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ELECTRON IMPACT AND MOLECULAR DISSOCIATION—XV[1]

THE MASS SPECTRA OF PHYSOSTIGMINE AND SOME RELATED COMPOUNDS

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THE mass-spectra of physostigmine, some derived and related molecules have been obtained. The spectra are listed in the following Table and the compounds studied are in Diagram I.

TABLE 1. PERCENTAGE ABUNDANCE

M/e	I	II	III	IV	V	VI	VII	VIII	IX	X
30	1·4									
31	0·7									
32										
33										
34										
35										
36										
37				0·35						
38				0·87						
39	1·0	2·3			0·32	7·78	14·62	3·24		
40	0·3	1·6			0·19	2·9	16·56	0·62		
41	1·1	3·1			0·61	21·48	3·22	1·75	2·85	
42	1·0	3·3	6·68	0·87	2·64	12·27	2·42	2·11	0·83	12·64
43	0·7	1·4	32·25	0·41	0·48	72·5	2·71	9·53	0·98	1·03
44	2·8	0·8			1·19	25·05	7·22	0·75		12·54
45	0·6						0·77	0·39		23·85
46										1·91
47										
48										
49										
50	1·4	0·7	0·69	2·44	0·26	6·73	4·32	1·26	1·37	
51	4·4	1·4	2·69	1·57	0·39	0·26	11·78	4·12	4·57	
52	2·2	0·7		0·41	0·16	1·19	5·28	1·36	2·02	
53	1·8	0·3			0·51		2·32	1·65	1·25	
54	1·0	0·2			0·32		1·29	0·65	0·65	1·33
55	1·8	0·7			0·48		0·77	1·00		2·54
56	1·3	0·9			1·45	2·11	0·10	0·65		6·72
57	1·3	0·7		1·8	4·21	0·79	0·13	1·20		2·92
57·5								0·32		
58	0·6				5·73	0·53	0·10	0·32		*100*
58·5	0·4		0·38				0·90	1·17	0·81	
59	0·6	1·4	0·69		0·32	1·32	0·19	0·16	0·21	8·03
59·5									0·15	

[1] Part XIV—in press.

TABLE 1 (*Cont.*)

M/e	I	II	III	IV	V	VI	VII	VIII	IX	X
60						3·03	0·19			
61				0·46		1·85	0·39			
62	0·6						1·93	0·65	0·65	0·38
63	2·6	1·1	1·23	0·17	0·32	0·79	7·99	3·14	3·29	1·44
64	1·0	0·5		0·46		1·19	1·87	1·62	1·48	
64·5							0·97	1·13	1·28	
65	4·7	1·8	2·07	0·58	0·64	1·32	11·92	6·19	5·67	1·74
65·5		0·1					1·93	1·39	1·98	
66	2·3	0·5	0·69		0·29		2·00	1·36	1·19	1·06
66·5							0·32		0·24	
67	1·8	0·7		4·53	0·35	2·50		0·49	3·26	1·59
68	1·2	0·6		2·26	0·39	1·98		0·32		1·13
69	1·0	1·1		23·52	0·16	30·2		0·65		1·69
70	0·7	0·8		4·64	0·26	6·7	0·32	0·52		4·28
70·5	0·1						0·39	0·97	0·24	
71	0·6	0·2		2·38	0·16	9·75	0·13	1·94		8·06
71·5	0·4	0·2					1·93	5·15	0·74	
72	0·4			0·70	0·16	2·11	1·03	6·42	0·42	14·03
72·5	0·4	0·2	0·38				0·32	1·81	0·24	
73	2·1	1·1	0·69	0·64	1·22	3·96	0·52	0·68	0·15	5·57
73·5							3·16	1·62	3·59	
74	0·4			0·93		4·22	2·97	1·00	1·16	0·96
75	1·5	0·9	0·78	1·04		2·37	4·57	2·27	1·16	0·20
76	2·2	1·4	0·69	5·45		12·93	5·41	2·98	1·54	0·30
77	14·6	7·6	10·60	27·74	1·13	8·57	26·16	16·98	7·98	6·47
78	4·1	2·3	0·54	2·72	0·39	3·43	6·83	5·41	2·55	1·26
78·5		0·5						1·98		
79	3·1	2·7		2·38	0·39	2·37	1·29	2·59	0·62	2·52
79·5	1·2	0·5						0·75		
80	2·2	3·8		0·52	0·42	1·71	0·32	1·30	0·15	1·84
80·5								7·94	0·03	
81	1·2	0·6		7·07	0·71	9·1		2·17		3·42
82	2·5	3·0		2·96	0·58	6·85		0·19		1·76
83	1·8	0·9		6·85		10·04		3·89		2·97
83·5									0·12	
84	0·2			0·70	0·19	4·08		0·23		3·10
84·5									0·09	
85				0·29	0·13	6·33		0·32		0·63
85·5		0·2							0·06	
86		1·3		0·35		1·32		0·23		
86·5		1·3						0·45	0·03	
87		0·2					0·84	2·92	0·33	0·48
87·5					0·13			1·07		
88	0·6						0·97	0·91	0·39	0·45
89	3·7	1·8	2·53	0·64	0·58	1·58	7·21	4·67	2·94	2·04
90	2·1	2·2	2·46	0·29	0·55	1·19	5·99	4·54	2·97	1·54
91	6·1	6·9	3·15	4·18	1·35	7·25	14·05	11·63	5·79	5·01
92	1·3	1·3		0·41	0·32	1·85	2·77	1·88	1·04	0·45
93	2·5	1·2		2·09	0·29	3·03	3·22	1·62	0·80	1·56
93·5		0·5								
94	1·0	1·5		1·04	1·16	1·58	0·64	1·10	0·30	1·84
94·5								1·07		

