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TRITERPENOIDS FROM TWO HONG KONG EUPHORBIACEAE SPECIES*

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Key Word Index—*Claoxylon polot*; Euphorbiaceae; friedelin; 3β-hydroxy-30-nor-lupan-20-one and its acetate; betulinic acid; sitosterol; *Fluggea virosa*; Euphorbiaceae; friedelin; friedelan-3α-ol; friedelan-3β-ol; lupeol; glochidonol; glochilocudiol; betulonic acid and sitosterol.

The petrol extracts of both the leaves and stems of *Claoxylon polot* were examined separately by column chromatography on alumina. The former yielded friedelin and sitosterol, while the latter gave 3β-acetoxy-30-nor-lupan-20-one, sitosterol and 3β-hydroxy-30-nor-lupan 20-one, according to the order of elution from the column. 3β-Acetoxy-30-nor-lupan-20-one has not previously been isolated as a natural product, and its corresponding alcohol has only been isolated twice, first from *Ricihus communi* (Euphorbiaceae) [1], and later from *Carlina corymbosa* (Compositae) [2]. The ethanol extracts were then examined for acidic triterpenoids, only betulinic acid was isolated from that of the leaves.

Fluggea virosa (snowberry) was also analysed for its triterpene content. *F. microcarpa* previously yielded hexacosane, friedelin, friedelan-3α-ol and sitosterol from the trunk bark [3] and bergenin from the leaves [4].

Both the leaves and stems of *Fluggea virosa* were examined as for *Claoxylon polot*. The petrol extracts of the leaves gave in succession friedelin, friedelan-3α-ol and sitosterol, while that of the stems yielded friedelin, friedelan-3β-ol, lupeol, sitosterol, glochidonol, glochilocudiol [lup-20(29)-ene-1α,3β-diol]. Only betulonic acid was isolated from the ethanol extract of the stems. Glochilocudiol has only been isolated once from *Glochidion multiloculare* (Euphorbiaceae) [5].

EXPERIMENTAL

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

Claoxylon polot (*Burm. f.*) *leaves.* Milled air-dried leaves (5 kg) were extracted 2 × with petrol for ten days. The combined extracts were concd and chromatographed on alumina (1.5 kg). Elution with petrol gave friedelin (0.03 g), mp 262–264°, IR ν_{max} cm^{-1}: 1720 ($\rangle O{=}O$): with petrol–C_6H_6, sitosterol (0.7 g), mp 139–140°, IR ν_{max} cm^{-1}: 3300 (OH). The residue after extraction with petrol was extracted 2 × at room temp. with EtOH. The acidic solid (5 g) isolated through the Na salt, was treated with CH_2N_2 in Et_2O, and the product was chromatographed on alumina (100 g). Elution with petrol–C_6H_6 (1:1) gave prisms of methyl betulinate (0.05 g), mp 229–230°, IR ν_{max} cm^{-1}: 3550 (OH), 1720, 1174 (COOMe), 3080, 1650, 880 ($\rangle C{=}CH_2$). *Stems.* The petrol extract from the stems (10 kg) was chromatographed on alumina (1 kg). Elution with petrol yielded plates (0.03 g), mp 262–263° (from $CHCl_3$), $[\alpha]_D$ + 9.0° (Found: M^+-470. Calc for $C_{31}H_{50}O_3$: M^+-470), IR ν_{max} cm^{-1}: 1735, 1250 (OAc), 1695 ($\rangle C{=}O$), NMR: δ 2.17 (3H, *s*, $C\underline{H}_3CO$), 2.04 (3H, *s*, $C\underline{H}_3OCO$), identical with a sample of 3β-acetoxy-30-nor-lupan-20-one prepared by ozonolysis of lupenyl acetate [6]. Elution with petrol–C_6H_6 yielded sitosterol (1.2 g); with C_6H_6, needles (0.02 g), mp 239–240°, $[\alpha]_D$ − 14.8°, MS: *m/e* 428 (M^+), IR ν_{max} cm^{-1}: 3470 (OH), 1695 ($\rangle C{=}O$), identical with a sample of 3β-hydroxy-30-nor-lupan-20-one obtained by hydrolysis of 3β-acetoxy-30-nor-lupan-20-one [6]. The EtOH extract was treated as stated for the leaves, no acidic triterpenoids could be isolated.

Fluggea virosa (*Willd*) *Baill. leaves.* The petrol extract from the leaves (0.5 kg) was chromatographed on alumina (1 kg). Elution with petrol gave friedelin (0.7 g), with petrol–C_6H_6 yielded friedelan-3α-ol (0.01 g), mp 293–297°, IR ν_{max} cm^{-1}: 3600 (OH), and sitosterol (0.8 g). No acidic triterpenoid was isolated from the EtOH extract. *Stems.* The petrol extract from the stems (10 kg) was chromatographed on alumina (700 g).

