

THE ANOMALOUS MASS SPECTRA OF  $\omega$ -AMINOKETONES

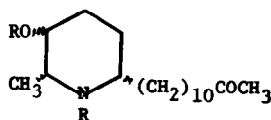
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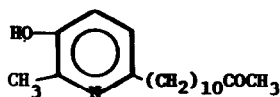
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The McLafferty rearrangement, which quite generally gives rise to important ions in the mass spectra of ketones bearing  $\gamma$ -hydrogen atoms, has been extensively studied (1). Recent investigations have demonstrated that it is directed by the charge on the carbonyl groups, and suppressed when the ionic charge is localized far from the ketone (2,3). In our studies on the alkaloids of *Cassia excelsa* (4,5) we observed that the mass spectra of these materials not only exemplify this effect, but show in addition ions resulting from the anomalous expulsion of the group  $\text{CH}_2\text{COCH}_3$  ( $m/e$  57).

The mass spectrum of cassine, 1 (Figure 1) has been described without comment on its anomalous character (6). The fragmentation is dominated by the anticipated cleavage of the alkyl



1. R=H; 2. R=Ac

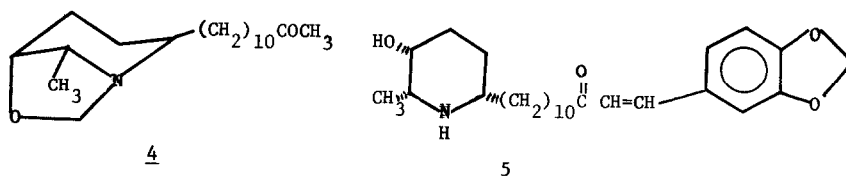


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chain adjacent to the nitrogen. However, the strongest ion of  $m/e$  greater than 114 is  $m/e$  240, arising from the loss of  $\text{CH}_2\text{COCH}_3$  from the molecular ion. Accurate mass measurements and the spectrum of pentadeutereocassine, which is identical with that of cassine below  $m/e$  250, confirm that the fragment lost is the terminal acetyl residue. Peaks which would result from the McLafferty rearrangement do not appear: There is no substantial peak at  $m/e$  239 ( $M-58$ ), and that at  $m/e$  58, when examined at high resolution (7), reveals no component corresponding to  $\text{C}_3\text{H}_6\text{O}$ .

In the spectra of the closely related compounds of the Table this mode of fragmentation is general. The acetylated derivative 2, and the synthetic analogue, 1-(N-piperidyl)decan-11-one, show the same major mode of fragmentation and anomalous ions of similar abundance. The aromatic derivative 3 differs only in that the benzylic ion is most abundant. In the spectra of the synthetic material at low ionizing voltages, the peak at  $m/e$  210 persists with the appearance of a metastable ion corresponding to the transition  $267 \rightarrow 210$ .

In the spectrum of bicyclocassine 4, (8) (Figure 2), in which the favorable nature of the cleavage adjacent to the nitrogen is evidently diminished by Bredt's rule, the effect is even more



striking, for the loss of acetyl now produces the most abundant ion. The fragmentation of the condensation product piperonylidene cassine, 5, retains the features of that of the parent alkaloid, the ion of  $m/e$  240, somewhat less abundant, arising from the loss of piperonylideneacetyl moiety, while a new ion of  $m/e$  175 corresponds to the cinnamoyl fragment.

The fragmentations observed in the series closely parallel those observed by Wolff and Caspar in a series of  $\omega$ -aminoesters (9). In each case, because the charge is localized at the nitrogen atom, McLafferty rearrangements are insignificant, and the fragmentations which involve the carbonyl group are directed by the stability of the radical expelled.

<u>Compound</u>	<u>Base peak</u>	<u>M-57</u>	<u>M</u>
Cassine, <u>1</u>	$m/e$ 114	$m/e$ 240 (14%)	$m/e$ 297 (2%)
O,N-Diacetylcassine, <u>2</u>	198	324 (8%)	381 (2%)
Dehydrocassine, <u>3</u>	122	234 (7%)	291 (2%)
Bicyclocassine, <u>4</u>	252	252 (100%)	309 (6%)
1-N-Piperidyl(dodecan-11-one)	98	210 (6%)	267 (2%)
Piperonylidinecassine, <u>5</u>	114	240 (4%)	429 (2%)

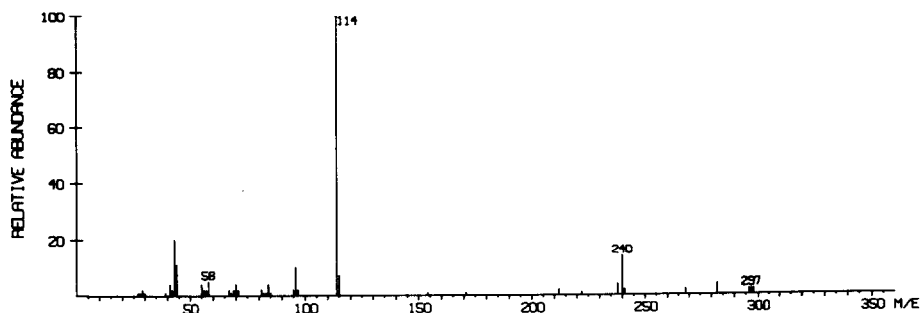


FIGURE 1. CASSINE.

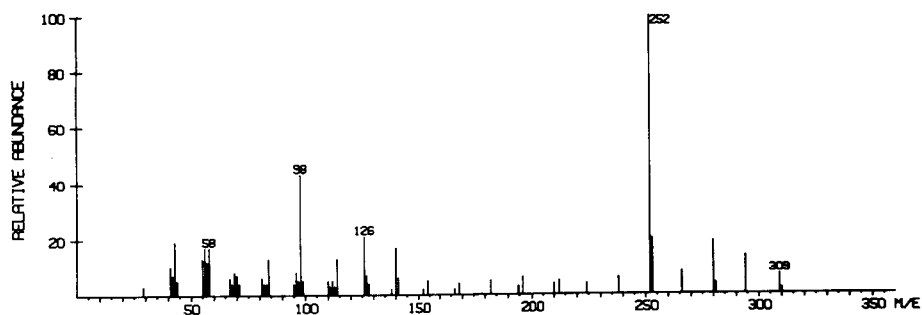


FIGURE 2. BICYCLOCASSINE.

### References

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- (6) D. Lythgoe and J. Vernengo, *Tetrahedron Lett.*, 1133 (1967).
- (7) We are indebted to Dr. H. M. Fales for these measurements.

- (8) This material is formed spontaneously on the addition of formaldehyde to a solution of cassine. Its structure rests on the molecular ion, ready hydrolysis by acid to cassine, hydrogenation to N-methylcassine, and an AB system in the nmr spectrum,  $\delta = 4.40, 4.62$ ;  $J = 7$  hz.; cf. ref. 4.
- (9) R. Wolff and A. Caspar, Tetrahedron Lett., Following paper. We are indebted to Dr. Wolff for informing us of his work before publication.