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STUDIES IN THE INDOLE SERIES—V[1]

THE MASS SPECTRA OF SOME VOBASINE-TYPE COMPOUNDS[2]

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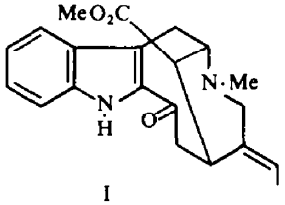
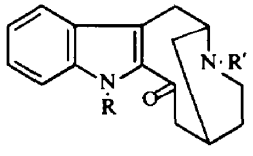
Abstract—The mass spectra of some vobasine-type compounds (II–XII) have been investigated, and the genesis of the major fragments has been rationalized; in several instances deuterium labelling has also been employed for purposes of substantiation. The analogy of the fragmentation processes between the synthetic compounds and natural vobasine-type alkaloids has confirmed the identity of their carbon skeleton.

THE advantages of the mass technique in structural studies in the field of the indole alkaloids has become extremely useful in the characterization and identification of the over-all skeleton, particularly since the determination of the sarpagine skeleton by Biemann[3] in 1960.

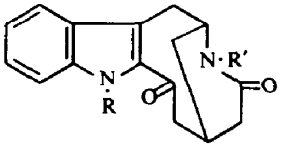
In our preceding report[1] we described the synthesis of some vobasine-type compounds (II–XII) having the full carbon skeleton of vobasine (I) and its congeners.[4]



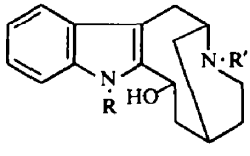
I



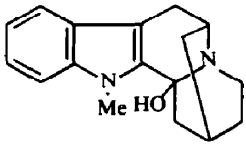
II: R = H, R′ = CH_2Ph
III: R = Me, R′ = CH_2Ph
IV: R = Me, R′ = Me



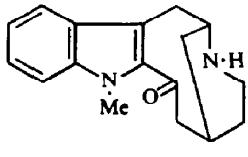
V: R = H, R′ = CH_2Ph
VI: R = Me, R′ = CH_2Ph
VII: R = Me, R′ = H



VIII: R = H, R′ = CH_2Ph
IX: R = Me, R′ = CH_2Ph
X: R = Me, R′ = H



XI

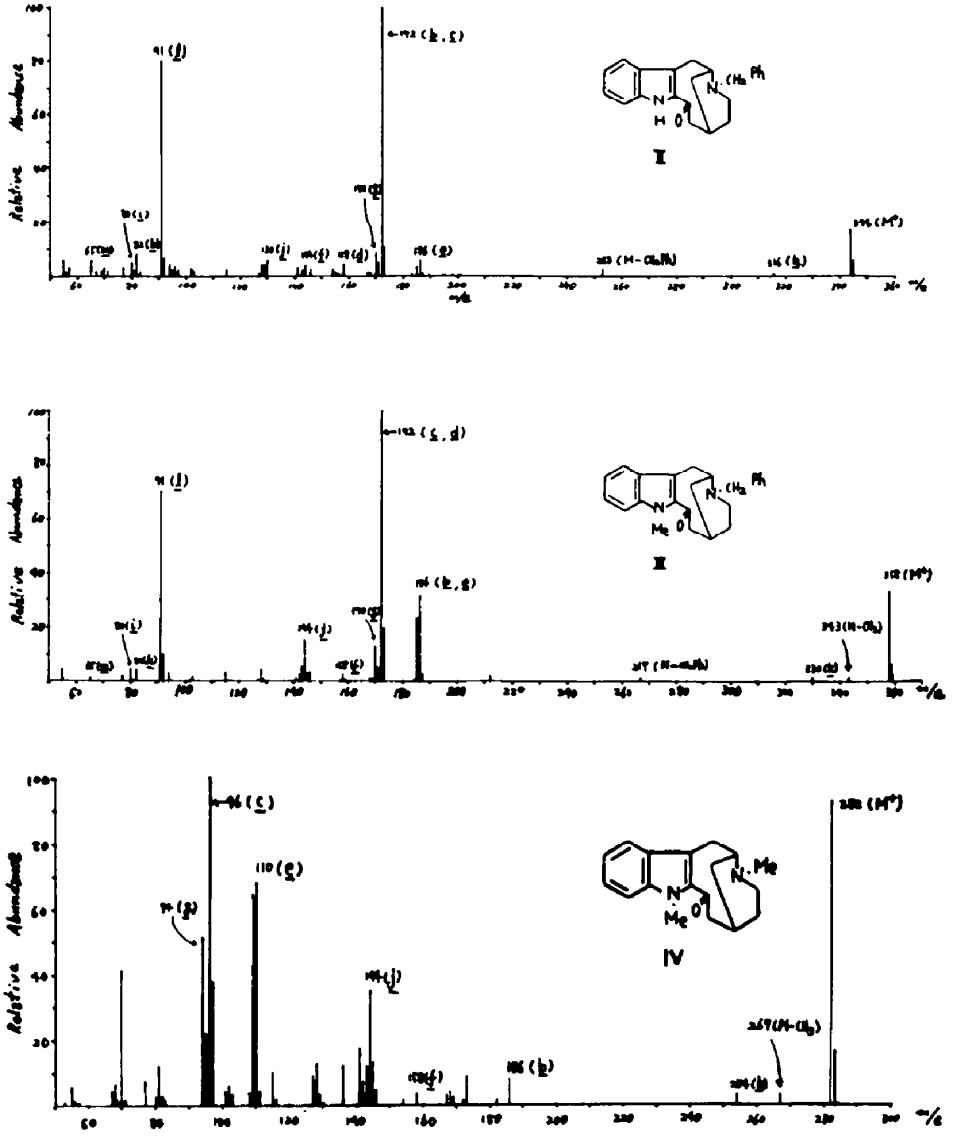


XII

To verify the carbon skeleton of the synthetic compounds (II–XII) their mass spectrometric behaviour has been investigated. The similar fragmentation processes of the compounds (II–XII) and natural vobasine-type alkaloids[5–8] have confirmed the identity of their skeletal structures. Suitable deuterium labelling has also made possible a mechanistic interpretation of the genesis of the principal fragments.

