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TRITERPENOIDS FROM *GLOCHIDION MACROPHYLLUM* AND *G. PUBERUM**

Wai-Haan Hui and Man-Moon Li
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

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Key Word Index—*Glochidion macrophyllum*; *G. puberum*; Euphorbiaceae; triterpenoids; glochilocudiol, methyl betulinate, lup-20(29)-ene-1,3-dione; lup-20(29)-en-3α-ol-1β-yl acetate, lup-20(29)-en-1β-ol-3α-yl acetate, sitosterol.

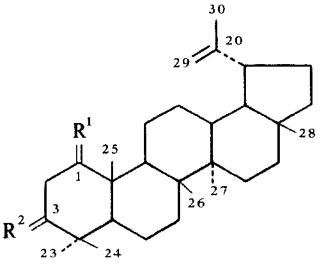
INTRODUCTION

G. macrophyllum contains friedelin, friedelan-3β-ol, sitosterol and stigmasterol in both the leaves and stems. The latter also contains glochidone, glochidonol [1β-hydroxy-lup-20(29)-en-3-one], glochidiol [lup-20(29)-ene-1β,3α-diol], lup-20(29)-ene-1β,3β-diol, two unidentified lupene derivatives (a ketol A and a diol B) [1], and lup-20(29)-ene-3α,23-diol [2]. Lupene derivatives have also been isolated from *G. dasyphyllum* [1], *G. hongkongense* [1], *G. wrightii* [3], and *G. eriocarpum* [4] and three new imidazole alkaloids were obtained from *G. phillippicum* [5].

RESULTS

Compounds A and B, previously isolated from *G. macrophyllum* Benth. [1], have been identified as methyl betulinate and glochilocudiol [lup-20(29)-ene-1α,3β-diol] respectively. The natural occurrence of glochicudiol has only been reported previously from two Euphorbiaceae species, *Glochidion multiloculare* [6] and *Fluggia virosa* [7].

Investigation of *G. puberum* Hutch. has shown that the petrol extract of the leaves on chromatography yielded, in succession, friedelin, friedelan-3β-ol, lupeol, compound **1** and sitosterol, while that of the stems gave friedelin, lupenone, glochidone, friedelan-3β-ol, sitosterol, two new compounds **2** and **3**, glochidonol (**4**), glochidiol (**5**) and lup-20(29)-ene-1β,3β-diol (**6**). The subsequent ethanol extracts of both the leaves and stems were examined for triterpene acids. No such compounds could be isolated. Compound **1**, $C_{30}H_{46}O_2$, was shown to be a β-diketone possessing the lup-20(29)-ene skeleton, and was proved to be identical with lup-20(29)-ene-1,3-dione prepared by oxidation of glochidonol (**4**) with Jones reagent. This is the first report of compound **1** as a natural product, though it has been partially synthesised from glochidiol (**5**) [8]. Compounds **2** and **3**, both of molecular formula $C_{32}H_{52}O_3$, were hydroxy-acetates of the lup-20(29)-ene series. On hydrolysis both yielded the same compound, glochidiol (**5**), while on acetylation both afforded glochidiol diacetate (**7**). Compound **3**, on oxidation with Jones reagent gave a keto-acetate, identical with glochidonyl acetate (**8**), and is therefore lup-20(29)-en-3α-ol-1β-yl acetate It follows that compound **2** is lup-20(29)-en-1β-ol-3α-yl acetate. These were finally confirmed when glochidiol on partial acetylation yielded a mixture which was separated by column chromatography into glochidiol diacetate, then in succession two monoacetates, identical with compounds **2** and **3** respectively, and finally unreacted glochidiol. Compounds **1**–**3** are examples of 1,3-dioxygenated lupene derivatives, which we have postulated to be characteristic of the *Glochidion* species [4].



	R^1	R^2
1	O	O
2	α-H, β-OH	α-OAc, β-H
3	α-H, β-OAc	α-OH, β-H
4	α-H, β-OH	O
5	α-H, β-OH	α-OH, β-H
6	α-H, β-OH	α-H, β-OH
7	α-H, β-OAc	α-OAc, β-H
8	α-H, β-OAc	O
9	α-OH, β-H	α-H, β-OH

EXPERIMENTAL

IR spectra were recorded for KBr discs; PMR spectra in $CDCl_3$ were determined at 60 MHz using TMS as int. stand ; UV spectra in 95 % EtOH, and optical rotations in $CHCl_3$ soln. Petrol had bp 60–80°. Known compounds were identified by TLC, mmp, IR and MS comparisons with authentic samples.

