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Studies on the Syntheses of Heterocyclic Compounds. CCX.[1] The Mass Spectra of 10-Substituted-dibenz[*b,f*]oxepine Derivatives

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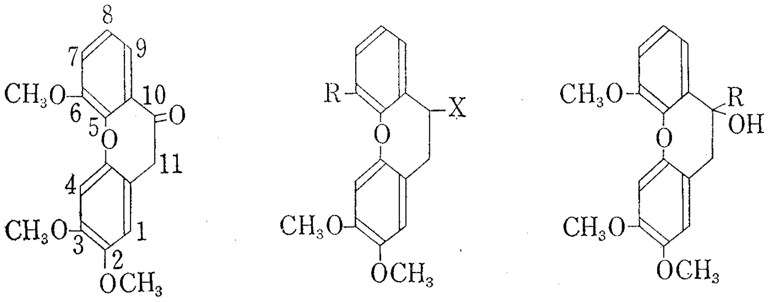
The mass spectra of several kinds of 10,11-dihydrodibenz[*b,f*]oxepine derivatives (I—VII) were investigated and the characteristic fragmentation patterns were revealed.

In the previous papers[3,4] the mass spectra of cularine and related compounds were investigated to reveal the process of its fragmentation. The purpose of the present investigation was to study the fragmentation pattern of dibenz[*b,f*]oxepine derivatives, one of components of the above alkaloids, by mass spectrum, namely, seven kinds of compounds (I—VII) being investigated. Therefore, we wish to report these results.



I

II : R=OCH_3, X=Cl
III : R=H, X=Cl
IV : R=H, X=NHCHO
V : R=H, X=NH_2

VI : R=H
VII : R=D

Chart 1

The base ion peak in the mass spectrum[5] of 2,3,6-trimethoxy-10,11-dihydrodibenz[*b,f*]-oxepin-10-one (I)[6] (molecular ion) occurs at *m/e* 300 and relatively strong peaks are shown at M^+-1, *m/e* 285, *m/e* 271, and *m/e* 257. The ion peak at M^+-1 is presumably due to the loss of one proton to form ion (a). The presence of metastable ion at *m/e* 298 seems to substantiate such a process. The peak at *m/e* 285 (M^+-15) is due to the loss of methyl unit by methoxyl-cleavage to the stable *p*-quinoid ion (b). Elimination of carbonyl group from ion (b) furnishes the ion (c)(*m/e* 257), which decomposed further through expulsion of a carbonyl radical (28 mass units) to give the ion (d) at *m/e* 229. On the other hand, the following

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[1] Part CCIX: *Chem. Pharm. Bull.* (Tokyo), **16**, 20 (1968).
[2] Location: *Kita-4-bancho, Sendai.*
[3] T. Kametani, S. Shibuya, C. Kibayashi, and S. Sasaki, *Tetrahedron Letters*, **1966**, 3215.
[4] T. Kametani, S. Shibuya, and S. Sasaki, *Yakugaku Zasshi*, **87**, 232 (1967).
[5] The mass spectrum was measured with a Hitachi mass spectrometer RMU-6D equipped with a direct inlet system: Accel. voltage, 1200 V; Chamber voltage, 70 V; total emission, 80 μA; target current, 60 μA; evaporation temp., 200°; ion-chamber temp., 250°.
[6] T. Kametani, K. Fukumoto, and T. Nakano, *Yakugaku Zasshi*, **82**, 1548 (1962); M. Kulka and R.H.F. Manske, *J. Am. Chem. Soc.*, **75**, 1233 (1953).

fragmentation process is supported by the existence of a metastable ion at *m/e* 243. That is, the peak at *m/e* 272 is due to the loss of a carbonyl group (28 mass unit) from M^+ ion to form ion (e), from which the methyl radical of methoxyl group was removed to give the ion (c). Furthermore, removal of one mass unit from the ion (e) gives the stable ion (f), whose stability is due to the conjugation as is shown in the mass spectrum of xanthene derivative.[7] Furthermore, elimination of CHO unit (29 mass unit) gives the ion (g) at *m/e* 242, which decomposed further through expulsion of a methyl radical to afford the *o*–quinoid ion (h) at *m/e* 227 as is shown in case of various compounds having vicinal dimethoxyl groups, for instance, veratrol.[8] With regards to the formation of ion (f), elimination mechanism of