1. *Fragmentation processes of amino-ketones* (II–IV; Figs 1–3)

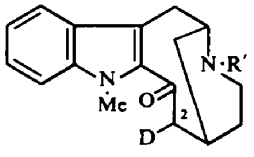
The mass spectra (Figs 1 and 2) of the N_b-benzyl-amino-ketones (II and III) resemble each other especially in the region below *m/e* 200. The most intense peak



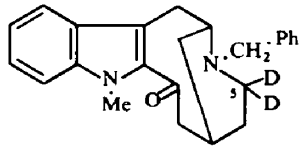
FIGS 1–3 Mass spectra of II–IV.

in each spectrum is displayed at *m/e* 172. The spectrum (Fig. 3) of the N_b-methyl-amino-ketone (IV) contains the base peak at *m/e* 96. As in the spectrum of vobasine[5] (I), the formation of these principal fragments can be interpreted by assuming the initial homolytic fission of the 7–8 bond connecting the indole nucleus with the basic N atom. Subsequent β-cleavage with migration of the γ-hydrogen atom to the carbonyl oxygen (arrows in the intermediate *a**) in a manner typical of aliphatic ketones[9] provides the most abundant ions *c* (*m/e* 172, 172 and 96 in the spectra of II, III and IV respectively) and the less abundant ions *b* (*m/e* 172, 186 and 186 in the respective spectra of II, III and IV), the latter of which may be produced via the enol ions *b'*. The characteristic peaks at *m/e* 186 in the spectra of II and III and at *m/e* 110 in that of IV can be explained by α-cleavage of the 1–2 bond in *a'* (typical of ketones[9]) accompanied with transfer of one hydrogen and depicted as *e*. Biemann *et al.*[5b] pointed out in the vobasine spectrum the presence of the ion *d* (*m/e* 158) which could be derived from the intermediate *a'*. The spectrum of II contains a characteristic but not abundant peak at *m/e* 158, while in the spectrum of III the overlap of the ions *c* and *d* at the same position (*m/e* 172) obscures the presence of the species *d* and no characteristic peak is found in that region of the spectrum of IV.

Deuteration of III and IV with sodium and deuterium oxide in dioxan[10] resulted in the replacement of one H atom adjacent to the CO group by deuterium. In the spectra of these 2-monodeuterio derivatives (XIII and XIV) the ions *b* and *e* are shifted by one mass unit, but the species *c* remains unaltered. The mass spectrum of the 5,5-dideuterio compound (XV), which was obtained from the keto-lactam (VI) by



