AN EXAMINATION OF THE EUPHORBIACEAE OF HONG KONG*

I. THE OCCURRENCE OF TRITERPENOIDS

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The Euphorbiaceae are a very large plant family, growing mostly in the tropics. Numerous papers have been published on the investigations of lipids, terpenoids, and alkaloids from various species of the family. A review on these investigations in connection with plant taxonomy was written by Ponsinet and Ourisson[1] in 1965. It is interesting that in the triterpene field, five pentacyclic (bauerenol, germanicol, epigermanicol, multiforenol, and phyllanthol)[2] and three tetracyclic (euphol, euphorbol, and tirucallol)[3] alcohols were first discovered in plants of this family. Seventy-eight species of Euphorbiaceae from 30 genera have been identified in Hong Kong.[4] Of these, some are used in Chinese medicine, and only three have previously been investigated for triterpenoids. We thus select this family for a search of new triterpenoids.

The first two plants under investigation are *Aleurites moluccana* (L.) Willd. and *Bischofia trifoliata* (Roxb.) Hk. f. The former is a large tree having oval-shaped leaves, white flowers, and fleshy fruits, with hard-shelled, oily seeds. The oil is used in the preparation of paints and varnishes, for illumination, and as dressing for ulcers. *B. trifolia* is also a large tree with fairly big, oval to oblong, leaves. It has not been reported as a medicinal plant.

Although we were unable to detect any new compound, we have isolated from the light petroleum extract of both the leaves and stems of the first plant, *Aleurites moluccana*, a triterpenoid, moretenone, which has not formerly been reported as a natural product. We also obtained the corresponding 3β-alcohol, moretenol, α-amyrin, and β-sitosterol from the leaves, and β-sitosterol from the stems of the same plant. Moretenol has only been reported once in 1965 by Ritchie *et al.*[5] who discovered it in *Ficus macrophylla* Desf. They also determined its structure to be 3β-hydroxy-21αH-hop-28-ene. Moretenone was obtained by oxidation of the alcohol. Ethanol extracts (after light petroleum extraction) of both the leaves and stems were also investigated, but no other triterpenoid compound could be isolated.

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[3] Ourisson, G., Crabbe, P., and Rodig, O. R., "Tetracyclic Triterpenes." pp. 153, 160, and 155. (Hermann: Paris 1964.)

[4] "Check List of Hong Kong Plants." p. 24. (Hong Kong Herbarium 1966.)

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From the light petroleum extract of the leaves of *Bischofia trifoliata* (Roxb.) Hk. f., the presence of friedelan-3α-yl acetate, friedelin, friedelan-3β-ol, friedelan-3α-ol, and β-sitosterol has been demonstrated; friedelin and friedelan-3β-ol occur in the stems. Ellagic acid, which has been reported to be present in several species of the family, was also isolated from the ethanol extract of the leaves of this plant.

Experimental

Moretenone, moretenol, α-amyrin, β-sitosterol, friedelan-3α-ol and its acetate, friedelan-3β-ol, friedelin, and ellagic acid were identified by i.r. spectral comparisons, and all the above except ellagic acid were also confirmed by mixed m.p. determinations with authentic samples. Microanalyses were carried out by the Microanalytical Laboratory, University of Singapore. Optical rotations are for chloroform solutions. Light petroleum had b.p. 60–80°.

(*a*) Aleurites moluccana (*L.*) *Willd.*

(i) *Leaves.*—Milled air-dried leaves (5·6 kg) were extracted twice at room temperature with light petroleum. The concentrated combined extracts were chromatographed on alumina (2·5 g). Elution with light petroleum gave low-melting waxy material.

Elution with light petroleum–benzene (9 : 1) yielded a solid (2·0 g) which crystallized from acetone to give colourless needles of moretenone, m.p. 203–205°, $[\alpha]_D$ +61·2° (*c*, 0·90), ν_{max} (Nujol) 1705, 1640, 875 cm^{-1} (Found: C, 84·7; H, 11·5. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4%). It formed an oxime, m.p. 261–262°, ν_{max} (Nujol) 1650, 3280 cm^{-1}. It was subjected to Wolff–Kishner reaction in diethylene glycol to give moretene, m.p. 201–204°, and reduction with lithium aluminium hydride to yield moretenol, m.p. 233–236°, $[\alpha]_D$ +28·7°.

