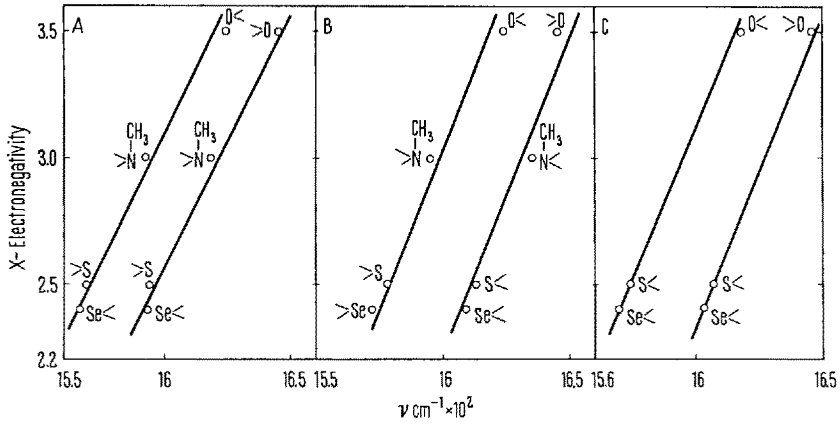


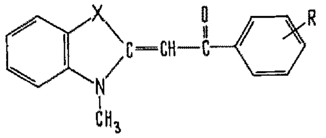
Fig. 2. The relation between the frequencies of $\nu_{C=O}$ and $\nu_{C=C}$, respectively, and the electronegativity of X in compounds I: A) R = H; B) R = 4'-NO_2 and C) R = 3',5' $(NO_2)_2$.

Table II. Frequencies[a] $\nu_{C=C}$ and $\nu_{C=O}$ in the compounds I

R	X ν cm^{-1} (in KBr)	O (3.5)	N-CH_3 (3.0)	S (2.5)	Se (2.4)
H	C=O	1624	1592	1569	1566
	C=C	1645	1618	1594	1593
4'-NO_2	C=O	1624	1595	1578	1573
	C=C	1645	1635	1613	1609
3',5'$(NO_2)_2$	C=O	1618	–	1574	1569
	C=C	1646	–	1607	1603

[a] The assignment of these bands was made on the analogy of the results of a previous paper[9].

Since there is a parallelism between the inductive effect and the electronegativity, we attempted to correlate the frequency of these absorption bands with the electronegativity of X. Surprisingly, we found a simple linear relation as is pictured in Figures 1 and 2.



Zusammenfassung. Der vom Heteroatom X auf die Elektronen- und IR-Spektren der 3-Alkyl-2-acylmethylenbenzazoline (I) ausgeübte Einfluss steht in einer linearen Abhängigkeit zum induktiven Effekt.

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Ecdysterone: an Insect Moulting Hormone from *Achyranthes aspera* (Amaranthaceae)

Following the recent clarification of the nature of the active principles (ecdysones) responsible for the metamorphosing phenomena in insects[1], it has become recognized that such substances (phytoecdysones) are widely distributed also in the plant kingdom[2-4]. Ecdysterone, a C_{27}-compound, has been isolated by IMAI et al.[5] from *Polypodium japonicum*, *Trillium smallii* and other plants, and together with cyasterone from *Ajuga* species. GALBRAITH and HORN[6] have isolated an insect moulting hormone, crustecdysone, from Australian brown pine which turned out to be identical with ecdysterone. In the present communication we report the isolation and identification of ecdysterone from *Achyranthes aspera*.

The roots (490 g) (supplied by Allied Chemical Co. Calcutta), in 1.5 l of methanol were homogenized with a Waring blender, and left at room temperature for 5 days. The filtered methanol extract was concentrated in vacuo

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and the residue subjected to chromatography on a silica gel column (3 × 40 cm). Elution with chloroform-methanol (4:1) furnished a small quantity of ecdysterone in fractions 7–9 (each fraction 100 ml), as indicated by thin-layer chromatography, developing with chloroform-ethanol-acetone, 6:2:1. Spraying the plate with 50% sulfuric acid and heating revealed ecdysterone as a green spot, Rf 0.44. The fractions were pooled and concentrated, and the residue (127 mg) recrystallized from ethyl acetate-ethanol, 1:1, to give crystals of ecdysterone of mp 240–241°, characterized further by UV-, NMR- and mass-spectrum.