XIII: R' = CH_2Ph
XIV: R' = Me



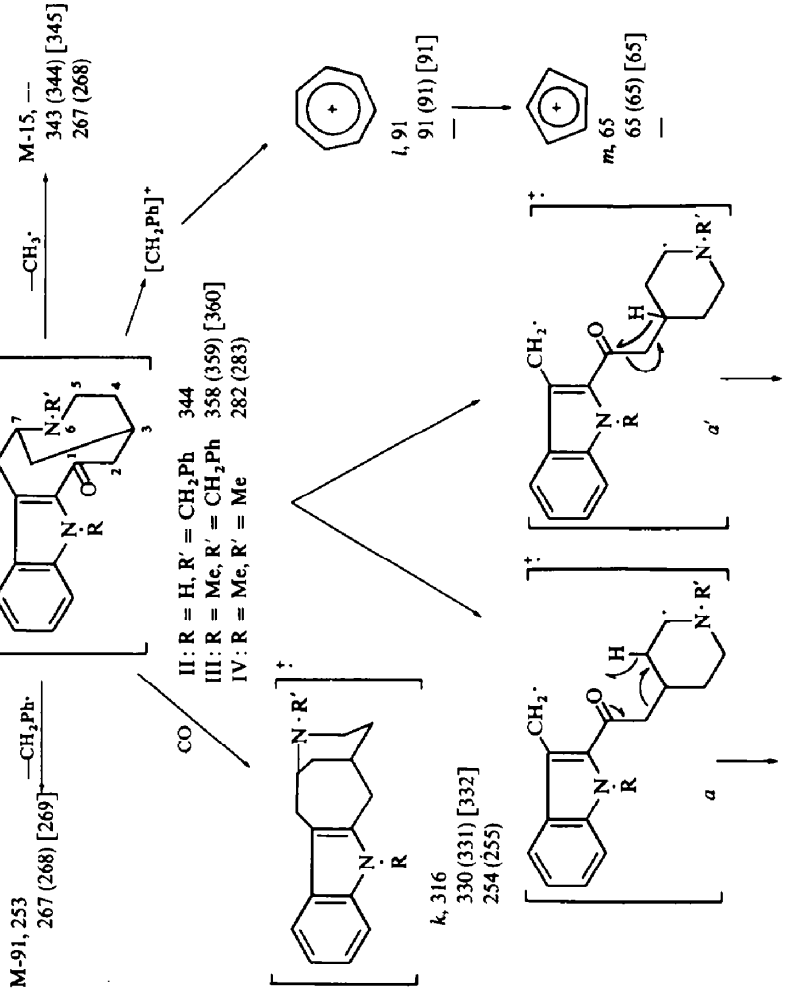
XV

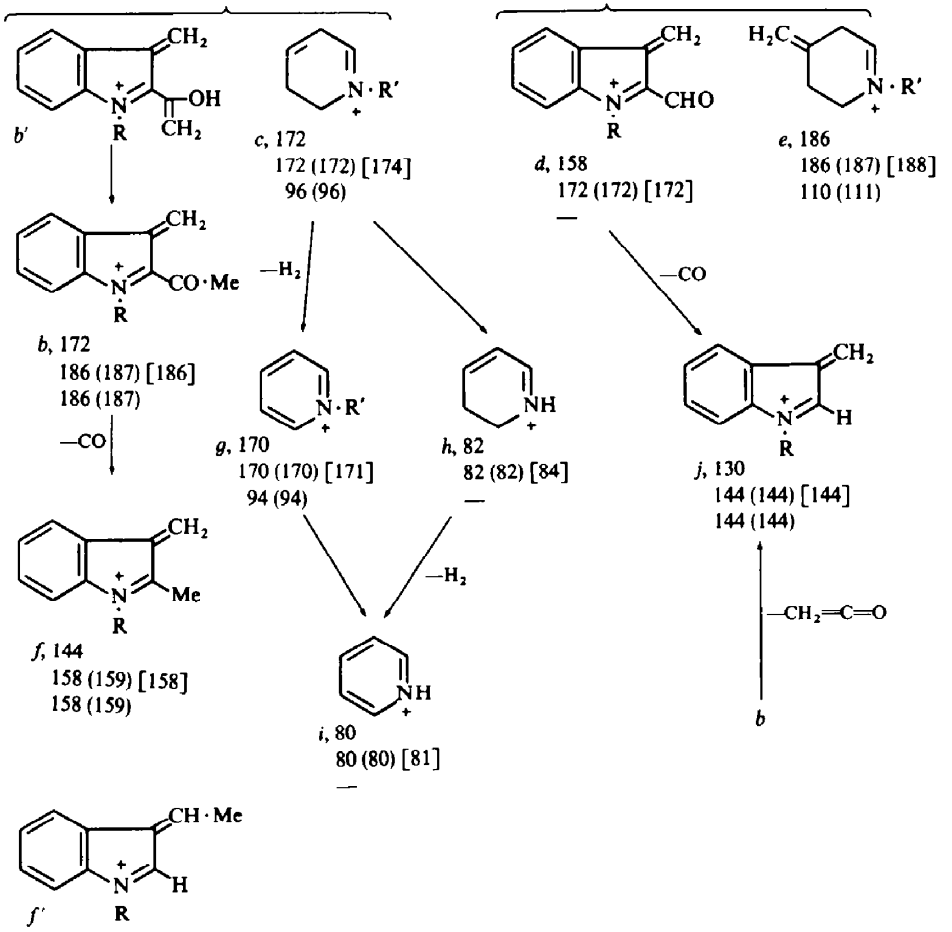
LAD reduction followed by CrO_3 oxidation, exhibits the species *c* at *m/e* 174 and the species *e* at *m/e* 188, both of which are two mass units higher than those in the spectrum of III. The labelling experiments support the above fragmentation processes.

The dihydropyridinium ion *c* would be degradated to the ions *g*, *h* and *i*.

Each peak at *m/e* 144, 158 and 158 in the respective spectra of II, III and IV might be represented by the species *f* which could be formed by expulsion of carbon monoxide from the methyl ketone species *b*, although no metastable ion could be found to substantiate this proposal and there are few examples[11] of loss of carbon monoxide from a methyl ketone species with migration of a Me group.

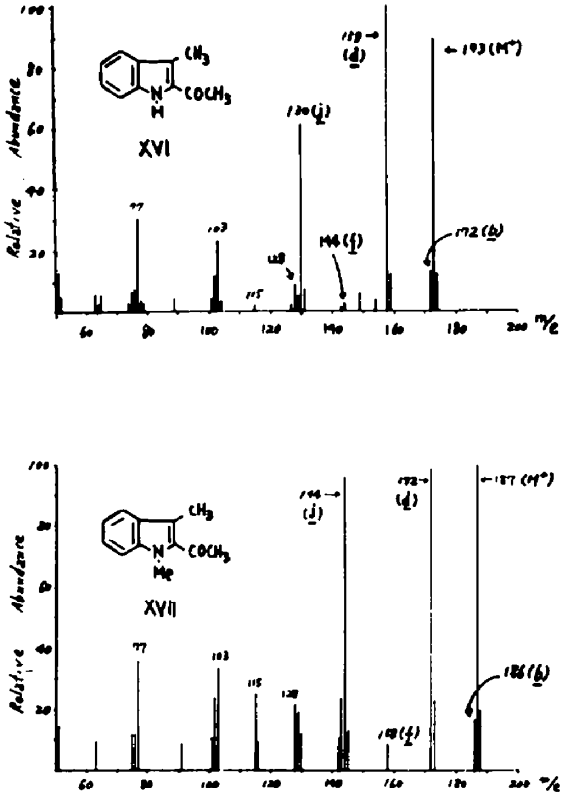
* One electron shifts are denoted by fish-hooks (⌒) following the convention adopted in Ref. 5*a*, p. 2.


M-91, 253
267 (268) [269]
—CH2Ph·
CO
II: R = H, R' = CH2Ph 344
III: R = Me, R' = CH2Ph 358 (359) [360]
IV: R = Me, R' = Me 282 (283)
—CH3·
M-15, —
343 (344) [345]
267 (268)
[CH2Ph]+
k, 316
330 (331) [332]
254 (255)
l, 91
91 (91) [91]
—
m, 65
65 (65) [65]
—
a
a'



* The arabic figures express *m/e* of each fragment in the spectra of II, III and IV respectively. The *m/e* in parentheses and brackets shows the peaks in the spectra of the monodeuterio (XIII and XIV) and dideuterio (XV) derivatives.