Glochidion macrophyllum. The previously reported compound A [3] had mp 229–231°, IR ν_{max}^{KBr} cm^{-1}: 3580 (OH), 1720, 1170 (COOMe), 3080, 1650, 880 ($>C{=}CH_2$), identical with methyl betulinate, and the diacetate of compound B, mp 234–235°, on hydrolysis with 5 % methanolic KOH gave the diol, mp 235°, MS· *m/e* 442 (M^+), IR ν_{max}^{KBr} cm^{-1}. 3350 (OH), 3080, 1650, 880 ($>C{=}CH_2$), identical with glochilocudiol (**9**) [7].

G. puberum *leaves*. Milled air-dried leaves (2 kg) were extracted 2 × with petrol at room temp for 10 days. The combined extracts were distilled to give a dry residue (130 g), which was chromatographed on Al_2O_3 (3 5 kg) in petrol. Elution with the same solvent gave needles of friedelin (1.2 g), mp 262–264°, IR ν_{max}^{KBr} cm^{-1}: 1715, then plates of friedelan-3β-ol (0.05 g), mp 289–290°, IR ν_{max}^{KBr} cm^{-1}. 3630, and finally needles of lupeol (0.9 g), mp 198–201°, IR ν_{max}^{KBr} cm^{-1}: 3380, 3050, 1650, 880. Elution with petrol C_6H_6 (1 : 1) yielded needles of compound **1** (0.04 g), mp 198–199° (from MeOH) (Found : M^+ 438. Calc. for $C_{30}H_{46}O_2$: M^+ 438), IR ν_{max}^{KBr} cm^{-1}: 3050, 1650, 880 ($>C{=}CH_2$), 1720 (C=O) 1700 (C=O), UV λ_{max}^{EtOH} nm : 225 (ε 12000) shifted to 285 (ε 28 500) in presence of alkali ($COCH_2CO$), PMR : δ 3 50 (2H, *ca q*, *J* = 20 Hz, $COCH_2CO$), 4.58 and 4.69 (1H *ea.*, *m*), 1.68 (3H, broad *s*) and 0.80–1.15 (6 × 3H, *s*) [lup-20(29)-ene system] then needles of sitosterol (0.3 g), mp 139–140°, IR ν_{max}^{KBr} cm^{-1}: 3360

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*Part 16 in the series 'An Examination of the Euphorbiaceae of Hong Kong'. For part 15, see ref. [7].

Stems. The residue (57 g) of the petrol extract of the stems (5 kg) was chromatographed on Al_2O_3 (1.5 kg) in petrol. Elution with petrol gave friedelin (1.9 g), followed by prisms of lupenone (0.03 g), mp 170–171°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}. 3050, 1710, 1650, 880, then prisms of glochidone (0.02 g), mp 169–170°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3050, 1660, 1620, 880 and finally plates of friedelan-3β-ol (0.9 g). Elution with petrol–C_6H_6 (1 : 1) yielded sitosterol (1.35 g), then prisms of compound **2** (0.04 g), mp 230–231° (from petrol), $[\alpha]_D$ + 13.6°, (Found: C, 79.4; H, 10.8 %; M^+ 484. $C_{32}H_{52}O_3$ requires C, 79.3; H, 10.8 %; M^+ 484). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3500 (OH), 1715, 1250 (OCOMe), 3050, 1650, 880 ($>C{=}CH$), PMR: δ 2.04 (3H, *s*, OCOC$\underline{H}_3$), 3.60 (1H, *ca q*, $W_{\frac{1}{2}}$ = 15 Hz, *ax*-C$\underline{H}$OH), 4.68 (1H, approx. *t*, $W_{\frac{1}{2}}$ = 7 Hz, *eq*-C$\underline{H}$OAc), followed by needles of compound **3** (0.03 g), mp 186–188° (from MeOH), $[\alpha]_D$ − 7.6°, (Found: C, 79.4; H, 10.6 %; M^+ 484, $C_{32}H_{52}O_3$ requires C, 79.3; H, 10.8 %; M^+ 484), IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3500 (OH), 1730, 1250 (OCOMe), 3050, 1650, 880 ($>C{=}CH_2$), PMR: δ 1.98 (3H, *s*, OCOC$\underline{H}_3$), 3.50 (1H, *ca t*, $W_{\frac{1}{2}}$ = 7.Hz, *eq*-C$\underline{H}$OH), 4.90 (1H, approx. *q*, $W_{\frac{1}{2}}$ = 15 Hz, *ax*-C$\underline{H}$OAc). Both compounds **2** and **3** showed δ 4.58 and 4.68 (1H, *ea*, *m*), 1.68 (3H, *br. s*) and ~0.8–1.5 (6 × 3H, *s*) [lup-20(29)-ene skeleton]. Elution with C_6H_6 gave needles of glochidonol (**4**) (0.05 g), mp 228–230°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3430, 3080, 1725, 1650, 880; with C_6H_6–$CHCl_3$ (1 : 1) needles of glochidiol (**5**) (0.02 g), mp 268–269°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3380, 3050, 1650, 880, then needles of lup-20(29)-ene-1β,3β-diol (**6**) (0.035 g), mp 251–252°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400, 3050, 1650, 880.