TABLE 1 (*Cont.*)

M/e	I	II	III	IV	V	VI	VII	VIII	IX	X
95	0·7			9·69	0·55	8·05		0·55		3·70
96	0·7			3·65	3·42	3·82		0·36		1·11
97	0·7			7·19	0·71	6·46		0·71		2·59
98				2·61	0·13	3·46		0·29		1·13
99				1·62		2·24		0·26		1·51
100				0·75		1·32	0·19	0·23	0·09	0·20
100·5					0·26					
101	1·8	0·9	1·84	0·52	0·64	0·92	2·51	2·04	0·98	0·48
101·5					1·90					
102	5·1	3·4	3·92	0·93	0·97	0·66	7·92	4·86	2·79	0·75
103	9·7	5·4	5·53	3·02	1·06	2·77	12·82	6·81	5·87	2·39
104	5·9	2·5		9·22	0·74	11·74	6·70	3·14	2·55	1·49
105	2·1	1·0		*100*	0·68	3·56	3·09	5·41	1·16	2·37
106	2·1	1·6		10·73	0·64	0·40	2·13	2·92	0·89	1·56
107	0·6	0·6		2·73	0·90	1·71		0·65		2·37
108	0·1	0·4		0·93	0·64	0·53		0·26		2·64
108·5										1·18
109	0·5			6·44	1·09	4·08		0·55		4·00
110	0·5			2·15	0·19	2·11		0·32		0·68
111	0·4			3·54		2·64		0·39		2·74
112	0·1			1·74		1·32		0·39		1·59
113	0·4			1·28		0·79		0·81	0·36	0·23
114	1·0	0·8	1·00	0·45		4·97	0·32	2·07	0·47	
115	10·6	9·3	11·59	4·82	1·26	7·60	9·35	13·51	4·39	2·19
116	4·7	4·8	4·84	1·68	1·13	2·36	3·93	6·51	2·05	2·52
117	10·8	9·0	6·68	3·95	2·55	6·68	15·46	11·47	9·46	5·11
118	7·6	6·9	3·61	1·74	1·62	4·98	13·59	7·97	5·58	3·07
119	3·2	0·9	0·23	7·60	1·09	9·83	21·25	2·17	4·99	2·01
120		1·0		0·93	0·84	0·92	3·16	1·56	1·69	1·91
121				1·28	0·51	1·19		0·32		1·44
122				0·58	0·68	0·26				1·49
123		0·7		3·48	0·45	3·28				1·32
124				1·16		1·06				1·66
125	0·3			0·29		2·11		0·32		1·89
126	0·4			0·58		1·45		0·55	0·39	0·18
127	2·2	1·5		0·45	0·26	2·38	1·67	2·59	1·39	0·91
128	7·5	5·9	4·76	2·94	0·58	5·94	8·05	6·81	5·93	1·66
129	10·1	8·6	4·76	2·32	0·64	7·13	7·21	5·77	7·33	2·27
130	72	19·6	11·59	4·98	2·06	40·00	87·2	17·44	48·20	5·72
131	46	9·3	5·91	7·36	4·05	25·47	33·18	13·35	*100*	5·26
132	18·9	6·1	4·76	3·48	6·60	5·54	25·99	13·84	43·77	15·74
133	9·7	1·8	0·54	2·96	2·55	2·64	2·96	3·34	6·97	5·64
134	1·5	0·4	0·3	0·75	1·32	0·79	0·13	7·13	0·71	3·83
135				2·67	0·39	0·92		2·92		2·90
136				0·46	0·29					0·91
137				1·39	0·16	1·32				2·01
138				0·58		0·66				
139				1·22		3·82		0·32		2·32
140	1·0	0·7		0·35	0·16	2·77		0·91	0·36	
141	1·6	1·4	0·77	2·61	0·32	6·99		1·56	0·56	1·54
142	6·2	5·0	4·07	2·90	0·97	5·93	3·16	5·31	1·25	1·76
143	14·3	17·3	15·59	6·09	1·39	12·13	10·17	17·82	4·45	2·54