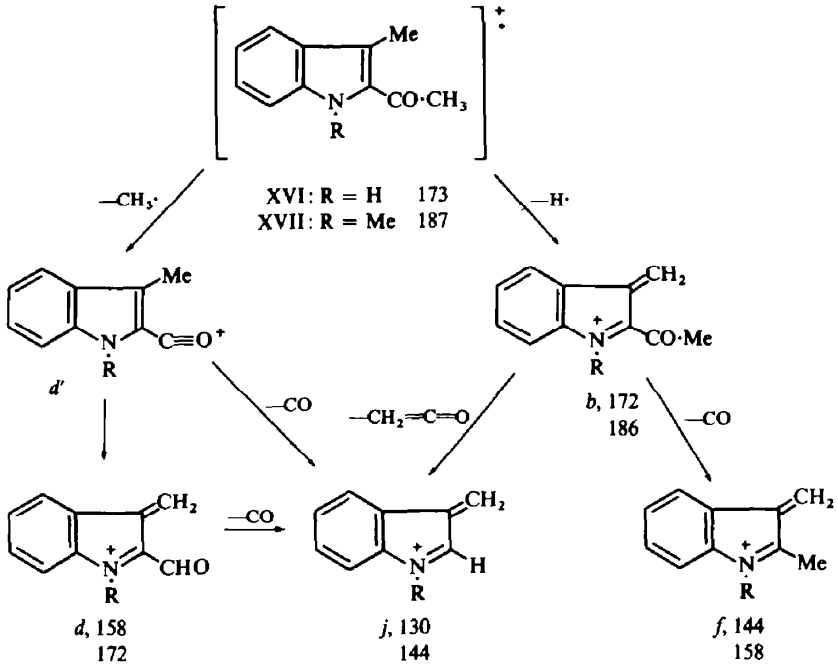
A clue to the fragmentation process comes from the spectra (Figs 4 and 5) of the model compounds: 2-acetyl-3-methylindole (XVI) and 2-acetyl-1,3-dimethylindole (XVII).[12] As expected from the mass spectrometric behaviour of 3-methylindole derivatives,[13] both of XVI and XVII yield the M-1 peak due to β-bond fragmentation.



FIGS 4 and 5 Mass spectra of XVI–XVII.

The M-1 ions correspond to the above ions *b*, which would produce the ions *f* at *m/e* 144 in the spectrum of XVI and at *m/e* 158 in that of XVII though not so intense. However, it should be mentioned that in the spectra of the amino-ketones (II–IV) we could not completely exclude the possibility of alternative species *f'* for *f*.

The ions *d* (or *d'*) are also found at *m/e* 158 and 172 in the respective spectra of XVI and XVII.

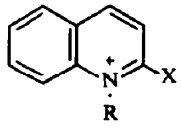


Each spectrum of the indole-N unsubstituted compounds (II and XVI) contains a peak at *m/e* 130, whereas the N_a-Me analogues (III, IV, XIII, XIV, XV and XVII) show the corresponding peak at *m/e* 144. This peak may be represented by *j*, which generally exists in the spectra of 3-alkylindole derivatives[5a, 13] and may be formed from both ions *b* and *d* by the loss of ketene and carbon monoxide respectively.*

All three spectra of the amino-ketones (II–IV) exhibit peaks corresponding to the M-28 ions, which may be formulated as *k* due to loss of carbon monoxide from the molecular ions. Deuterium labelling (spectra of XIII–XV) excluded the possible loss of ethylene from the molecular ions and the presence of metastable peak in each spectrum also confirmed the above assignments.

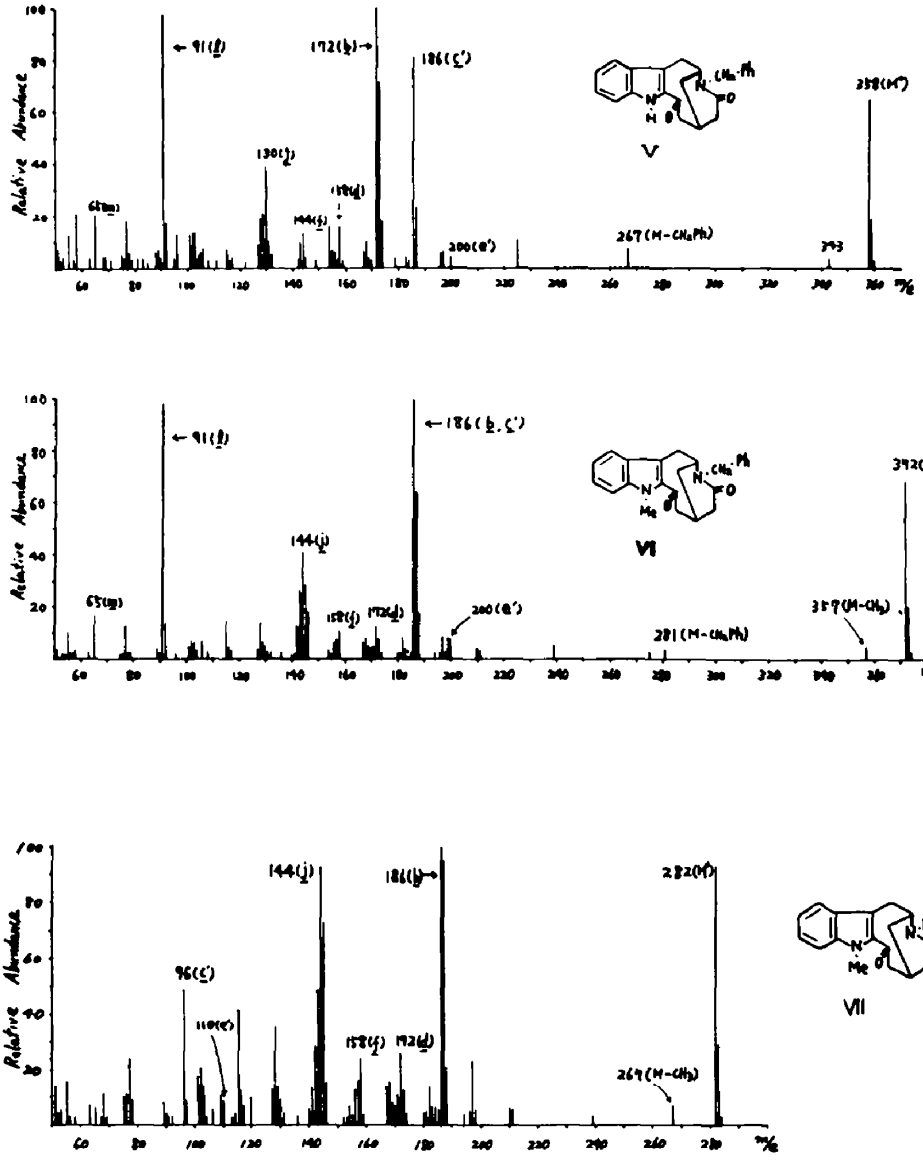
The N_b-benzyl-amino-ketones (II, III, XIII and XV) show an intense peak at *m/e* 91 and a weak peak at *m/e* 65, which can be respectively ascribed to the tropylium cation *l* and cyclopentadienyl cation *m*. The M-91 peaks in the spectra of the N_b-benzyl compounds can arise from the loss of benzyl group from the molecular ions. Each spectrum of the N_a-Me (III, XIII and XV) or N_a,N_b-dimethyl compounds (IV and XIV) contains a weak M-15 (M-CH_3) peak.

