Structure of the Phytoecdysone, Ajugasterone B[1]

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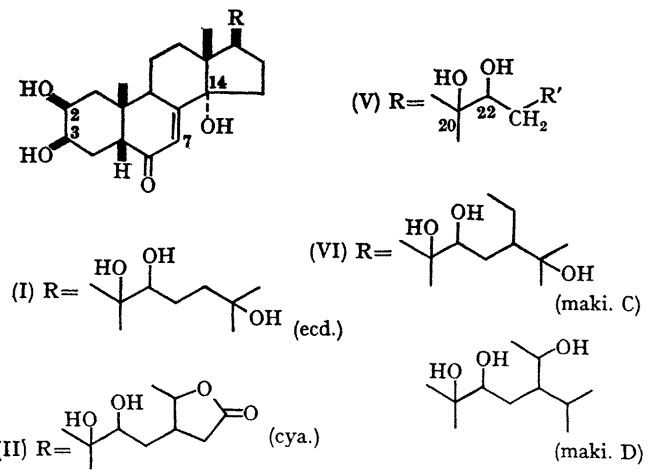
ADDITIONAL sources of phytoecdysones[2] have been discovered by the screening of 1056 species, selected from 186 families, of Japanese plants. We have recently reported[3] the isolation and characterization of ecdysterone (I) and cyasterone (II)[4] from *Ajuga decumbens* ("kiranso" in Japanese), *A. incisa* ("hiiragiso") and *A. nipponensis* ("junihitoe") (Labiatae). *A. incisa* affords, in addition, two minor phytoecdysones which we designate ajugasterone A and B. The C_{29} structure (III) is assigned to ajugasterone B on the basis that, of the total of 17 zoo- and phyto-ecdysones characterized to date,† it is the first to possess a double-bond in addition to the ubiquitous 7-ene.



Ajugasterone B is isolated from fresh leaves of *A. incisa* (0·0008% yield) and the order of activity according to the *Chilo* dipping method[5] is comparable to other ecdysones. Ajugasterone B (III) and its tetra-acetate (IV) possess the following physical properties. Ajugasterone B (III), m.p. 240° (decomp.), $C_{29}H_{46}O_7$ (M^+ 506), i.r. (KBr) 3400 and 1650 cm.$^{-1}$; u.v. (MeOH) 244 nm. (log ϵ 10,675); α (dioxan) $= +54{\cdot}7$ ($n \rightarrow \pi^*$). Ajugasterone B 2,3,22,26-tetra-acetate (IV), m.p. 165—167° (decomp.), $M - 18$ at m/e 656.

By comparison of the following results with those obtained from structural studies with other ecdysones identification of the component (V), common to the majority of ecdysones is possible:[6,7] (i) u.v. and i.r. (7-en-6-one); (ii) HCl–MeOH treatment give two products absorbing at *ca.* 240 and 295 nm. as a result of dehydration involving the 14α-OH;[8] (iii) n.m.r. chemical-shifts of Me, carbonyl,

† Undoubtedly this number will continue to increase. See Reference 7 for recent publication describing the structures of four new phytoecdysones.

TABLE 1. *N.m.r. chemical shifts (p.p.m. from internal* Me_4Si) *in the component* (V).

Free ecdysones (in pyridine)	C(18)-Me	C(19)-Me	C(21)-Me	2-H	3-H	7-H	22-H
General for (V)	1·19	1·06	1·54	4·05 ($w_{\frac{1}{2}}$ 20)	4·13 ($w_{\frac{1}{2}}$ 8)	6·20	3·80 dd
Ajugasterone B	1·16	1·05	1·54	4·05 ($w_{\frac{1}{2}}$ 20)	4·14 ($w_{\frac{1}{2}}$ 8)	6·18	3·85 dd
2,3,22-Acetates (in $CDCl_3$)							
General for (V)	0·85	1·02	1·24	5·05 ($w_{\frac{1}{2}}$ 22)	5·32 ($w_{\frac{1}{2}}$ 8)	5·86 d	4·82 dd
Ajugasterone B (also 27-acetate) ..	0·82	1·01	1·21	ca 5·07 ($w_{\frac{1}{2}}$ 22)	5·35 ($w_{\frac{1}{2}}$ 9)	5·82 d	ca 4·85 dd

$w_{\frac{1}{2}}$: half-band width in c./sec.

TABLE 2. *Additional n.m.r. peaks in* (III) *and* (IV)

	C(29)-Me	$=CH_2$	CH_2·OR
(III) (in pyridine)	0·86 t, 7	5·03, 5·53	4·36
(IV) (in $CDCl_3$)	0·86 t, 7	4·91, 5·09	4·28, 4·69 (AB q, *J* 14)

and olefinic protons (Table 1); (iv) sign and amplitude of Cotton effects ($n\rightarrow\pi^*$, also $\pi\rightarrow\pi^*$) (A/B cis);[9] (v) strong mass peaks (frequently base peak) at *m/e* 363, 345, and 327 due to fission-(a) [*e.g.* in (III)] followed by losses of H_2O. Since ajugasterone B was typical in all these respects presence of part structure (V) is established.

The mass fragments due to the side-chain of ajugasterone appeared at *m/e* 143, 125, and 107 [fission-(a) in (III)], *i.e.* at 2 mass units lower than the corresponding peaks in makisterone C (VI) and D (VII),[7] and two other C_{29}-ecdysones; also, two additional olefinic protons were present in the n.m.r. spectrum (Table 2). The lack of 26-Me and 27-Me n.m.r. singlets, and presence of a Me triplet (29-Me), and a clear AB type quartet (confirmed by decoupling) centred at 4·51 p.p.m. in the acetate (Table 2) leads unambiguously to structure (III) (side-chain stereochemistry undefined) for ajugasterone B.

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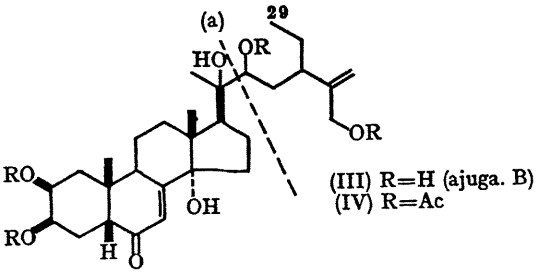

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[1] Part of the series on "Insect Hormones" from Department of Chemistry, Tohoku University, previous Paper, see ref. 7.
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