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[*] Part 15 in the series 'An Examination of the Euphorbiaceae of Hong Kong.' For Part 14, see Hui, W. H. and Li, M. M. (1977) *Phytochemistry* **16**, 113.

Elution with petrol gave friedelin (1.1 g), friedelan-3β-ol (0.05 g), mp 283–286°, IR ν_{max} cm^{-1}: 3630 (OH), and lupeol (0.04 g), mp 210–211°, IR ν_{max} cm^{-1}: 3380 (OH), 3080, 1645, 882 cm^{-1} ($>$C=CH$_2$). Elution with petrol–C$_6$H$_6$ (1:1) gave sitosterol (0.6 g); with C$_6$H$_6$, glochidonol (0.03 g), mp 229–231° (from C$_6$H$_6$), IR ν_{max} cm^{-1}: 3430 (OH), 1720 ($>$C=O), 3075, 1650, 887 ($>$C=CH$_2$). Elution with CHCl$_3$ gave needles of glochilocudiol (0.04 g), mp 239–240°, $[\alpha]_D$ + 19° (Lit. [5], mp 235°, $[\alpha]_D$ + 17°), MS. m/e 442 (M$^+$), IR ν_{max} cm^{-1}: 3360 (OH), 3035, 1645, 882 ($>$C=CH$_2$) which on hydrogenation (in EtOAc using Adam's catalyst), yielded a diol, C$_{30}$H$_{52}$O$_2$, mp 235–236°, $[\alpha]_D$ − 5°, MS: m/e 444 (M$^+$), IR ν_{max} cm^{-1}: 3380 (OH), identical with an authentic sample of lupane-1α,3β-diol [7]. The methylated product (4 g) from the EtOH extract was chromatographed on alumina (80 g). Elution with petrol–C$_6$H$_6$ (1:1) gave prisms of methyl betulonate (0.02 g), mp 167–168°, IR ν_{max} cm^{-1}. 1720 ($>$C=O), 1740, 1160 (COOMe), 3080, 1650, 880 ($>$C=CH$_2$).

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THE STRUCTURE OF A TRITERPENOID KETOL FROM *CETRARIA NIVALIS*

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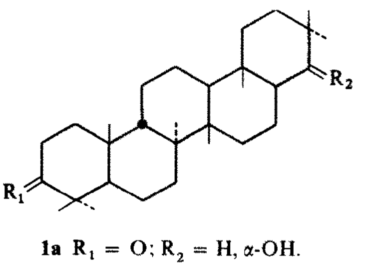
Key Word Index—*Cetraria nivalis*; *Pseudocyphellaria coronata*; *Pseudocyphellaria colensoi*; Stictaceae; Parmeliaceae; triterpenoids; 22α-hydroxystictan-3-one.

Abstract—A triterpenoid ketol isolated from a Norwegian species of *Cetraria nivalis* is identified as 22α-hydroxystictan-3-one, a triterpenoid present in some *Pseudocyphellaria* lichens.

Bruun [1] has previously reported the isolation of a number of known triterpenoid compounds (viz. friedelan-3-one, friedelan-3β-ol, lupeol, α-amyrin and ursolic acid), and a new triterpenoid ketol, C$_{30}$H$_{50}$O$_2$, mp 221–222°, $[\alpha]_D$ + 105°, from *Cetraria nivalis*. As the original extraction yielded only 150 mg of the new ketol, an effort was made to accumulate further quantities of the compound. However, the extraction of other *C. nivalis* material, including specimens gathered from the same narrow region, gave different triterpenoids [1]. In an unrelated investigation [2] of New Zealand Stictaceae lichens, a triterpenoid ketol was isolated from *Pseudocyphellaria coronata* and *P. colensoi*. This ketol was shown to possess a hither-to unreported pentacyclic triterpane skeleton, and the detailed structural analysis subsequently undertaken [2–4] lead to the determination of the stictane skeleton, and the assignment of structure **1a** to this ketol.

A considered analysis (Table 1) of the constants reported for some derivatives of Bruun's ketol, and of 22α-hydroxystictan-3-one (**1a**), leads to the conclusion that the *Pseudocyphellaria* and *Cetraria* ketols are identical. In addition a comparison of the constants reported [5] for retigeradione, previously considered to be taraxerane-3,19-dione, but recently established [6] to be stictane-3,22-dione (**1b**), further substantiates the identity.



1a R$_1$ = O; R$_2$ = H, α-OH.
1b R$_1$ = R$_2$ = O.
1c R$_1$ = O, R$_2$ = H, α-OAc.
1d R$_1$ = H$_2$; R$_2$ = H, α-OH.
1e R$_1$ = H$_2$; R$_2$ = H, α-OAc
1f R$_1$ = H$_2$; R$_2$ = O

Similarly the chemical, and spectroscopic data reported [1] for the *Cetraria* ketol are fully consistent with the proposed stictane structures. For example the dominant peaks at m/e 207, 205 and 189 (207-H$_2$O) in the MS of the ketol [1] (as in 22α-hydroxystictan-3-one)