* The indolenium ions *b*, *d*, *f* and *j* can be also expressed as the quinolinium ions:



X = CO·Me, CHO, Me, H

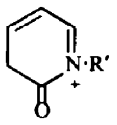
Thus, energetically plausible fragmentations can be suggested for most of the characteristic ions in the spectra of the amino-ketones (II–IV).



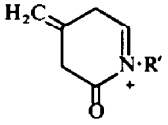
FIGS 6–8 Mass spectra of V–VII.

2. *Fragmentation processes of keto-lactams* (V–VII; Figs 6–8)

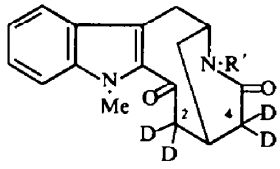
The keto-lactams (V–VII) have a fragmentation pattern very similar to that of the amino-ketones (II–IV). The genesis of the major peaks (*b*, *c'* and *e'*) can be easily understood by assuming the similar electron shifts as those in the intermediates *a* and *a'*, the latter of which is less important. The species *c'* and *e'* respectively correspond to *c* and *e* in the spectra of the amino-ketones.



c'



e'



XVIII: R' = CH_2Ph
XIX: R' = H

In contrast to the spectra of II–IV, it is noteworthy that the most abundant ion in each spectrum is *b* rather than *c'*. The species *e'* is weak and not characteristic in the spectra of the keto-lactams (V–VII).

The species *f* and *j* are found in all spectra. The formation of *j* by loss of ketene from *b* is confirmed, at least in part, by the presence of a metastable ion in each spectrum.

Deuteration of the keto-lactams (VI and VII) under a similar reaction condition to that of the amino-ketones (III and IV) afforded the 2,2,4,4-tetradeuterio derivatives (XVIII and XIX), whose spectra exhibit a two mass unit shift of each species *b*, *c'* and *f* and a four of the species *e'*.

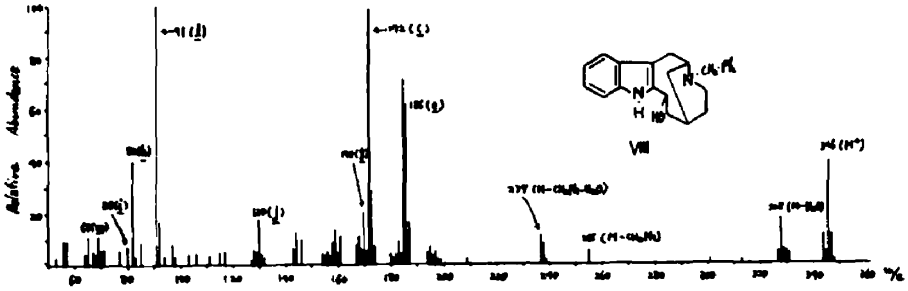
The characteristic M-CO peak in the spectra of the amino-ketones is absent in any spectrum of the keto-lactams. The different behaviour between the amino-ketones and the keto-lactams toward the deuterium labelling and the generation of the M-CO peak might suggest that conformational factors govern them to a large extent.

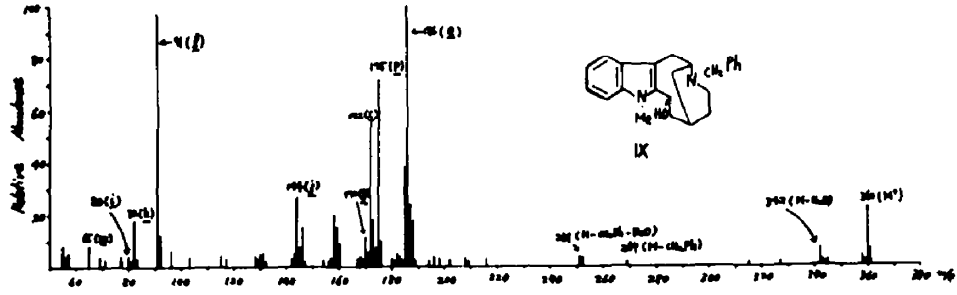
The spectra of the N_b-benzyl-keto-lactams (V, VI and XVIII) contain the peaks *l*, *m* and M-91, while the M-15 peak is observed in all spectra. We cannot offer a reasonable explanation for the presence of the M-15 ion in the spectrum of V.

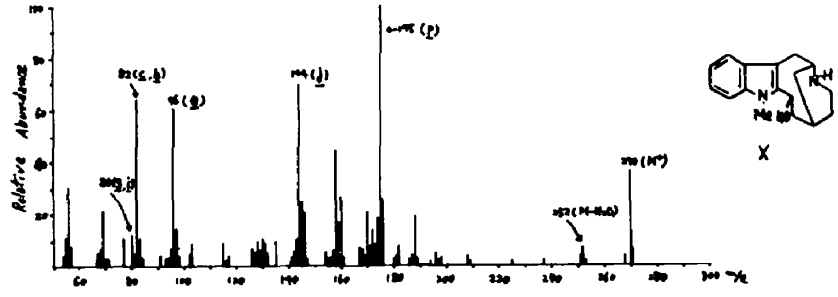
3. *Fragmentation processes of amino-alcohols* (VIII–X; Figs 9–11)

The carbinol function of the amino-alcohols (VIII–X), which is confirmed by the presence of the characteristic M-18 (M-H_2O) peak, does not influence in any major way the mass spectrometric fragmentation of the molecule. Two major peaks *c* and *e* can arise from analogous intermediates to *a* and *a'* in the spectra of the amino-ketones (II–IV).

