The Structures of Two Ecdysone Analogues, Cheilanthones A and B, from the Fern *Cheilanthes tenuifolia*

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Summary Cheilanthones A and B are shown to be 7,8-dihydroecdysone (II) and 25-deoxy-7,8-dihydroecdysone (V), respectively.

The insect moulting hormone ecdysone (I)[1] also occurs in certain ferns.[2] We now report that the fern *Cheilanthes tenuifolia* (Burm.f.) Swartz of Northern Queensland contains ecdysone and two related compounds, cheilanthones A and B. Cheilanthone A, m.p. 235—238°, for which we suggest the structure (II), has the same R_F value (0·20) as ecdysone† in t.l.c. [silica gel with chloroform–96% ethanol (4–1) as solvent], shows no strong u.v. absorption, and has i.r. absorption (KBr) at 1684 cm^{-1}, which we attribute to an isolated carbonyl group, since by comparison ecdysone with a conjugated double bond shows an i.r. absorption at 1651 cm^{-1}.

The mass spectrum of cheilanthone A shows peaks at *m/e* 99 and 81 corresponding to side-chain fragments as in the spectrum of ecdysone,[3] and a series of prominent peaks at *m/e* 448 (P − 18), 430, 412, 394, 379, 332, and 302, which are all 2 mass units higher than the corresponding prominent peaks in the mass spectrum of ecdysone.† The n.m.r. spectrum of cheilanthone A has strong signals (Table) assigned to $C(OH)(CH_3)_2$ and 18-, 19-, and 21-H_3. The o.r.d. curve of cheilanthone A in dioxan shows a negative Cotton effect with the large amplitude (a −167) typical of 6-oxo-steroids with the 5β-configuration.[4,5] These data and the absence of enone absorption indicate that cheilanthone A corresponds to a 7,8-dihydroecdysone.

Acetylation of cheilanthone A afforded a triacetate (III), ν_{max} 1735, 1725 (OAc), 1705 (C=O) cm^{-1}, with an R_F value (0·36) in t.l.c. [chloroform–96% ethanol (9–1)] the same as that of ecdysone triacetate. The chemical shifts of 18- and 19-H_3 are close to the values calculated (Table) from those of compound (IV),[4] by allowing for the contribution[6] from an extra 14α-hydroxy-group. The other chemical-shift values, apart from that of the proton at C-7, are closely similar to those of ecdysone triacetate. As cheilanthone A occurs with ecdysone it is likely that it has the same configuration at C-22 and other asymmetric centres as ecdysone, and it is assigned structure (II).

Table

Chemical shifts of protons (δ)

	2α-H	3α-H	7-H	18-H_3	19-H_3	21-H_3	22-H	26/27-H_6
Cheilanthone A[a]				0·83	1·01	1·24[b]		1·36
Cheilanthone B[a]				0·85	1·03	1·24[b]		0·84[b]
Ecdysone[a]				0·70	1·05	1·25[b]		1·38[1]
2,3,22-*Triacetates*								
Cheilanthone A[c]	5·35[d]	*ca.* 5·10[e]		0·80	0·96	*ca.* 0·94[e]	*ca.* 4·9	1·24
Cheilanthone B[c]	5·24[d]	*ca.* 5·0[e]		0·79	0·94	*ca.* 0·91[e]	*ca.* 4·9	0·88[b]
Cheilanthones calc.				0·78	0·95			
Ecdysone[c]	5·3[d]	*ca.* 5·0[e]	5·86	0·67	1·03	0·95[e]	*ca.* 5·0	1·24

[a] [$^2H_5$]Pyridine; [b] J 6 Hz; [c] triacetate in $CDCl_3$; acetyl peaks of each compound appeared at δ2·00, 2·05, and 2·09; [d] $W_{\frac{1}{2}}$ 8 Hz; [e] $W_{\frac{1}{2}} > 16$ Hz.

Cheilanthone B, m.p. 225—228°, for which structure (V) is suggested, has a higher R_F value (0·50) in t.l.c. [chloroform–96% ethanol (4–1)] than cheilanthone A, no strong u.v. absorption, o.r.d. (dioxan) a −192, and i.r. absorption (KBr) at 1684 cm^{-1}. The mass spectrum of cheilanthone B

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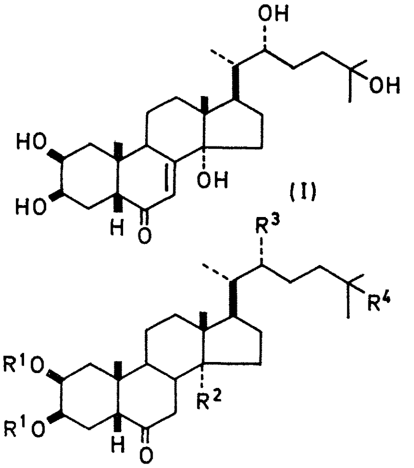
(parent ion m/e 450) has prominent peaks at m/e 332 and 302 attributed to nuclear fragments like those in the spectrum of cheilanthone A, and peaks at m/e 432, 414, 396, and 381, which are 16 mass units less than similar peaks in the spectrum of cheilanthone A. The n.m.r. spectrum of cheilanthone B (Table) does not show a six-proton methyl signal at δ1·24 but instead a doublet at δ 0·84 which on irradiation at δ1·73 collapses to a six-proton singlet. Thus cheilanthone B, unlike cheilanthone A, does not have a hydroxy-group at C-25. Otherwise the n.m.r. spectra of cheilanthone B and its triacetate (VI) are closely similar to those of cheilanthone A and its triacetate, respectively, (Table) and cheilanthone B is assigned structure (V).



(I)

	R¹	R²	R³	R⁴
(II)	H	OH	OH	OH
(III)	Ac	OH	OAc	OH
(IV)	Ac	H	H	H
(V)	H	OH	OH	H
(VI)	Ac	OH	OAc	H

Cheilanthones A and B were biologically inactive when tested up to 0·6 μg. per animal in isolated abdomens of *Calliphora stygia*.[7] Also unlike ecdysone, cheilanthone A injected into larvae did not accelerate puparium formation.[8] It thus appears that *Calliphora* are unable to introduce a 7-double bond into cheilanthone A and it is likely that in the biosynthesis of ecdysone in *Calliphora* the 7-double bond is introduced before the introduction of all of the hydroxy-groups. In the biosynthesis of ecdysone in *Cheilanthes* the introduction of the 7-double bond may take place at a later stage.

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