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LUPENE TRITERPENOIDS FROM *GLOCHIDION ERIOCARPUM**

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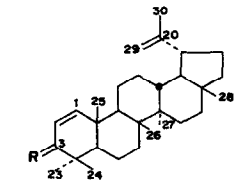
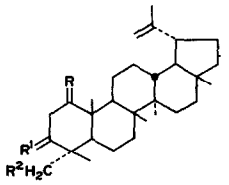
Key Word Index—*Glochidion eriocarpum*; Euphorbiaceae; lupene triterpenoids; glochidol [lupa-1,20(29)-dien-3β-ol].

Previous investigations of various *Glochidion* species [1–7] have shown that this genus is characteristic in yielding lupene derivatives, which include six new compounds: glochidone [lupa-1,20(29)-dien-3-one] (**2**) [4] glochidiol [lup-20(29)-en-1β,3α-diol] (**3**) [4], glochidonol [1β-hydroxylup-20(29)-en-3-one] (**4**) [1], lup-20(29)-en-1β,3β-diol (**5**) [2] [4], lup-20(29)-en-3α,23-diol (**6**) [3] and glochilocudiol [lup-20(29)-en-1α,3β-diol] (**7**) [4] [5]. The present work is a study of the fifth, rather rare local species, *G. eriocarpum* Champ., which is also known as the hairy-fruited abacus plant.

Chromatography of the stems of *G. eriocarpum* gave lupenone (**8**), glochidone (**2**), lupeol (**9**), sitosterol, and a new compound glochidol (**1**), glochidonol (**4**), glochidiol (**3**) and lup-20(29)-en-1β,3β-diol (**5**) respectively according to their order of elution from the column. Similar investigation of the leaves led to the isolation of sitosterol and (**3**).

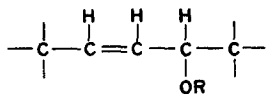


R
(1) α-H, β-OH
(2) O
(10) α-H, β-OAc



	R	R¹	R²
(3)	α-H, β-OH	α-OH, β-H	H
(4)	α-H, β-OH	O	H
(5)	α-H, β-OH	α-H, β-OH	H
(6)	H_2	α-OH, β-H	OH
(7)	α-OH, β-H	α-H, β-OH	H
(8)	H_2	O	H
(9)	H_2	α-H, β-OH	H

Glochidol (**1**), $C_{30}H_{48}O$, gave positive reactions to both tetranitromethane and Liebermann–Burchard. (**1**) contained an OH group and formed an acetate (**10**). The PMR spectra of both (**1**) and (**10**) showed signals at δ4·59, 4·68 (1H each, *m*) and 1·68 (3H, broad *s*), characteristic of the isopropenyl group of lup-20(29)-ene derivatives. The partial structure



(**1**) R = H
(**10**) R = OAc

was indicated by signals at δ5·27 (1H, *d*, *J* 10, 1·5) 5·83 (1H, *d*, *J* 10, 2·5) and 3·86 (1H, t, *J* 1·5 2·5 Hz) in the spectrum of (**1**) shifted to δ5·18, 5·89 and 5·07 respectively in that of (**10**). This partial structure can exist only in ring A. (**1**) was thus either lupa-1,20(29)-dien-3ξ-ol or lupa-2,20(29)-dien-1ξ-ol, and it was proved to be the former by allyllic oxidation with MnO_2 in $CHCl_3$ to give a conjugated ketone, identical with (**2**). The configuration of the OH group at C-3 was proved to be β by the formation of (**1**) from (**2**) through $LiAlH_4$ reduction, which involved hydride attack from the less hindered α face, leading to the formation of the β-OH group. Further confirmation of this was achieved by catalytic hydrogenation of (**10**), when a saturated acetate $C_{32}H_{54}O_2$, identical with lupan-3β-yl acetate prepared from lupenyl acetate, was obtained. The structure (**1**) for glochidol was thus confirmed.

The NMR proton signals of the six tertiary Me groups in the following lupene derivatives are assigned as in Table 1.

This investigation adds further evidence to our postulation [3] that *Glochidion* species are characteristic in yielding lupene derivatives. The number of new compounds isolated from this species is now seven and all those possessing two oxygen functions have these existing in a 1,3 relationship which might be another significant feature of this genus.

EXPERIMENTAL

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

Extraction and isolation of compounds. Milled air-dried stems of *G. eriocarpum* (14 kg) were extracted 2× at room temp.

Table 1. NMR Signals of tertiary methyl groups in *Lupene* derivatives

Compound	C-23	C-24	C-25	C-26	C-27	C-28
(**1**)	0·98	0·80	0·98	1·07	0·94	0·80
(**10**)	0·88	0·88	1·00	1·07	0·94	0·79
(**2**)	1·07	1·07	1·11	1·11	0·96	0·80
(**4**)	1·05	1·05	0·84	1·05	0·98	0·80
Acetate of (**4**)	1·07	1·04	0·89	1·07	0·97	0·80
(**3**)	0·90	0·82	0·90	1·04	0·97	0·78
Diacetate of (**3**)	0·84	0·90	1·04	1·04	0·98	0·79
(**5**)	0·96	0·74	0·91	1·06	0·96	0·79
Diacetate of (**5**)	0·85	0·85	1·03	1·03	0·92	0·79

* Part 11 in the series "An Examination of the Euphorbiaceae of Hong Kong." For part 10, see Hui, W. H., Li, M. M. and Ng, K. K. (1975) *Phytochemistry* **14**, 816.