The result of the following labelling experiments is consistent with the mechanism. The mass spectrum of the 1,5,5-trideuterio compound (XX), obtained by LAD reduction of the keto-lactam (VI), shows both fragments *c* and *e* at two mass units higher (*m/e* 174 and 188). These ions *c* and *e* were respectively moved to two and four higher mass number in the spectrum of the 2,2,4,4-tetradeuterio derivative

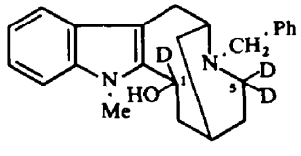




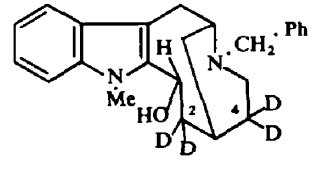


FIGS 9–11 Mass spectra of VIII–X.

(XXI), which was provided by LAH reduction of XVIII. Interestingly the ions *e* in the spectra of the amino-alcohols (VIII–X) are considerably abundant in contrast with those of the amino-ketones (II–IV) and the keto-lactams (V–VII).

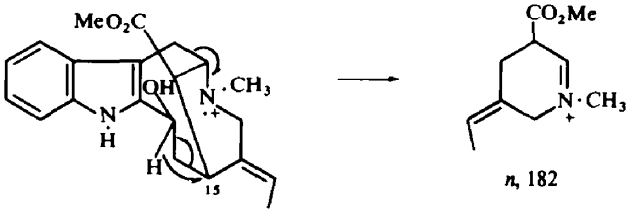


XX

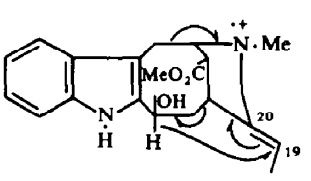


XXI

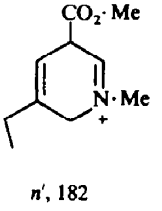
In the vobasinol (XXII) and 16-epivobasinol spectra there is a very intense peak at *m/e* 182; this peak was ascribed to the ion *n* or *n'* resulting from transfer of the C-3 hydrogen to C-15[5a,c] (arrows in XXIIa) or C-19[5b] (arrows in XXIIb). Since the



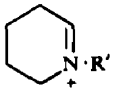
XXIIa *n*, 182



XXIIb



n', 182

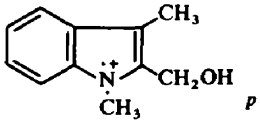


o

amino-alcohols (VIII–X) have no ethylidene function, only the electron shifts analogous to these of XXIIa can be expected to give the species *o* corresponding to the species *n*. Actually the species *o* (*m/e* 174, 174, 177, 176 and 84 in the spectra of VIII, IX, XX, XXI and X respectively) are weak and not characteristic, which shows the fragmentation analogous to that of XXIIa occurring to a little extent and might support the mechanism in XXIIb in the spectrum of vobasinol. The spectrum of 19,20-dihydrovobasinol[5c] contains a weak *m/e* 184 peak corresponding to *n* or *n'*, and also confirms the electron shifts in XXIIb.

The ions *g*, *h* and *i* derived from the ion *c* are present, and the tropylium cation *l* (*m/e* 91) and the cyclopentadienyl cation *m* (*m/e* 65) as well as the M-91 peak are found in the spectra of the N_b-benzyl-amino-alcohols (VIII, IX, XX and XXI). The weak M-109 (M-CH_2Ph–H_2O) peaks are also observed in their spectra. The M-15 peaks are not characteristic in comparison with those in the amino-ketones.

Each mass spectrum of the N_a-methylindole derivatives (IX and X) displays a prominent peak at *m/e* 175, which is increased by one unit in the spectrum of the 1,5,5-trideuterio compound (XX) but remains unaltered in that of the 2,2,4,4-tetradeuterio one (XXI). High-resolution mass spectrometry* established $C_{11}H_{13}ON$ as the composition of this ion in both spectra of IX and X. From the above data the



p

* Kindly measured by Dr. Y. Itagaki at Japan Electron Optics Laboratory Co. Ltd.

fragment at *m/e* 175 can be formulated as the ion *p*. It is interesting that there is no significant peak (*m/e* 161) corresponding to *p* in the spectrum of VIII.

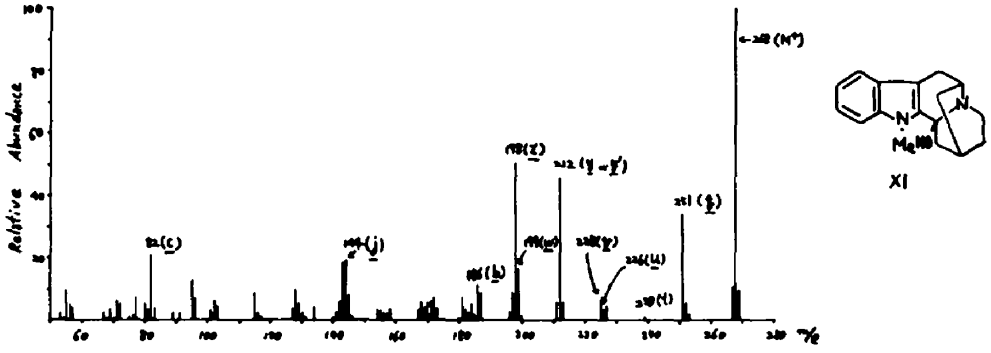


FIG. 12 Mass spectrum of XI.