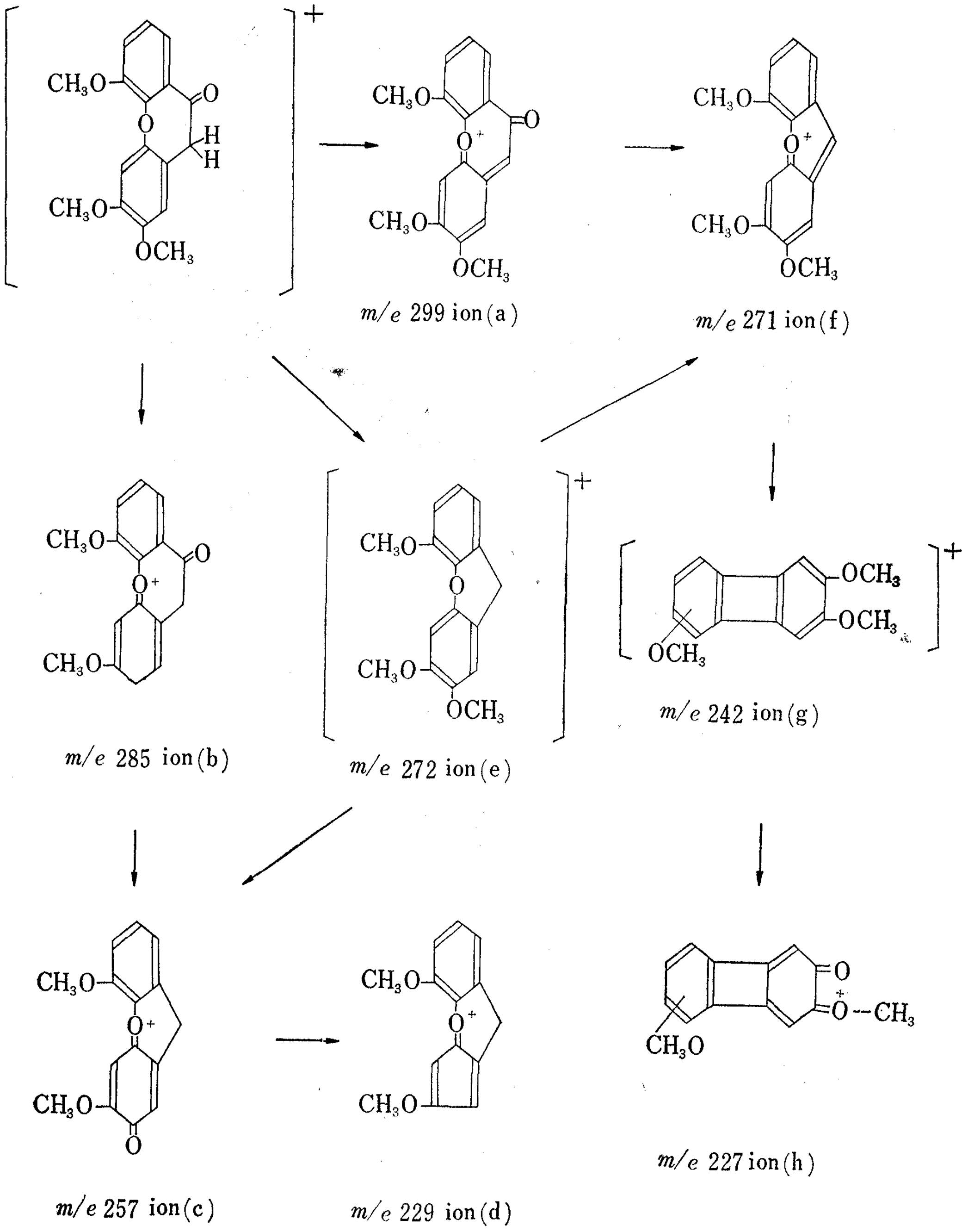

Chart 2

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7) S. Sasaki, "Mass Spectrum," Hirokawa Shoten, 1965, p. 186.

