

and its ureide (VI) with those of desureaviomycin and viomycin respectively has provided strong support for this proposal<sup>22</sup>.

The sequence of the amino-acids in viomycin has been determined from the evidence of end group analyses of viomycin itself and of the structure of the dipeptides obtained from partial base hydrolysis. The molecular structure is shown in formula (VII) and the assignment is in accord with the physical and spectral properties of the antibiotic.

Investigations on the capreomycin complex are still in progress and will be reported at a later date, although all the components have been shown to contain the chromophoric system (IV). The units (III) and (IV) are derived from dehydroarginine and dehydroserine respectively and the related biosynthesis of the dehydroamino-acid units and D-amino acid units frequently found in microbial peptides has been discussed elsewhere<sup>23</sup>.

*Zusammenfassung.* Die Struktur von Viomycin wird durch seine Zerfallseigenschaften bestimmt und das Vorhandensein von Guanidin-Carbinol sowie von Dehydroserin oder Formylglycin bestätigt.

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## The Influence of the Second Heteroatom on the Spectra of 3-Alkyl-2-Acylmethylenbenzazoles

The influence of the second heteroatom on the chemical properties<sup>1</sup>, IR-<sup>2</sup>, electronic<sup>3-6</sup> and NMR<sup>7</sup>-spectra of the benzazoles have been already investigated. The differences observed have been interpreted in terms of the electron-releasing mesomeric effect of these atoms. For instance, the fact that the benzthiazoles absorb at higher wavelengths than the corresponding benzoxazoles has been explained either by the larger +M effect of the sulfur atom in the excited state<sup>3-5</sup> or by its ability to be a conjugation transmitter<sup>6</sup>.

In contrast with these findings, our measurements on 3-alkyl-2-acylmethylenebenzazoles (I) led us to the conclusion that the influence exerted by the heteroatom X on the electronic- and IR-spectra may be correlated with the inductive effect of X. This effect outweighing the mesomeric one, controls the phenomena observed. Thus, the increasing order of the frequency of the  $\lambda_{max}$  absorptions (Table I) and of  $\nu_{C-C}$  and  $\nu_{C-O}$  (Table II), respectively, is as expected, taking into account the inductive effect of the heteroatom X, namely: Se < S < N < O.

Table I.  $\lambda_{max}$  Absorption bands<sup>a</sup> of the compounds I

R	X <sup>b</sup> O (3.5) $\lambda_{max}$ nm ( $\nu$ cm <sup>-1</sup> )	$\epsilon$	N-CH <sub>3</sub> (3.0) <sup>c</sup> $\lambda_{max}$ nm ( $\nu$ cm <sup>-1</sup> )	S (2.5) $\lambda_{max}$ nm ( $\nu$ cm <sup>-1</sup> )	$\epsilon$	Se (2.4) $\lambda_{max}$ nm ( $\nu$ cm <sup>-1</sup> )	$\epsilon$
H <sup>a</sup>	357.1 (28,000)	39,700	368 (27,173)	381 (26,247)	37,200	382.2 (26,164)	37,900
4'-NO <sub>2</sub> <sup>a</sup>	386 (25,906)	18,600	401 (24,937)	411 (24,330)	28,300	414 (24,154)	31,300
3',5'-(NO <sub>2</sub> ) <sub>2</sub> <sup>b</sup>	384.6 (26,000)	18,200	-	411.2 (24,319)	21,900	413.9 (24,160)	21,000

<sup>a</sup> Measurements made in: a) methanol; b) DMF. <sup>b</sup> PAULING'S<sup>8</sup> electronegativities scale. <sup>c</sup> The optical density varies with time.

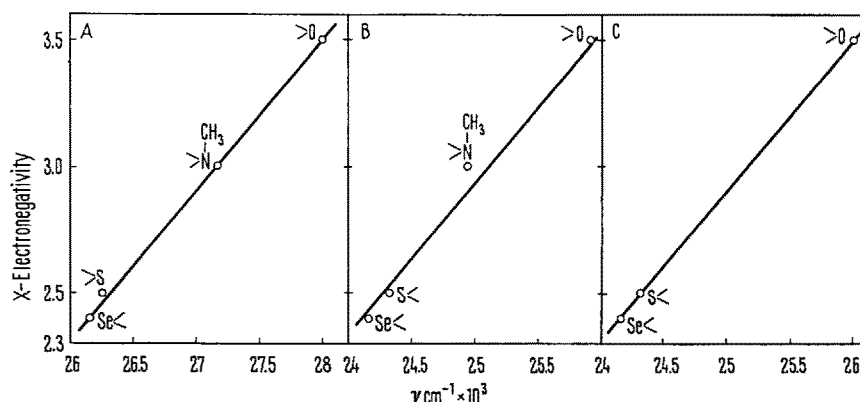


Fig. 1. The relation between the frequencies of  $\lambda_{max}$  absorption bands and the electronegativity of X in compounds I: A) R = H; B) R = 4'-NO<sub>2</sub> and C) R = 3'm5'-(NO<sub>2</sub>)<sub>2</sub>.