4. *Fragmentation processes of carbinolamine* (XI; Fig. 12)

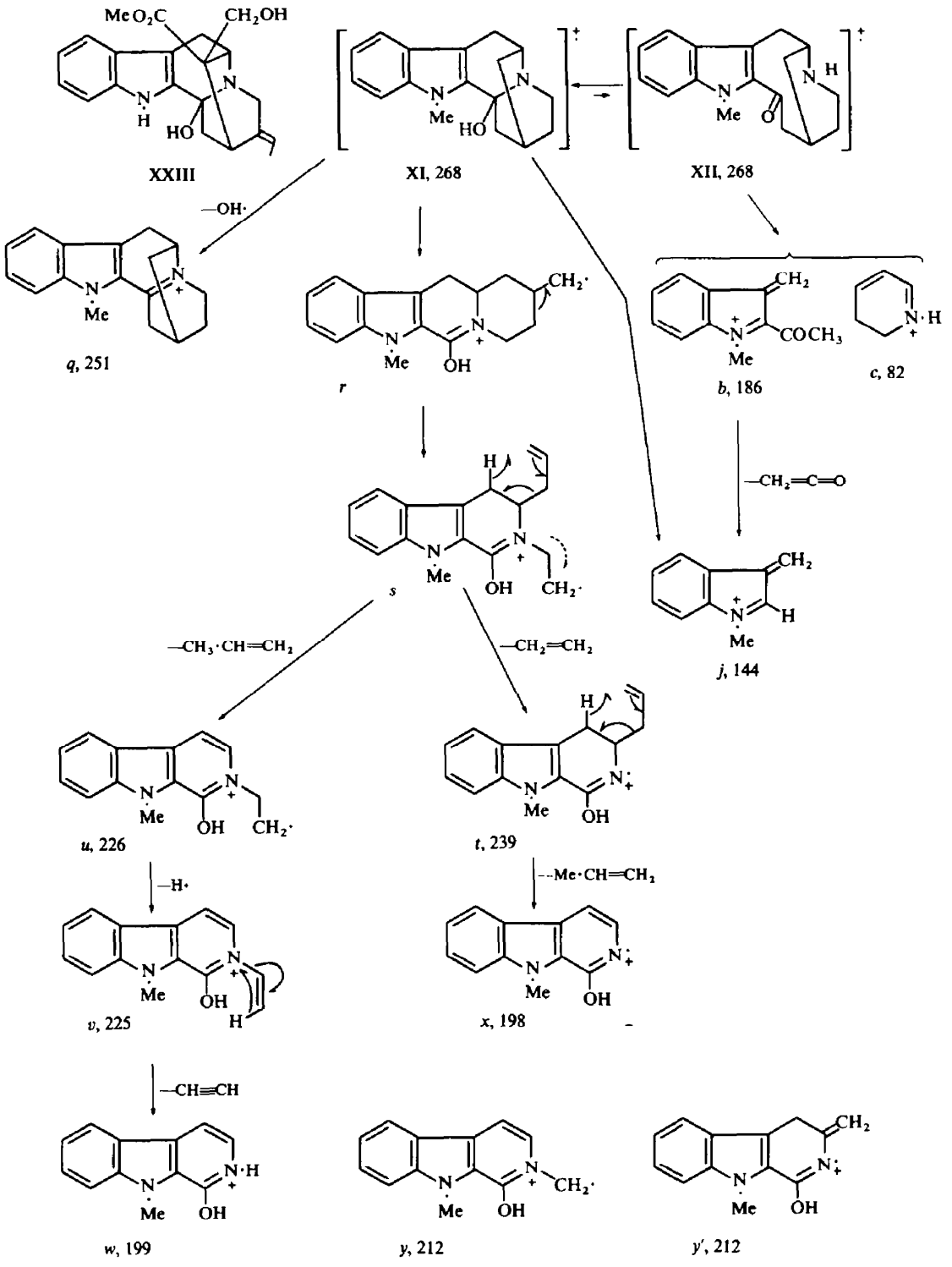
As reported in our preceding paper,[1] debenzylation of the amino-ketone (III) or oxidation of the amino-alcohol (X) furnished an equilibrated mixture of the carbinolamine (XI) and the amino-ketone (XII). The IR and UV spectra revealed that the product was almost entirely in the carbinolamine (XI) in the solid state but in solution the amino-ketone (XII) exists a little in equilibrium with the carbinolamine (XI).

On electron impact the compound undergoes a very characteristic decomposition path, which has been mostly explained by that of the carbinolamine (XI). A diagnostic fragment is found at *m/e* 251, which is attributed to the M-OH ion (*q*) corresponding to the pronounced M-1 peak generally appeared in the spectra of the tetrahydro-β-carboline alkaloids.[14] Voacarpine (XXIII) also has been reported[8] to contain the M-OH ion in its mass spectrum.

The other noteworthy features are the peaks at *m/e* 239, 226, 225, 199 and 198, which can be ascribed to the β-carboline fragments and depicted as *t*, *u*, *v*, *w* and *x* respectively. The genesis of these ions can be visualized as the analogous fragmentation mechanism via intermediates *r* and *s* to that in the spectra of sarpagine,[3] voacarpine[8] (XXIII) and related alkaloids.[14]

A peak at *m/e* 212 seems to represent a cleavage specific to this compound and might be formulated as *y* or *y'*.

If the compound were mainly consisted of the amino-ketone (XII), a peak at *m/e* 82 would be prominent because of its correspondence to the most abundant ions *c* in the spectra of the amino-ketones (II–IV). Actually the *m/e* 82 ion is observed in company with the weak peak *b* at *m/e* 186, but not abundant. This supports that the equilibrium between the carbinolamine (XI) and the amino-ketone (XII) largely inclines to XI upon electron impact.


XXIII
XI, 268
XII, 268
q, 251
r
b, 186
c, 82
s
j, 144
u, 226
t, 239
v, 225
x, 198
w, 199
y, 212
y', 212
—OH·
—CH₂=C=O
—CH₃·CH=CH₂
—CH₂=CH₂
—H·
—Me·CH=CH₂
—CH≡CH

The usual indole-containing fragment *j* is also found at *m/e* 144.

The above extensive study of fragmentation processes of the vobasine-type compounds not only identified their carbon skeleton with that of vobasine, but also will contribute to the structure elucidation of the vobasine-type alkaloids which will be found in the future.