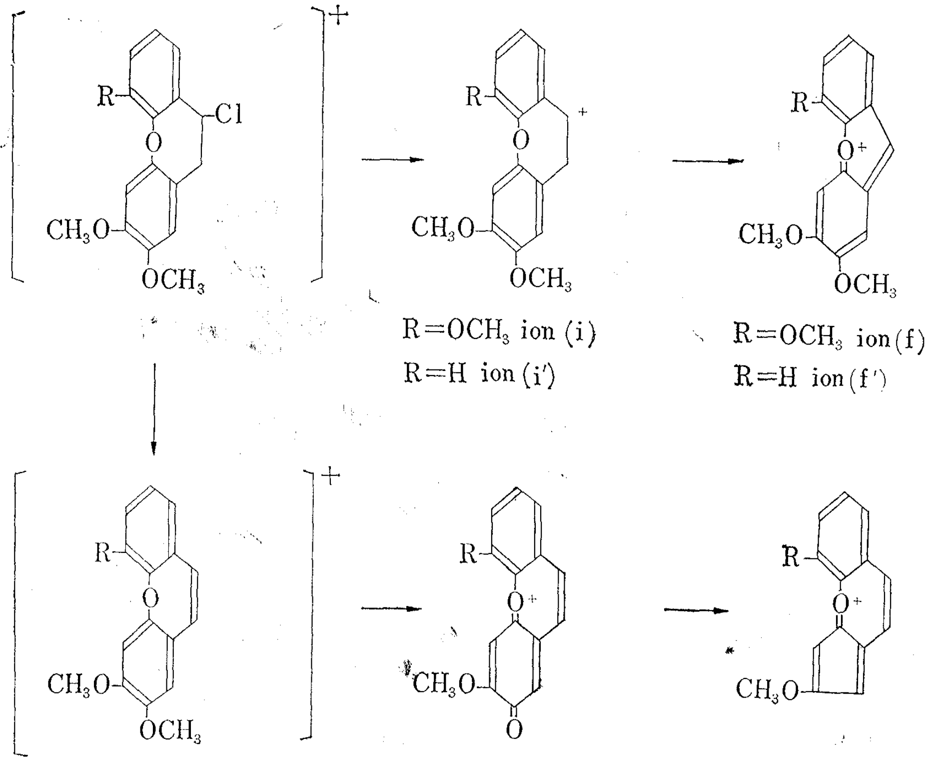
8) H. Budzikiewicz, C. Djerrasi, and D.H. Williams, "Interpretation of Mass Spectra of Organic Chemistry," Holden–Day, Inc., San Francisco, 1964, p. 181.

carbonyl group from the ion (a) and removal of one proton from the ion (e) may be supported by the existence of the metastable ions at *m/e* 245 and *m/e* 270, respectively. These fragmentation process is shown in Chart 2 and calculated and experimental values of metastable ions are summarized in Table I.

Table I. The Data of the Metastable Ions in the Mass Spectrum of the Compound (I)

	Calculated values	Found
$M^+ \longrightarrow$ ion a	$299^2/300=298.0$	298
ion a $\longrightarrow$ ion f	$271^2/299=245.6$	245
ion e $\longrightarrow$ ion f	$271^2/272=270.0$	270
$M^+ \longrightarrow$ ion b	$285^2/300=270.7$	271
ion e $\longrightarrow$ ion c	$257^2/272=242.8$	243

The mass spectra of 10-chloro-derivatives (II) and (III)⁹⁾ showed the characteristic fragmentation pattern as was shown in Chart 3, which was elucidated by shift technique and investigation of metastable ion. In case of compound (II), the base ion peak (molecular ion at *m/e* 320 and 322) occurs at *m/e* 271, and the mass sepctrum of III also shows the base ion peak at *m/e* 241 which is decreased by 30 mass unit from the former peak. These ions (f and f′) seem to be formed by loss of 14 mass unit by the repulsion of methylene group at C_{11}-position from the ions (i and i′), which formed by the elimination of chlorine atom from M^+. Removal of CHO unit from the ion (f and f′) furnishes the ring ion (g) (*m/e* 242) as is shown in



$R=OCH_3$ ion (i)
R=H ion (i′)

$R=OCH_3$ ion (f)
R=H ion (f′)

$R=OCH_3$ ion (j) *m/e* 284
R=H ion (j′) *m/e* 254

$R=OCH_3$ ion (k)
R=H ion (k′)

$R=OCH_3$ ion (l)
R=H ion (l′)

Chart 3

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9) T. Kametani, S. Shibuya, and W.D. Ollis, *J. Chem. Soc.*, in press.

