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THE OCCURRENCE OF TRITERPENOIDS AND STEROIDS IN THREE *GLOCHIDION* SPECIES*

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Abstract—From the stems of *Glochidion dasyphyllum*, *G. hongkongense* and *G. macrophyllum*, twenty-two compounds have been isolated. These include eleven triterpenoids (nine related to lup-20(29)-ene and two to friedelane), and two sterols. One of the triterpenoids, lup-20(29)-ene-1β,3β-diol, has not previously been found in nature, and another, glochidonol, has only been isolated once before. Two others, a ketol and a diol, obtained in minute quantities, appear to be new compounds of the lupene series. Triterpenoids and stigmasterol were found in the leaves of only one of the species, while β-sitosterol was obtained from those of all three.

INTRODUCTION

The *Glochidion* genus (Euphorbiaceae) is found in tropical Asia and Australia, and its species are commonly known as Abacus plants. Of the seven listed[1] local species, three are rare, and one[2] has recently been investigated in this laboratory. We report here the work on the remaining three. *G. dasyphyllum* K. Koch. and *G. hongkongense* Muell. are very similar plants, with ovate, obtusely acuminate leaves and shortly pedunculate flower-clusters. The difference is that the former is usually taller and perfectly glabrous in every part. *G. macrophyllum* Benth. is also quite glabrous; it can be distinguished from the other species by its stout branches and quite sessile fruiting-clusters.

RESULTS AND DISCUSSION

The concentrated light petroleum extract of each plant was examined by column chromatography on alumina. The distribution of all compounds found in these species is listed in Table 1. *Glochidion macrophyllum* yielded the triterpenoid lup-20(29)-ene-1β,3β-diol, which has never been reported to occur naturally, but has been prepared by reduction of glochidonol[2] and lup-20(29)-ene-1,3-dione.[3] Glochidonol (I), which was obtained from both *G. hongkongense* and *G. macrophyllum*, has only been isolated once in this laboratory; its structure has been proved to be 1β-hydroxylup-20(29)-ene-3-one. Glochidone [lupa-1,20(29)-dien-3-one] and glochidiol [lup-20(29)-ene-1β,3α-diol], isolated from all the three plants, have been reported to occur in two other *Glochidion* species.[2, 3] Glochidiol could not be crystallized from solvents, hence it has only been characterized as its diacetate. We have now

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* Part VII in the series "An Examination of the Euphorbiaceae of Hong Kong", for Part VI, see *J. Chem. Soc.* (C),1710 (1969).

[1] H. C. Tang and W. T. K. Leung, *Check List of Hong Kong Plants*, p. 25, Urban Council and Urban Services Department, Hong Kong (1967).

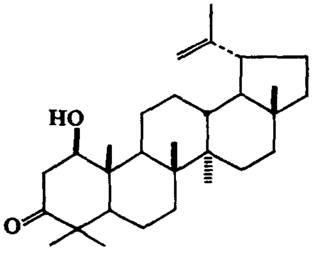
[2] See *An Examination of the Euphorbiaceae of Hong Kong*, Part VI.

[3] A. K. Ganguly, T. R. Govindachari, P. A. Mohamed, A. D. Rahimtulla and N. Viswanathan, *Tetrahedron* **22**, 1513 (1966).

isolated the pure diol from *G. hongkongense* and *G. dasyphyllum* by repeatedly boiling the crude product with light petroleum in which it is sparingly soluble. The residue had m.p. 266–267°, $[\alpha]_D + 17{\cdot}0°$, and gave one single spot on TLC. *G. macrophyllum* also afforded two apparently new lupene derivatives in minute quantities. One was a ketol A, m.p. 229–231°, $[\alpha]_D - 8{\cdot}7°$, ν_{max} 3580 (OH), 1720 (C═O), 3090, 1650, 865 (═CH_2) cm^{-1}, the other a diol B, which formed a diacetate, m.p. 234–235°, $[\alpha]_D + 77{\cdot}5°$, ν_{max} 1750, 1730, 1265, 1245 (acetates), 1650, 880 (═CH_2) cm^{-1}. Diol B was eluted from the alumina column together with lup-20(29)-ene-1β,3β-diol as needle-shaped crystals. On TLC, the mixture gave a single spot; however, after acetylation, the product showed an appreciable tailing effect, and was finally separated by column chromatography on alumina, B being the minor and slower moving constituent.