EXPERIMENTAL

The mass spectra were obtained with a Hitachi RMU-6D instrument using a direct inlet system except using an indirect one in the case of XVI and XVII. The ionizing energy was maintained at 70 eV, and the ionizing current at 80 μA. The chamber was heated at 210–215°.

The samples, except those described below, were prepared according to our previous reports.[1,12]

General procedure for deuterium exchange of amino-ketones (III *and* IV) *and keto-lactams* (VI *and* VII). The deuteration reagent was prepared by adding Na (50 mg) to a mixture of D_2O–dioxan (1:1; 4 ml) according to the method of Djerassi *et al.*[10]

To each carbonyl compound (10 mg) in dioxan (1·5 ml) was added the reagent (1 ml) and further D_2O (0·2 ml). The mixture was stirred at 70–75° (bath temp) under N_2 for 13 hr, and evaporated *in vacuo*. To the residue was added D_2O (1 ml), and the mixture was extracted with AcOEt (15–20 ml). The AcOEt layer was washed with sat. NaCl aq, dried and evaporated to an oil which crystallized by tritulation with Me_2CO. Mass spectrometry showed the amino-ketones (XIII and XIV) to contain 79 and 71% d_1 species respectively, while the keto-lactams (XVIII and XIX) respectively contained 84 and 78% d_4 species.

Mass spectrum of XIII: *m/e* 359 (12%, M^+), 344 (1, M-CH_3), 331 (1, M-CO), 268 (1, M-CH_2Ph), 187 (14, *b* and *e*), 186 (13), 173 (12), 172 (79·5, *c* and *d*), 170 (7·5, *g*), 159 (2, *f*), 158 (2), 144 (9, *j*), 91 (100, *l*), 82 (3·5, *h*), 80 (4, *i*), 65 (6, *m*).

Mass spectrum of XIV: *m/e* 283 (20%, M^+), 268 (2, M-Me), 255 (2, M-CO), 187 (3, *b*), 159 (1, *f*), 158 (2), 144 (12, *j*), 111 (19, *e*), 110 (15·5), 97 (11), 96 (100, *c*), 94 (14, *g*), 70 (13).

Mass spectrum of XVIII: *m/e* 376 (40, M^+), 361 (2, M-Me), 285 (3, M-CH_2Ph), 204 (5, *e'*), 190 (15), 189 (53), 188 (100, *b* and *c'*), 187 (14), 173 (6), 172 (6), 160 (4, *f*), 159 (5), 158 (5), 145 (33), 144 (30, *j*), 143 (10), 91 (60, *l*), 65 (7, *m*).

Mass spectrum of XIX: *m/e* 286 (67%, M^+), 271 (3, M-Me), 190 (28·5), 189 (59), 188 (100, *b*), 173 (12), 172 (9), 160 (9·5, *f*), 159 (11), 158 (9), 145 (54), 144 (58, *j*), 143 (29), 128 (21), 115 (15), 98 (15·5, *c'*), 97 (27).

LAD Reduction of keto-lactams (VI). The keto-lactam VI (0·20 g) was reduced with LAD (0·10 g) in refluxing THF (10 ml) for 4 hr. The soln was cooled, and remaining deuteride was decomposed with a mixture of D_2O–THF. The mixture was dried over Na_2SO_4, filtered, and the filtrate was evaporated to the residue, which was recrystallized from benzene. The crystals of XX were washed with Et_2O and dried. Mass spectrometry showed XX to contain 68% d_3 species. Mass spectrum: *m/e* 363 (8%, M^+), 345 (2, M-H_2O), 272 (2, M-CH_2Ph), 255 (2·5), 254 (2, M-CH_2Ph-H_2O), 189 (33), 188 (74·5, *e*), 187 (22), 176 (68, *p*), 175 (20), 174 (34, *c*), 171 (11·5, *g*), 161 (20), 159 (21), 145 (15·5), 144 (31, *j*), 92 (17), 91 (100, *l*), 84 (8·5, *h*), 65 (2, *m*).

CrO_3 *Oxidation of* 1,5,5-*trideuterio-amino-alcohol* (XX). To compound XX (0·07 g) in pyridine (7 ml) was added a slurry of CrO_3 (0·14 g) in pyridine (3 ml). The mixture was kept at room temp for 5 min with occasional shaking, poured into water (50 ml), and extracted with AcOEt (50 ml). The AcOEt extract was washed with water, sat. NaCl aq, dried over Na_2SO_4 and evaporated. The residual oil (0·07 g) after solidification with Me_2CO was chromatographed on silicagel (3·5 g). Elution with benzene–$CHCl_3$ (10:1) (20 ml) gave XV as crystals, shown by mass spectrometry to contain 82% d_2 species. Mass spectrum: *m/e* 360 (34·5%, M^+), 345 (4, M-Me), 332 (5, M-CO), 269 (4, M-CH_2Ph), 188 (29, *e*), 187 (24), 186 (8, *b*), 175 (28), 174 (95, *c*), 172 (12, *d*), 171 (8·5, *g*), 158 (4, *f*), 144 (16, *j*), 91 (100, *l*), 84 (5, *h*), 81 (4·5, *i*), 65 (6, *m*).

LAH *reduction of* 2,2,4,4-*tetradeuterio-keto-lactam* (XVIII). Compound XVIII (0·05 g) was reduced with LAH (0·03 g) in refluxing THF (4 ml) for 4 hr. The cooled mixture was treated as usual procedure. The resultant XXI was shown by mass spectrometry to contain 64% d_4 species. Mass spectrum: *m/e* 364 (12%, M^+), 346 (4·5, M-H_2O), 345 (5·5, M-DHO), 273 (2, M-CH_2Ph), 255 (4, M-CH_2Ph-H_2O), 191 (20), 190 (73·5, *e*), 189 (37·5), 175 (49, *p*), 174 (35, *c*), 173 (25), 172 (20), 158 (18), 154 (25), 144 (30, *j*), 106 (22), 105 (26), 91 (100, *l*), 84 (14, *h*), 83 (14), 81 (9, *i*), 77 (35), 71 (35), 65 (9, *m*), 57 (36).

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