Oxidation of glochidonol (**4**). Glochidonol (0.025 g) was treated with Jones reagent, the product was recrystallized from MeOH to give needles of lup-20(29)-ene-1,3-dione (0.016 g), mp 196–199°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3050, 1720, 1700, 1650, 880, identical with compound **1**.

Hydrolysis of compounds **2** and **3**. Compounds **2** (0.015 g) and **3** (0.010 g) were refluxed separately with 5 % methanolic KOH (20 ml) for 2 hr. In each case the product, mp 263–265° (from MeOH) IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3380, 3050, 1650, 880, was identical with glochidiol (**5**).

Acetylation of compound **2**. Compound **2** (0.025 g) was treated with Ac_2O and C_5H_5N at room temp. for 2 days. The product (0.02 g), mp 258–260°, $[\alpha]_D$ + 17.5°, MS: *m/e* 526 (M^+); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1750, 1255, 3085, 1650, 880, was identical with glochidiol diacetate (**7**).

Acetylation of compound **3**. Compound **3** (0.015 g) was acetylated as for **2**. The product (0.012 g) was again identified as **7**.

Oxidation of compound **3**. Compound **3** (0.025 g) was treated with Jones reagent. The product (0.015 g) mp 196–197°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3080, 1750, 1650, 1230, 880 was identical with glochidonyl acetate (**8**).

Partial synthesis of compounds **2** and **3**. Glochidiol (**5**), (0.15 g) was acetylated with Ac_2O and C_5H_5N at room temp. for 1 hr. The product was chromatographed on Al_2O_3 (10 g). Elution with petrol–C_6H_6 (3 : 2) prisms of lup-20(29)-en-1β-ol-3α-yl acetate (0.02 g), mp 229–230°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3500, 3050, 1715, 1650, 1250, 880 identical with compound **2**, with petrol–C_6H_6 (2 : 3) needles of lup-20(29)-en-3α-ol-1β-yl acetate (0.03 g) mp 187–189°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3500, 3050, 1730, 1650, 1250, 880, identical with compound **3** and finally with C_6H_6 needles of unreacted glochidiol (0.03 g) mp 263–265°.

PMR signals of tertiary Me groups. The chemical shifts of the tertiary Me signals of a number of lupene derivatives from *Glochidion* species have been assigned [4] Those of compounds **1–3** and **9** are listed as follows:

	C-23	C-24	C-25	C-26	C-27	C-28
(1)	1.10	1.10	1.15	1.00	0.99	0.80
(2)	0.80	0.86	0.90	1.04	0.98	0.80
(3)	0.91	0.84	0.93	1.02	0.97	0 78
(9)	0.91	0.76	0.97	1.06	0.97	0.80

Test for acidic triterpenoids in G. puberum. Both the leaves and stems after extraction with petrol, were further extracted 2 × with 95 % EtOH at room temp. for 10 days. The combined extracts of each were distilled to dryness and extracted with Et_2O. The ethereal solns were separately shaken with M NaOH soln. The aq. layer in each case gave no ppt on acidification.

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