Elution with light petroleum–benzene (1 : 1) afforded α-amyrin (0·1 g), m.p. 185–186°, $[\alpha]_D$ +78·7°, ν_{max} (CCl_4) 3650, 1640 cm^{-1}. It formed α-amyrenyl acetate, m.p. 223–224°.

Further elution with the same solvent mixture yielded crystals (0·08 g) which crystallized from light petroleum to give needles of moretenol, m.p. 235–237°, $[\alpha]_D$ +28·7° (*c*, 0·40), ν_{max} (Nujol) 3500, 1640, 890 cm^{-1} (Found: C, 84·0; H, 12·0. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%).

Elution with light petroleum–benzene (1 : 4) gave β-sitosterol (0·24 g), m.p. 140°, $[\alpha]_D$ −35°. It formed an acetate, m.p. 127–129°, and a benzoate, m.p. 153–154°.

(ii) *Stems.*—The light petroleum extract of the stems on chromatography yielded moretenone (0·74 g, m.p. 203°, $[\alpha]_D$ +61·0°) when eluted with light petroleum–benzene (9 : 1). Further elution with light petroleum–benzene (1 : 1) afforded β-sitosterol (0·1 g), m.p. 137–140° (acetate, m.p. 129–130°).

(*b*) Bischofia trifoliata (*Roxb.*) *Hk. f.*

(i) *Leaves.*—The concentrated light petroleum extract of the powdered dried leaves (7·0 kg) was chromatographed on alumina (3 kg). Elution with light petroleum–benzene (9 : 1) yielded a substance (0·6 g) which on rechromatography and recrystallization from benzene–light petroleum gave friedelan-3α-yl acetate, m.p. 298–300°, $[\alpha]_D$ −12·0°, ν_{max} (Nujol) 1740, 1250 cm^{-1}. Further elution with the same solvent mixture afforded friedelin (3·0 g), m.p. 265–266°, $[\alpha]_D$ −25°, ν_{max} (CCl_4) 1720 cm^{-1}. Fractions from light petroleum–benzene (7 : 3) yielded needles (1·1 g) which crystallized from benzene, afforded friedelan-3β-ol, m.p. 286–288°, $[\alpha]_D$ +14·5°, ν_{max} (CCl_4) 3630 cm^{-1}. Fractions from light petroleum–benzene (1 : 1) deposited crystals (0·42 g) which crystallized from chloroform–methanol to give friedelan-3α-ol, m.p. 308–310°, $[\alpha]_D$ +13·0°, ν_{max} (CCl_4) 3625 cm^{-1}. Further elution with light petroleum–benzene (1 : 4) yielded needles of β-sitosterol (0·7 g), m.p. 139–140°.

The leaves, after extraction with light petroleum, were further twice extracted with ethanol at room temperature. The concentrated extracts deposited a brownish solid (7·3 g), m.p. > 360°, which was insoluble in light petroleum, benzene, and chloroform, and very sparingly soluble in alcohols. It gave a yellow colour with sodium hydroxide solution, and a blood-red solu-

tion with nitric acid containing a little nitrous acid. A dilute solution of the substance in ethanol gave a bluish green colour with neutral ferric chloride. Recrystallization from pyridine–ethanol afforded needles of ellagic acid, ν_{max} (Nujol) 3500, 1720, 1590, 1520 cm^{-1}.

(ii) *Stems.*—The concentrated light petroleum extract of the powdered dried stems (5·2 kg) on chromatography in the usual way yielded friedelin (0·2 g), m.p. 263–265, $[\alpha]_D$ −20·0°, and friedelan-3β-ol (0·4 g), m.p. 282–284°, $[\alpha]_D$ +15·0°.

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