Résumé. L'ecdystérone, hormone de mue des insectes a été extraite de l'*Achyranthes aspera* et identifiée par des méthodes chromatographiques et spectroscopiques.

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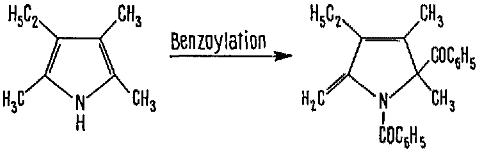
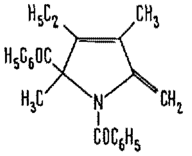
Benzoylation Studies in Pyrroles: Benzoylation of Phyllopyrrole

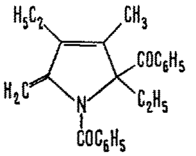
We have reported[1,2] the benzoylation of 2,3,4,5-tetramethyl pyrrole. The present report deals with the benzoylation of an unsymmetrically substituted pyrrole viz 2,3,5-trimethyl-4-ethylpyrrole (I) (Phyllopyrrole)



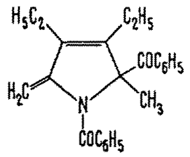
(I) (II)



(III)



(IV)



(V)

which can be expected to give 2 different products (II) and (III).

However benzoylation of phyllopyrrole gave only one product, mp 156–157°, colourless needles, 80% yield, analyzed for $C_{23}H_{23}NO_2$ (Found C, 79.49; H, 8.10; N, 5.57. Calcd. C, 79.63; H, 7.94; N, 5.80). The IR-spectrum did not exhibit O–H or N–H absorption but showed carbonyl absorption bands at 1690 and 1645 cm^{-1}. Structure (II) was assigned to the product on the bases of its nuclear magnetic resonance spectrum and the comparison of its chemical shift with the benzoylated product of 2,4-dimethyl-3,5-diethyl pyrrole[3] (IV) and 2,5-dimethyl-3,4-diethyl pyrrole[4] (V). The nuclear magnetic resonance (NMR) spectral data of the benzoylation product of (II), (IV) and (V) are presented in the Table. The NMR-spectrum of the product was taken in $CDCl_3$ (TMS as internal standard) and has been recorded in varian A-60 machine.

The ethyl groups in position 4 of (II), (IV) and (V) have a common triplet around 1.11–1.15 ppm and quartet at 2.29 ppm. Two methylene protons in these compounds show doublets around 3.41 and 4.29 ppm. The methyl group in position 3 of compound (II) shows a singlet at 1.79 which is very similar to the singlet at 1.78 ppm for the methyl in position 3 of (IV). The methyl group at position 2 in compound (II) and (V) both show a singlet at 1.84 ppm. It is worth mentioning that the benzoyl groups in all these compounds show multiplet in the low field around 6.9–7.8 ppm. The probable explanation of the preferential benzoylation at position 2 in preference to position 5 may be due to the steric effect of the ethyl group at position 4 of the phyllopyrrole[5].

Chemical shifts of different group protons[a] in ppm in $CDCl_3$

Compound	2		3		4		5	
II	1.84 (s)		1.79 (s)		1.11 (t)	2.29 (q)	3.41 (d)	4.29 (d)
IV	0.75 (t)	2.63 (q)	1.78 (s)		1.12 (t)	2.36 (q)	3.4 (d)	4.28 (d)
V	1.84 (s)		1.0 (t)	2.28 (q)	1.15 (t)	2.32 (q)	3.42 (d)	4.32 (d)

[a] d, doublet; q, quartet; t, triplet and s, singlet.

Zusammenfassung. Vergleichende NMR-Untersuchungen zeigten, dass die Benzoylierung von Phyllopyrrole die Verbindung II und nicht I liefert.

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16 November 1970.*

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