Chart 2. On the other hand, the ion (f′) gives the ion (g′) at *m/e* 212, in which 30 mass unit is decreased compared with the ion (g). Furthermore, elimination of HCl unit from M^+ ion affords the ions (j and j′), whose relative intensities are shown with 67% and 20%, respectively. The peaks at *m/e* 269 and 239 are due to the loss of methyl radical by methoxyl cleavage to form the ions (k and k′). The presence of metastable ion at *m/e* 255 (Calcd., $269^2/284=254.8$) [*m/e* 225 (Calcd., $239^2/254=224.9$) in case of III] seems to substantiate such a process. Further decarbonylation of the ions (k and k′) furnishes the ions (l and l′) at *m/e* 241 and 211, as is shown in the cleavage of most dienone–type compounds.[10,11]

The mass spectra of 10–amino– (V) and 10–formamido–deirvatives (IV) are almost the same each other in low mass field and the ion (j′) is observed as the base peak at *m/e* 254. Since the ion (j′) is formed as an intermediate as is shown in Chart 4, the mass spectra of IV and V are similar to that of compound (III). Furthermore, the peak of M^+-15 in the spectrum of V is shown at *m/e* 284 to form ion (o), from which the ion (p) is observed at *m/e* 256 through expulsion of CO unit.

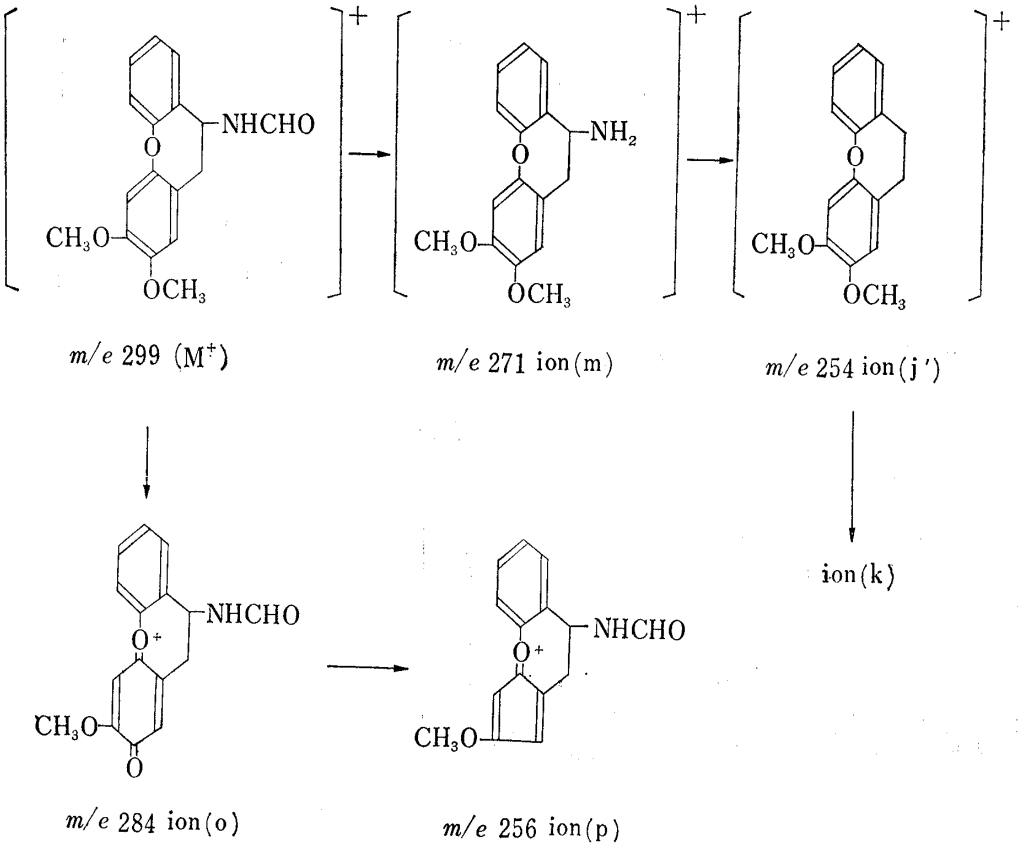

Chart 4

The base ion peaks in the mass spectra of 10–hydroxy–derivatives (VI) and (VII) (molecular ions at *m/e* 302 and 303) occur at *m/e* 284 and 285 and is presumably due to the loss of H_2O unit to form ions (j and q), respectively. Further cleavage of methoxy group of ions (j and q) gives the ions (k and r) at *m/e* 269 and 270, respectively, from which the ions (l and s) are formed further through repulsion of CO unit.

These facts revealed that the fragmentation pattern in the mass spectra of 10–substituted–dibenz[*b,f*]oxepine derivatives was considerably different from cularine and its related compounds.

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10) J.D. Mc Collum and S. Meyerson, *J. Am. Chem. Soc.*, **85**, 1739 (1963).

11) M. Tomita, A. Kato, T. Ibuka, and H. Furukawa, *Tetrahedron Letters*, **1965**, 2825.

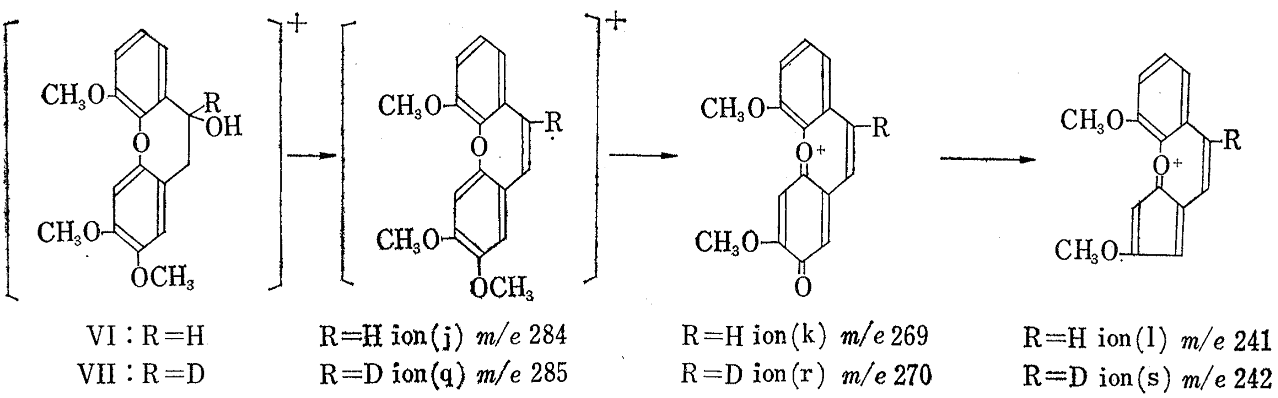

Chart 5

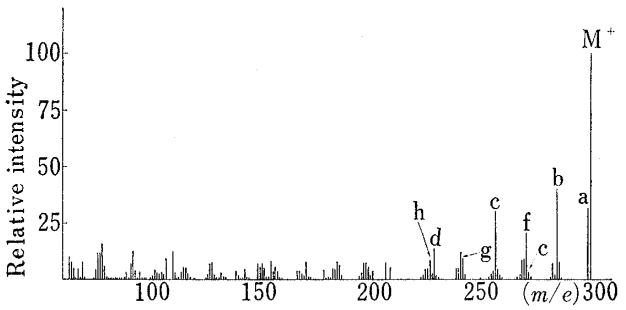

Fig. 1. The Mass Spectrum of 2,3,6-Trimethoxy-10,11-dihydrodibenz[*b,f*]oxepin-10-one (I)