with petrol for 7 days. Combined extracts were evaporated to give a residue (30 g), which was chromatographed on Al_2O_3 (600 g). Elution with petrol gave lupenone (30 mg), mp 170—171° $[\alpha]_D$ 56·0°; then glochidone (1 g), mp 169–170°, $[\alpha]_D$ + 69·0°. Elution with petrol-C_6H_6 (1:1) yielded first lupeol (10 mg), mp 199–202°, next sitosterol (2 g), mp 139–140°, and finally a solid, which on repeated recrystallisation from $CHCl_3$–MeOH gave needles of glochidol (**1**, 70 mg), mp 201–203°, $[\alpha]_D$ + 93·7° (Found: M^+ 424. $C_{30}H_{48}O$ requires: M^+ 424) IR ν_{max}: 3380 (OH), 3080, 1645, 885 cm^{-1} (=CH_2); MS: *m/e* (%) 424 (100), 409 (70), 381 (8), 285 (32), 229 (83), 218 (28), 205 (37), 203 (46), 189 (57). Elution with C_6H_6 afforded glochidonol (25 mg), mp 228–231°; with C_6H_6–$CHCl_3$ glochidiol (100 mg), mp 268–269°, then lup-20(29)-en-1β,3β-diol (30 mg), mp 250–251°, $[\alpha]_D$ + 28·0°. The residue (60 g) of the petrol extract of leaves (5·5 kg) was chromatographed on alumina (1·2 kg). Elution with petrol–C_6H_6 (1:1) gave sitosterol (2·5 g), with C_6H_6–$CHCl_3$ (1:1) glochidiol (10 mg).

Acetylation of (**1**). (**1**) (30 mg) was treated with Ac_2O and C_5H_5N at room temp. for 2 days. The product was recrystallized from petrol to give plates of glochidyl acetate (**10**, 30 mg), mp 207–208°, $[\alpha]_D$ + 117·8° (Found: C, 82·6; H, 10·6. $C_{32}H_{50}O_2$ requires: C, 82·35; H, 10·8%), IR ν_{max}: 1745, 1250 (OAc), 3080, 1645, 880 cm^{-1} (=CH_2), MS: *m/e* (%) 466 (27), 451 (13), 423 (11), 407 (100), 406 (95), 391 (29), 285 (35), 247 (12), 229 (86), 218 (17), 203 (57), 189 (60), 187 (37), NMR: δ 2·07 (3H, *s*, $OCOCH_3$).

MnO_2 oxidation of (**1**) *to glochidone* (**2**). (**1**) (25 mg) in $CHCl_3$ (25 ml) was shaken with MnO_2 (30 mg) at room temp. for 3 days. The product was recrystallized from petrol to give prisms (18 mg), mp 169–171°, $[\alpha]_D$ + 68·0°, M^+ 422, IR ν_{max}: 1670, 1630 (C=C–C=O), 3050, 1650, 880 cm^{-1} (=CH_2), UV λ_{max}: 229 (ϵ9,850), identical with glochidone (**2**).

Reduction of (**2**) *to* (**1**). (**2**) (50 mg) in dry Et_2O (30 ml) was refluxed with $LiAlH_4$ (50 mg) for 3 hr. The product (45 mg), mp 201–203° (from $CHCl_3$–MeOH), M^+ 424, IR ν_{max}: 3380 (OH), 3080, 1645, 885 cm^{-1} (=CH_2), was identical with (**1**) [acetate, mp 207–208°, identical with (**10**)].

Hydrogenation of (**10**) *to lupan-3β-yl acetate.* (**10**) (25 mg) in $CHCl_3$ (20 ml) was shaken with Adam's catalyst in H_2 for 2 hr. The product (20 mg), mp 247–248°, $[\alpha]_D$ − 3·0°, M^+ 470, IR ν_{max}: 1740, 1255 cm^{-1} (OAc), NMR: δ 4·48 (1H, q, $J_{ax/eq}$ 8 Hz, $J_{ax/ax}$ 9 Hz, C<u>H</u>OAc), was identical with lupan-3β-yl acetate prepared from lupenyl acetate by hydrogenation.

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ISOLATION OF TINGENONE AND PRISTIMERIN FROM *MAYTENUS CHUCHUHUASCA*

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Key Word Index—*Maytenus chuchuhuasca*; Celastraceae; tingenone, pristimerin; quinonoid triterpenes.

Plant and source: *Maytenus chuchuhuasca* Raymond Hamet (syn. *Maytenus krukovii* A. C. Smith (?) The plant was collected on the upper Rio Napo, Valley of Misahualli, Ecuador, and identified by one of us (A.P.) A voucher sample is deposited under the number T-10 in the Laboratory of Phytochemistry, Escuela Politecnica Nacional, Quito (Ecuador).

The plant is known locally as "chuchuhuaso" or "curicaspi" and is used in alcoholic solution for skin cancer treatment.

Previous work. This species was studied by Raymond-Hamet and Colas [1] who have described the isolation of an alkaloid maytenine, which was later demonstrated to be a dicinnamoyl spermidine [2]. No other substances were investigated.

Present work. In the course of our research on American species of Celastraceae [3] we examined a sample of *Maytenus chuchuhuasca*. The powdered bark of the trunk (100 g) was extracted at room temperature with a mixture (1/1) of hexane–EtOAc and gave on evaporation a residue (2·5 g), showing two orange pigments by TLC (C_6H_6–EtOAc 9:1). The residue was chromatographed on silica gel. Elution with the above solvent led to isolation of pristimerin (**1**) (250 mg) and tingenone (**2**)(200 mg) identified by TLC IR and NMR in comparison with authentic samples.

Pristimerin and tingenone were previously isolated from various species belonging to the closely related families of Celastraceae and Hippocrateaceae. [4]. It is of interest to find high concentration of the two phenol