Table 1. Triterpenoids and steroids isolated from three *Glochidion* species

Compounds isolated	Stems	Leaves
Lupenone	*G. dasyphyllum*, *G. hongkongense*	
Glochidone [lupa-1,20(29)-dien-3-one]	All three species	
Epilupeol	*G. hongkongense*	
Lupeol	*G. hongkongense*	
Glochidonol [1β-hydroxylup-20(29)-en-3-one]	*G. hongkongense*, *G. macrophyllum*	
Glochidiol [lup-20(29)-ene-1β,3α-diol]	All three species	
Lup-20(29)-ene-1β,3β-diol	*G. macrophyllum*	
β-Sitosterol	All three species	All three species
Stigmasterol	*G. dasyphyllum*, *G. macrophyllum*	*G. macrophyllum*
Friedelin	*G. macrophyllum*	*G. macrophyllum*
Friedelan-3β-ol	*G. macrophyllum*	*G. macrophyllum*
New ketol A	*G. macrophyllum*	
New diol B	*G. macrophyllum*	



Glochidonol (I)

From Table 1, it can be seen that *G. dasyphyllum* yielded three, *G. hongkongense* and *G. macrophyllum* six compounds of the lupene series, while the last also afforded two friedelane derivatives. All three species contained β-sitosterol and two stigmasterol. Previous papers[2, 3] have reported the isolation of three lupene compounds from *G. hohenackeri* and of five lupene and two friedelane derivatives and β-sitosterol from *G. wrightii*. It thus appears that the *Glochidion* genus is characteristic in yielding lupene derivatives and β-sitosterol. Tetracyclic triterpenoids, which occur commonly in *Euphorbia* species, and oleanane and ursane derivatives, which are often found in the Euphorbiaceae family, have not so far been found in *Glochidion*.

EXPERIMENTAL

Infra-red spectra were recorded in Nujol mulls on a Perkin–Elmer 337 spectrophotometer, and u.v. spectrum of glochidone in 95% ethanol on a Unicam SP800 spectrophotometer. Melting points were taken on a Kofler hot-stage apparatus. Specific rotations were determined in $CHCl_3$. Alumina for chromatography was B.D.H. preparative grade; light petroleum had b.p. 60–80°. Known compounds were identified by mixed m.p. and comparison of i.r. spectra.

Extraction

For all three species, air-dried plant material was milled, then extracted twice at room temperature with light petroleum. The combined extracts were evaporated to a small volume.

G. macrophyllum

The concentrated extract of the stems (9 kg) was chromatographed on alumina (1 kg). Elution with light petroleum–benzene (9:1) yielded friedelin (0·44 g), m.p. 257–258°, $[\alpha]_D - 24°$; light petroleum–benzene (4:1), glochidone (0·69 g), m.p. 168–172°, $[\alpha]_D + 67{\cdot}5°$, λ_{max} 229 (log 3·99) and 334 (1·9) nm, ν_{max} 1660, 880 cm^{-1}, in the earlier fractions, and friedelan-3β-ol (0·02 g), m.p. 289–292°, in the later fractions; light petroleum–benzene (2:3), a sterol mixture (0·60 g), m.p. 144–147°, identified as stigmasterol (formation of acetate tetrabromide, m.p. 204°) and β-sitosterol, m.p. 139° (by debromination and deacetylation of the filtrate after removal of stigmasteryl acetate tetrabromide); light petroleum–benzene (3:7), a compund A (0·02 g), m.p. 229–231° (recrystallized from light petroleum–benzene mixture), $[\alpha]_D - 8{\cdot}7°$, ν_{max} 3580, 1720, 1650, 865 cm^{-1}; benzene–chloroform (4:1), glochidonol (0·10 g), m.p. 226–230° (from light petroleum), ν_{max} 3430, 3080, 1725, 1650, 880 cm^{-1} (acetate prepared at room temp. had m.p. 194–195°, ν_{max} 1750, 1725, 1230, 1650, 880 cm^{-1}); benzene–$CHCl_3$ (3:2), an amorphous solid (0·21 g), m.p. ~ 240°, ν_{max} 3350, 1640, 885 cm^{-1}, which with cold Ac_2O–pyridine gave glochidiol diacetate, m.p. 258–259°, $[\alpha]_D + 16{\cdot}0°$, ν_{max} 1750, 1255, 1650, 880 cm^{-1} (Found: C, 77·24; H, 10·14. Calc. for $C_{34}H_{54}O_4$: C, 77·52; H, 10·33%); benzene–$CHCl_3$ (2:3), needle-shaped crystals (0·15 g), m.p. 247–250°, ν_{max} 3360, 880 cm^{-1} (Found: C, 80·89; H, 11·58. Calc. for $C_{30}H_{50}O_2$: C, 81·38; H, 11·38%). TLC of the crystals on silica gel G developed with benzene gave a single spot. The crystals (0·10 g) were treated with Ac_2O and pyridine at room temp. for 2 days, the product was recrystallized from light petroleum–benzene mixture to give needle-shaped crystals, m.p. 224–225°, TLC of which on silica gel G developed with EtOAc–$CHCl_3$ (1:4) showed a distinct tailing effect. The acetate mixture (0·08 g) was dissolved in light petroleum–benzene (1:1) and applied to a column of alumina (20 g); elution with the same solvent mixture yielded in the earlier fractions 1β,3β-diacetoxy-lup-20(29)-ene (0·05 g), m.p. 210–213°, ν_{max} 1750, 1250, 880 cm^{-1}, and in the later fractions compound B which crystallized from ethanol as needle-shaped crystals (0·017 g), m.p. 234–235°, $[\alpha]_D + 77{\cdot}5°$, ν_{max} 1750, 1730, 1650, 1265, 1246, 880 cm^{-1}.

