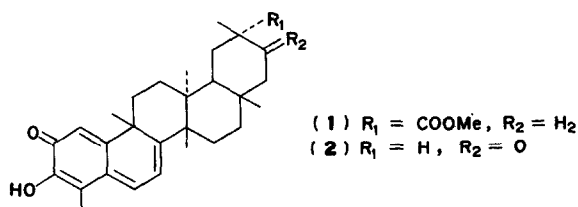


dienone triterpenes in the trunk bark and particularly tingenone (0.22%), which has been shown to be an inhibitor of tumor growth. [5,6].



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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 paper-bark tree. *Previous work.* Betulinic acid from bark [1] and in that of *M. parviflora*, *M. pubescens*, *M. raphiophylla*, *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 epitaraxeryl acetate, friedelin, taraxerone, taraxastenone, sitosterol and betulin. Neither epitaraxeryl 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 $\text{C}_6\text{H}_6\text{-CHCl}_3$ (1:1), needles (0.035 g), mp 221–223° (from $\text{CHCl}_3\text{-MeOH}$), $[\alpha]_D + 77.0^\circ$, $M^+ 442$, IR ν_{max} : 3380 (OH), 1650, 820 cm^{-1} ($>\text{C}=\text{CH}-$), 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), $[\alpha] - 37.0^\circ$ (Found: $M^+ 468$. Calc. for $\text{C}_{32}\text{H}_{52}\text{O}_2$: $M^+ 468$). IR ν_{max} : 1740, 1245 (OAc), 3070, 1650, 818 cm^{-1} ($>\text{C}=\text{CH}-$), identical with a sample of epitaraxeryl 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 epitaraxeryl acetate (0.015 g), mp 165–166° (from $\text{CHCl}_3\text{-MeOH}$), 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), $[\alpha]_D + 117.0^\circ$ (Found: $M^+ 424$. Calc. for $\text{C}_{30}\text{H}_{48}\text{O}$: $M^+ 424$). IR ν_{max} : 1720 cm^{-1} ($>\text{C}=\text{CH}_2$), 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} ($>\text{C}=\text{CH}_2$) 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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