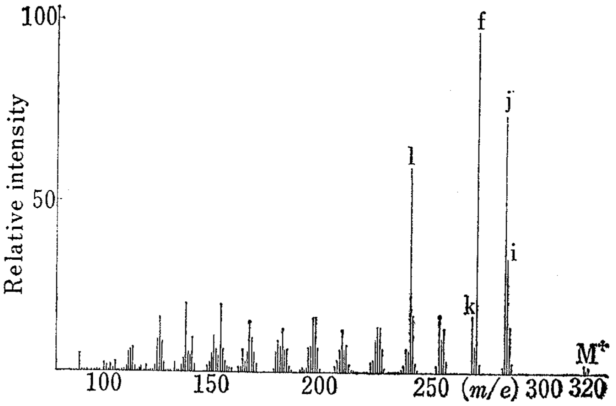

Fig. 2. The Mass Spectrum of 10-Chloro-2,3,6-Trimethoxy-10,11-dihydrodibenz[*b,f*]oxepin (II)

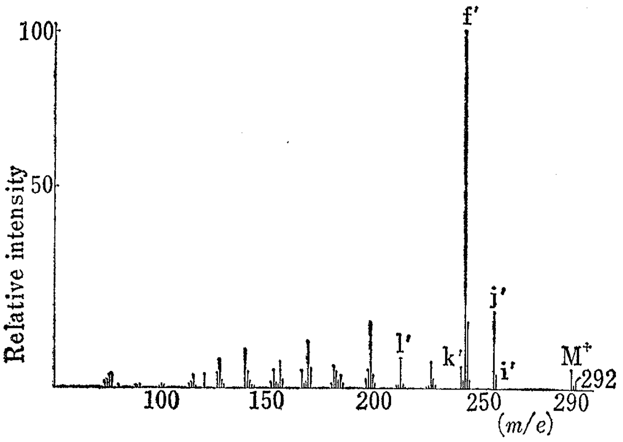

Fig. 3. The Mass Spectrum of 10-Chloro-2,3-dimethoxy-10,11-dihydrodibenz[*b,f*]oxepine (III)

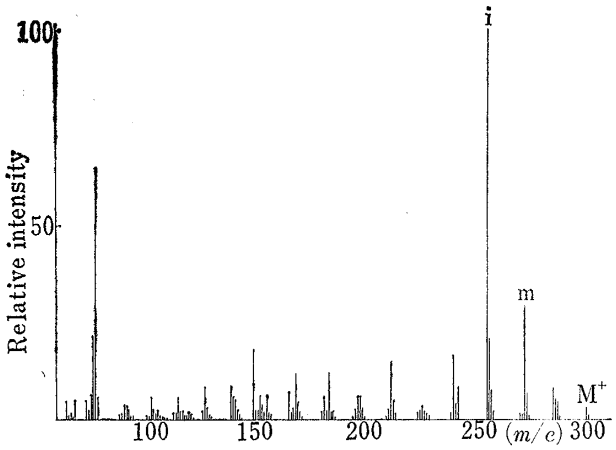

Fig. 4. The Mass Spectrum of 10-Formylamido-2,3-dimethoxy-10,11-dihydrodibenz[*b,f*]oxepine (IV)

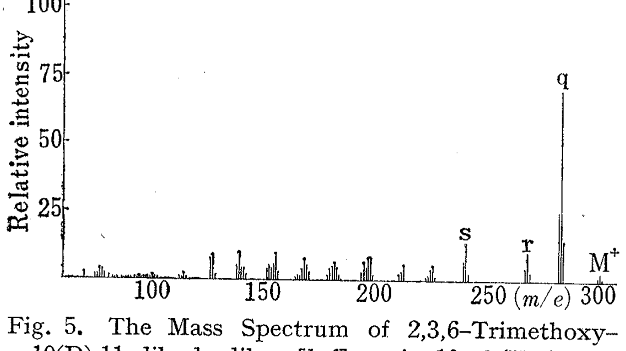

Fig. 5. The Mass Spectrum of 2,3,6-Trimethoxy-10(D),11-dihydrodibenz[*b,f*]oxepin-10-ol (VII)

Especially, it is characteristic that the fragmentation patterns in the lower mass field are very similar between the above compounds (II—VII) due to the formation of the ions (j, j′, k and k′).

Finally, the representative mass spectra of the above compounds (I, II, III, IV, and VII) were shown in Fig. 1—5.