The concentrated extract of the leaves (2 kg) was treated as for the stems. Alumina used was 3 kg. Elution with light petroleum–benzene (9:1) yielded friedelin (0·26 g), m.p. 257–258°; light petroleum–benzene (4:1) friedelan-3β-ol (0·003 g), m.p. 290–291°; light petroleum–benzene (2:3) a sterol mixture (1·07 g), m.p. 114–147°, as for the stems.

G. hongkongense

The residue (23 g) from the concentrated extract of the stems (4 kg) was redissolved in light petroleum and chromatographed on alumina (1100 g). Elution with light petroleum–benzene (4:1) gave lupenone (0·22 g), m.p. 171–172°, $[\alpha]_D + 59{\cdot}6°$, ν_{max} 1710, 890 cm^{-1}; light petroleum–benzene (7:3), glochidone (0·21 g), m.p. 171°, $[\alpha]_D + 66{\cdot}8°$, ν_{max} 1670, 890 cm^{-1}; light petroleum–benzene (2:3), an amorphous solid (0·25 g) which, after rechromatography and recrystallization from 95% ethanol, gave epilupeol (0·08 g), m.p. 198–201°, $[\alpha]_D + 16{\cdot}4°$, ν_{max} 3630, 3450, 888 cm^{-1}, characterized as the acetate, m.p. 163°, $[\alpha]_D - 7{\cdot}8°$, ν_{max} 1740, 1245, 883 cm^{-1}; light petroleum–benzene (1:4), lupeol (0·11 g), m.p. 215°, $[\alpha]_D + 30{\cdot}5°$, ν_{max} 3300, 883 cm^{-1} (acetate, m.p. 219–220°, $[\alpha]_D + 42{\cdot}2°$, ν_{max} 1740, 1245, 880 cm^{-1}); benzene, β-sitosterol (0·05 g), m.p. 139–140°, $[\alpha]_D - 34°$ (acetate, m.p. 130–131°, $[\alpha]_D - 38{\cdot}7°$); benzene–$CHCl_3$ (9:1), glochidonol (0·90 g), m.p. 225–226°, ν_{max} 3430, 1720, 880 cm^{-1}; benzene–$CHCl_3$ (4:1) a gel (0·30 g), ν_{max} 3350, 885 cm^{-1} which, after repeatedly boiling in light petroleum, left a residue of pure glochidiol, m.p. 266–267°, $[\alpha]_D + 17{\cdot}0°$ (diacetate, m.p. 258–259°, ν_{max} 1750, 1255, 880 cm^{-1}). TLC of the diol on silica gel G developing with $CHCl_3$ showed a single spot.

The leaves (4 kg) were similarly investigated; only β-sitosterol (0·3 g) was obtained from the light petroleum–benzene (1:1) fractions.

G. dasyphyllum

Chromatography of the concentrated extract of the stems (6 kg) on alumina (600 g) gave, on elution with light petroleum–benzene (4:1), lupenone (0·05 g) in the earlier fractions and glochidone (0·50 g) in the later fractions; light petroleum–benzene (1:4) a sterol mixture (0·7 g) which yielded stigmasterol and β-sitosterol as for *G. macrophyllum*; chloroform, glochidiol (0·02 g). The leaves (3 kg), investigated in the usual manner, gave only β-sitosterol (1·0 g).

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