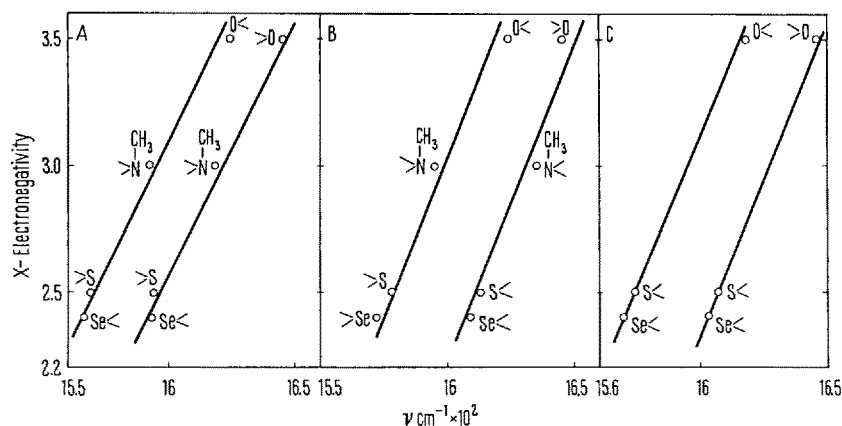


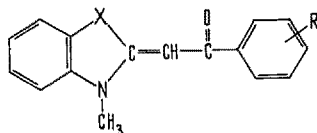
Fig. 2. The relation between the frequencies of  $\nu_{C=O}$  and  $\nu_{C=C}$ , respectively, and the electronegativity of X in compounds I: A) R = H; B) R = 4'-NO<sub>2</sub> and C) R = 3',5'-(NO<sub>2</sub>)<sub>2</sub>.

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

R	X	O $\nu$ cm <sup>-1</sup> (in KBr)	N-CH <sub>3</sub> (3.0)	S (2.5)	Se (2.4)
H	C=O	1624	1592	1569	1566
	C=C	1645	1618	1594	1593
4'-NO <sub>2</sub>	C=O	1624	1595	1578	1573
	C=C	1645	1635	1613	1609
3',5'-(NO <sub>2</sub> ) <sub>2</sub>	C=O	1618	—	1574	1569
	C=C	1646	—	1607	1603

\* The assignment of these bands was made on the analogy of the results of a previous paper<sup>9</sup>.

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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- M. FOA, A. RICCI, P. E. TODESCO and P. VIVARELLI, *Boll. scient. Fac. Chim. ind. Univ. Bologna* 23, 89 (1965).
- D. G. O'SULLIVAN, *J. chem. Soc.* (1960), 3278.
- A. CERNIANI and R. PASSERINI, *J. chem. Soc.* (1954), 226.
- P. E. TODESCO, *Boll. scient. Fac. Chim. ind. Univ. Bologna* 23, 107 (1965).
- R. GUGLIEMMETTI, E. PRETELLI and J. METZGER, *Bull. Soc. chim. Fr.* (1967), 2812.
- E. B. KNOTT, *J. chem. Soc.* (1955), 916.
- F. L. TOBIASON and J. H. GOLDSTEIN, *Spectrochim. Acta* 23A, 1385 (1967).
- L. PAULING, *The Nature of the Chemical Bond* (Cornell University Press 1960), p. 93.
- GH. CIURDARU, M. FARCASAN and V. I. DÉNES, *Rev. Roumaine chim.*, in press.

### 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<sup>1</sup>, it has become recognized that such substances (phytoecdysones) are widely distributed also in the plant kingdom<sup>2-4</sup>. Ecdysterone, a C<sub>27</sub>-compound, has been isolated by IMAI et al.<sup>5</sup> from *Polypodium japonicum*, *Trillium smailii* and other plants, and together with cyasterone from *Ajuga* species. GALBRAITH and HORN<sup>6</sup> 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

- P. KARLSON, H. HOFFMEISTER, H. HUMMEL, P. HOCKS and G. SPITELLAR, *Chem. Ber.* 98, 2394 (1965).
- K. NAKANISHI, M. KOREEDA, S. SASAKI, M. L. CHANG and H. Y. HSU, *Chem. Commun.* 1966, 915.
- M. N. GALBRAITH and D. H. S. HORN, *Chem. Commun.* 1966, 905.
- T. TAKEMOTO, S. OGAWA and N. NISHIMOTO, *J. pharm. Soc. Japan* 87, 1469 (1967).
- S. IMAI, T. TOYOSATO, M. SAKAI, Y. SATO, S. FUJIOKA, E. MURATA and M. GOTO, *Chem. pharm. Bull.*, Tokyo 77, 340 (1969).
- M. N. GALBRAITH and D. H. S. HORN, *Aust. J. Chem.* 22, 1045 (1969).