ULTRAVIOLET ABSORPTION SPECTRA OF DIHYDROINDOLE ALKALOIDS

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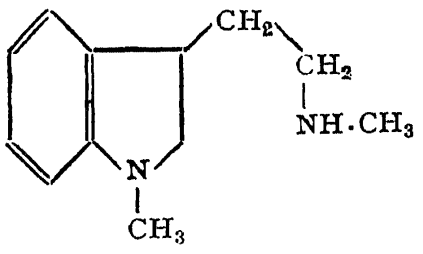
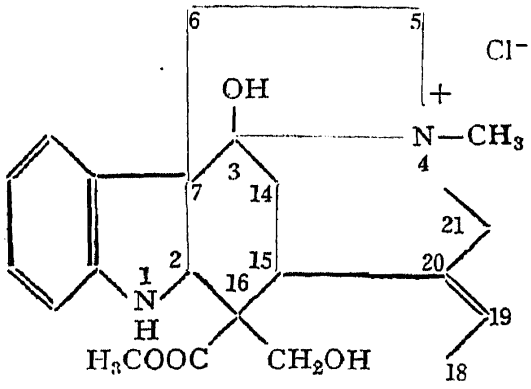
It is well known that alkaloids having the dihydroindole chromophore exhibit in neutral solution, absorption maxima near about 250 and 300 mμ. Hodson and Smith[1] have observed that the nature of the spectra of these alkaloids in acid solution is dependent on the number of carbon atoms separating N_a and N_b. Thus the absorption maxima of eserine-type compounds undergo a hypsochromic shift of about 10 mμ on addition of acid, while those of hexahydro-β-carbolines are unchanged. The indoline absorption of compound (I) in which N_a and N_b are separated by more than three carbon atoms undergoes a dramatic change to benzenoid absorption on addition of acid. Bearing these observations in mind, it was proposed[2–3] on the basis of ultraviolet absorption characteristics that echitamine contained a N_a–C–N_b system. Some further degradation experiments[4] also appeared to support this proposal. Recently, Conroy and co-workers[5] have proposed structure (II) for echitamine chloride, which satisfactorily explains all the experimental data, with the exception of u.v. absorption



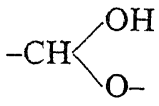
I



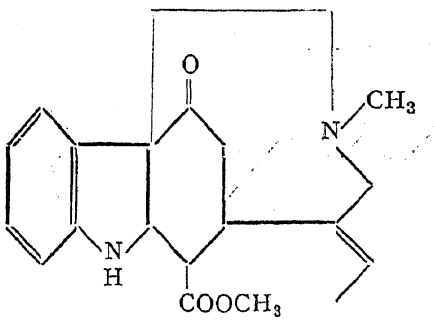
II

characteristics. Echitamine chloride shows only indoline absorption even in strong acid and this has been attributed to steric hindrance to protonation at N_a. It was therefore of interest to examine the u.v. spectra of several products derived from echitamine (Table I) and some other dihydroindole alkaloids in acid solution.

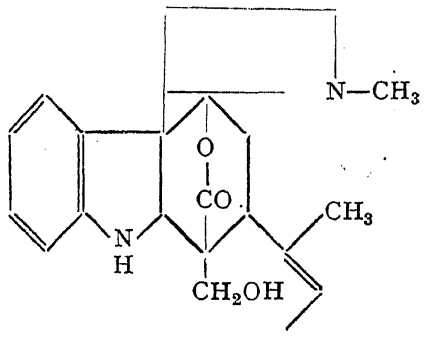
TABLE I

Compound	Substituents at C_{16}		u.v. in 0·1 N acid	u.v. in 5 N acid
1. Echitamine ..	CO_2CH_3,	CH_2OH	Indoline	Indoline
2. Echitinolide ..	COO– ,	CH_2OH	,,	,,
3. Lithium aluminium hydride reduction product of echitinolide	CH_2OH,	CH_2OH	,,	,,
4. Alloechitamine[5] ..	H,	CO_2CH_3	,,	Benzenoid
5. Lithium aluminium hydride reduction product of alloechitamine	H,	CH_2OH	Benzenoid	..
6. Hemitoxiferine-I[6] ..	H,		,,	..

It is seen from the data recorded that ultraviolet absorption behaviour of compounds of the N_a-C-C-C-N_b type (β-indole type alkaloids) is dependent on the number and nature of the substituents at C_{16} and also on the strength of the acid. For example, while alloechitamine (III) exhibits indoline absorption in 0·1 N HCl, and benzenoid absorption in 5 N HCl, the corresponding lithium aluminium hydride reduction product exhibits only benzenoid absorption even in 0·1 N acid. Compounds of the type of



III



IV

echitinolide (IV) and its lithium aluminium hydride reduction product, bearing two substituents at C_{16} exhibit only indoline absorption in 5 N acid.

Ajmaline in which N_a and N_b are separated by only two carbon atoms, shows indoline absorption in 0·1 N acid and benzenoid absorption in 5 N acid. Finally, calycanthine[7] in which N_a and N_b are separated by a single carbon atom exhibits indoline absorption even in strong acid.

The ability of N_a to protonate in dihydroindole alkaloids, with consequent change to benzenoid absorption, appears therefore to be influenced not only by the distance from N_b, but also on the degree and nature of substitution in the neighbourhood of N_a.

Summary

The ease of protonation of N_a of dihydroindole alkaloids is shown to depend not only on the distance from N_b, but also on the degree and nature of substitution in the neighbourhood of N_a, from a study of their u.v. spectra in acid solution.

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