol, germanicol³ (mixed m.p.). The more polar fraction was identified as β -sitosterol, by converting it into its acetate which was found to be identical (mixed m.p.) with β -sitosterol acetate.

EXPERIMENTAL

Isolation of Neutral Fraction from E. pulcherimma.—Dried and powdered whole plant of *E. pulcherimma* (920 g.) was extracted with benzene in a Soxhlet apparatus for 36 hr. Benzene was distilled and the dark resinous mass obtained was taken in ether. The ether solution was washed with 10% NaOH solution and then with water. It was dried over anhydrous sodium sulphate and evaporated to furnish the gummy neutral residue (35.5 g.).

The above gummy residue was chromatographed over a column of alumina (1200 g. deactivated with 48 ml of 10% aqueous acetic acid solution). On elution with light petroleum* a crystalline solid (A, 1.2 g.), m.p. 235-40°, was obtained. Further elution with a mixture of light petroleum-benzene (3:2) furnished a second crystalline solid (1.8 g.), m.p. 130-32°.

Germanicol Acetate.—The first crop of the crystalline solid (A, 1.2g.), m.p. 235-40°, on repeated crystallisation from chloroform and methanol gave crystals, m.p. 275-6°, $[\alpha]_D^{20} +20^\circ$, which showed positive test with tetranitromethane and was found to be identical with an authentic specimen of germanicol acetate (mixed m.p.). (Found: C, 81.51; H, 11.05. Calc. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18%) (lit³ m.p. 279-80°, $[\alpha]_D^{19} +19^\circ$).

*The petroleum used had b.p. 60°-80°. All the rotations were taken in chloroform unless otherwise stated. All melting points are uncorrected.

1. Part III: Sengupta and Khastgir, *Tetrahedron*, 1963, **19**, 123.

2. Cowan and Cowan, "The Trees of North Bengal", Government of Bengal, 1929, p. 118.

3. Simonsen and Ross, "The Terpenes", vol. IV, The University Press, Cambridge, 1957, p. 247.

Germanicol.—To a solution of above acetate (0.1 g.) in benzene (20 ml) was added 5% methanolic KOH solution (20 ml) and the mixture refluxed for 3 hr. On working up in the usual way, a solid, m.p. 168-70°, was obtained. The solid was chromatographed over deactivated alumina (6 g.). Elution with light petroleum-benzene mixture (2:3) gave a solid (0.07 g.) of m.p. 173-74°, which on crystallisation from methanol furnished needle-shaped crystals of germanicol, m.p. 175-76°, $[\alpha]_D + 8^\circ$. (Found C, 84.26; H, 11.79. Calc. for $C_{30}H_{50}O$: C, 84.44; H, 11.81%) (lit.³ m.p. 180°-81°, $[\alpha]_D + 7^\circ$).

Acetylation of Germanicol.—Germanicol (0.2 g.) was acetylated with pyridine (2 ml) and acetic anhydride (2 ml). After working up in the usual way, the solid was chromatographed over alumina (25 g. of alumina deactivated with 1 ml of 10% aqueous acetic acid). Elution with light petroleum gave a solid (0.18 g.) of m.p. 272-74°, which on crystallisation from chloroform and methanol provided a solid of m.p. 275-76°, identical with the germanicol acetate isolated above, (mixed m.p.).

Germanicol Benzoate.—Germanicol (0.2 g.) was benzoylated in the usual manner with benzoyl chloride (2 ml) and pyridine (6 ml). The product after crystallisation from acetone gave germanicol benzoate (0.14 g.), m.p. 268-9° $[\alpha]_D + 33.3^\circ$. (Found C, 83.74; H, 10.04. Calc. for $C_{37}H_{54}O_2$: C, 83.72; H, 10.25%) (lit.³ m.p. 270°, $[\alpha]_D + 38^\circ$).

Germanicone.—A solution of germanicol (0.2 g.) in pyridine in (2 ml) cooled to 15° was added to a complex prepared from chromium trioxide (0.2 g.) and pyridine (2 ml) at 15°. The mixture was allowed to stand overnight and worked up as usual. The crude solid was chromatographed over active alumina (12 g.) Elution with light petroleum gave a solid (0.16 g.), which on crystallisation from methanol-chloroform mixture had m.p. 186-87°, $[\alpha]_D + 36^\circ$. (Lit.³ m.p. 188°-89° $[\alpha]_D + 37^\circ$. (Found: C, 84.80; H, 11.23. Calc. for $C_{30}H_{48}O$: C, 84.84; H, 11.39%).

Germanicol Acetate Oxide.—To gormanicol acetate (0.1g.) was added a chloroform solution of perbenzoic acid (20 ml). The solution was kept for 48 hr. in the frigidaire and the mixture was treated with 1% sodium iodide solution (20 ml) and glacial acetic acid (2 ml). The solution was taken in a separating funnel, the aqueous layer removed, and the chloroform layer was washed with dilute sodium hydroxide solution and water. The chloroform layer was dried over anhydrous sodium sulphate and evaporated to dryness, when a solid (0.09g.), m.p. 255°, was obtained. The crude solid was chromatographed over deactivated alumina (6 g. alumina deactivated with 0.2 ml of 10% aqueous acetic acid). On elution with light petroleum a solid, m.p. 271-73°, was obtained. On crystallisation from chloroform and methanol it gave crystals of the acetate oxide, m.p. 286-87°, $[\alpha]_D + 21.6^\circ$ (lit.³ m.p. 287-5°).

β -Sitosterol.—The second fraction (1.8 g.), m.p. 130-32° was crystallised from chloroform and methanol to furnish fine crystals of m.p. 139-40°, $[\alpha]_D - 33^\circ$ (lit. m.p. 136.5-37.5°, $[\alpha]_D - 36^\circ$. (Found C, 84.07; H, 11.92. Calc. for $C_{29}H_{50}O$: C, 83.98; H, 12.15%).

β -Sitosterol acetate.—The above solid (0.1 g.) of m.p. 139-40° was acetylated with pyridine (1 ml) and acetic anhydride (1 ml) in the usual manner. The acetate on crystallisation from acetone furnished β -sitosterol acetate (0.09 g.), m.p. 127-28°, $[\alpha]_D - 41.3^\circ$, identical (mixed m.p.) with an authentic sample. (Found: C, 81.63; H, 11.51. Calc. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48%) (lit m.p. 126-27, $[\alpha]_D - 42^\circ$).

The authors' best thanks are due to Dr. Alfred Bernhardt for the microanalytical data and to Dr. S. Nakamura, Nagoya University, Chikusa, Japan, for supplying them the authentic samples of germanicol and germanicol acetate. One of them (B. P. Pradhan) is grateful to the Council of Scientific and Industrial Research, New Delhi, for the grant of a junior fellowship. Thanks are also due to Dr. S. K. Sengupta, East India Pharmaceutical Works Ltd., Calcutta for the optical rotation study.

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Received August. 1, 1966.