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°, $[\alpha]_D + 69{\cdot}0°$. 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°, $[\alpha]_D + 93{\cdot}7°$ (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°, $[\alpha]_D + 28{\cdot}0°$. 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°, $[\alpha]_D + 117{\cdot}8°$ (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 ŌAc), 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*, $OCO\underline{C}\underline{H}_3$).

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°, $[\alpha]_D + 68{\cdot}0°$, 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°, $[\alpha]_D - 3{\cdot}0°$, 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, $C\underline{H}OAc$), 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.

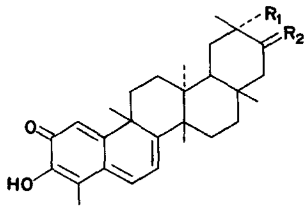
Plant and source: *Maytenus chuchuhuasca* Raymond Hamet (syn. *Maytenus krukovii* A. C. Smith (?) The plant was collected on the upper Rio Napo, Valley of Misahualli, Ecuador, and identified by one of us (A.P.) A voucher sample is deposited under the number T-10 in the Laboratory of Phytochemistry, Escuela 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 dienone triterpenes in the trunk bark and particularly tingenone (0·22%), which has been shown to be an inhibitor of tumor growth. [5,6].



(1) R_1 = COOMe, $R_2 = H_2$
(2) R_1 = H, R_2 = O

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NEUTRAL TRITERPENOIDS FROM *MELALEUCA LEUCADENDRON*

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Key Word Index—*Melaleuca leucadendron*; Myrtaceae; pentacyclic triterpenoids.

Plant. Melaleuca leucadendron L. Known as paperbark tree. *Previous work.* Betulinic acid from bark [1] and in that of *M. parviflora*, *M. pubescens*, *M. rhaphiophylla*, *M. cuticularis* and *M. viminea*; melaleucic acid [2] [3] also isolated from the last three species.

Present work. The light petrol extracts of both the leaves and stems of *M. leucadendron* were examined separately by column chromatography on alumina. The former gave friedelin, sitosterol, betulin and uvaol according to the order of elution from the column. The latter similarly yielded *epi*taraxeryl acetate, friedelin, taraxerone, taraxastenone, sitosterol and betulin. Neither *epi*taraxeryl acetate nor taraxastenone has formerly been isolated as a natural product.

EXPERIMENTAL

IR spectra were recorded for KBr discs; NMR spectra in $CDCl_3$ solutions at 60 MHz using TMS as internal standard; optical rotations in $CHCl_3$ solutions. Light petrol had bp 60–80°. Known compounds were identified by TLC, mmp, IR and MS spectral comparisons with authentic samples.

Leaves. Milled air-dried leaves (7.2 kg) were extracted 2 × with light petrol, combined extracts were concentrated and chromatographed on alumina (1 kg). Elution with light petrol gave friedelin (0.9 g), mp 261–262°, with light petrol–C_6H_6 (1:1), sitosterol (0.7 g), mp 139–140°, with C_6H_6, betulin (0.1 g), mp 253–255°, and with C_6H_6–$CHCl_3$ (1:1), needles (0.035 g), mp 221–223° (from $CHCl_3$–MeOH), $[\alpha]_D$ + 77.0°, M^+ 442, IR ν_{max}: 3380 (OH), 1650, 820 cm^{-1} (>C=CH–), identical with uvaol prepared from methyl ursolate by LAH reduction.

Stems. Milled air-dried stems (9 kg) were extracted with light petrol and chromatographed on alumina (1.5 kg) as for the leaves. Early elution with petrol yielded plates (0.01 g), mp 163–164° (from light petrol), $[\alpha]$ – 37.0° (Found: M^+ 468. Calc. for $C_{32}H_{52}O_2$: M^+ 468). IR ν_{max}: 1740, 1245 (OAc), 3070, 1650, 818 cm^{-1} (>C=CH–), identical with a sample of *epi*taraxeryl acetate prepared from taraxerone (a soln of freshly distilled Al isopropoxide (0.5 g) and taraxerone (0.15 g) in iso PrOH (50 ml) was refluxed at 110° for 2 hr. The product was acetylated and the mixture (0.1 g) separated by preparative TLC into *epi*taraxeryl acetate (0.015 g), mp 165–166° (from $CHCl_3$–MeOH), and taraxeryl acetate (0.083 g) mp 303–304°). Further elution with light petrol gave friedelin (0.3 g), then taraxerone (0.07 g), mp 248–250°, and finally needles (0.03 g), mp 184–185° (from light petrol), $[\alpha]_D$ + 117.0° (Found: M^+424. Calc. for $C_{30}H_{48}O$: M^+ 424). IR ν_{max}: 1720 cm^{-1} (>C=CH_2), identical with taraxastenone obtained by oxidation of taraxasterol with Jones' reagent. The needles (0.02 g) was stirred with $NaBH_4$ in isopropanol (20 ml) for 2 hr. The product 0.015 g), mp 224–226°, IR ν_{max}: 3600 (OH), 3080, 1650, 880 cm^{-1} (>C=CH_2) was identical with taraxasterol. Elution with petrol–C_6H_6 (1:1) afforded sitosterol (0.01 g), and with C_6H_6 betulin (0.07 g).

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