TABLE 1 (*Cont.*)

M/e	I	II	III	IV	V	VI	VII	VIII	IX	X
144	72	87·0	*100*	51·5	2·74	35·75	*100*	*100*	20·79	5·01
145	44·4	72·2	35·93	18·73	4·15	24·00	16·75	41·25	5·94	5·29
146	26·7	17·3	6·83	5·20	7·56	88·90	31·70	31·43	11·25	6·40
147	5·1	5·8	0·69	1·91	3·67	14·78	19·64	5·67	14·02	5·97
148	0·4			1·74	1·62	3·82	2·77	1·00	2·88	7·03
149				2·09	0·93	2·11		0·29		4·96
150				0·35	0·23	1·19				3·70
151				2·44		2·37				2·69
152				0·64		1·19				1·64
153	0·1			1·10		0·92				0·91
154	1·0	1·3	1·38	0·93	0·26	3·96		0·62	0·65	0·76
155	1·5	1·4	1·15	1·80	0·51	5·80		0·84	0·30	0·78
156	7·3	5·3	7·45	4·18	0·84	9·10	2·32	2·20	1·01	1·74
157	6·4	8·6	9·90	5·37	1·42	8·05	2·25	8·75	0·39	2·97
158	10·3	64·1	42·76	23·34	3·06	12·40	1·67	63·93	1·34	2·30
159	22·7	30·0	28·10	24·75	6·60	6·2	0·45	13·51	1·16	5·34
160	5·0	12·0	71·48	5·45	40·70	2·11	2·51	4·86	3·30	40·52
161	0·9	2·2	12·59	9·10	36·65	1·19	0·19	2·59	2·61	15·19
162	0·4		1·07	2·44	10·24			0·65	0·50	8·03
163			0·54	1·10	1·71					4·28
164				0·46	0·32					1·99
165				2·32		1·45				1·99
166				1·28		1·06				0·83
167			0·69	0·81		1·06				0·83
168		0·5	0·84	0·70	1·61	0·53		0·26	0·12	0·78
169	0·4	1·3	1·54	4·06	0·48	5·41		0·26	0·09	0·93
170	0·6	3·8	3·69	1·74	1·10	1·71		0·71	0·98	0·96
171	1·8	5·2	6·07	2·32	1·10	2·77		0·65	0·47	1·26
172	2·6	5·2	19·73	2·96	2·03	2·64	0·32	2·95	0·27	2·32
173	19·8	10·0	7·06	0·75	5·60	9·90	0·39	1·65	0·21	3·80
174	*100*	2·9	1·46	0·58	44·95	2·70	5·67	8·10	2·52	8·01
175	18·8	0·2		0·29	14·66		85·15	2·01	0·30	4·05
176	1·1			0·46	3·67		14·17	0·32		13·04
177			0·84	0·58	1·29		2·84			6·87
177·4			Metastable							
178			0·69	1·04	0·26	1·06				7·66
179			1·00	1·33		1·06				6·04
180				1·52		1·32				1·61
181				3·66		5·40				0·68
182				1·16		1·06				0·53
183				0·17	0·16					0·35
184				0·29	0·39					0·76
185		1·1		1·10	0·32	1·32				3·53
186		2·3	1·54	0·87	4·50	1·32		0·13	0·18	3·50
187		14·5	8·75	2·44	4·67	3·56		0·75	0·47	2·87
188		*100*	2·23	1·68	7·5	90·9		6·48	4·10	10·07
189		15·2	0·84	0·35	2·84	20·04		35·94	58·15	33·77
190		2·1		0·87	2·06	3·30		8·49	18·91	17·07
191				0·93	0·48	0·66		1·30	2·97	5·31
192				0·81		0·53				2·52
193				1·39		1·19				1·26
194				1·10		0·79				0·23

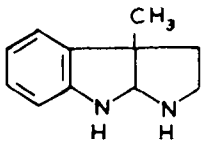
TABLE 1 (*Cont.*)

M/e	I	II	III	IV	V	VI	VII	VIII	IX	X
195				0·29		0·53				0·23
196				0·87						
197				0·12						
198					0·32					
199					0·61					1·30
200			0·78		0·64					1·26
201			1·54		2·95	2·37				3·02
202			44·76		2·77	1·45				12·52
203			9·60		8·98	0·53				4·81
204			1·23		2·71	0·13				8·21
205			0·78		0·39	1·06				23·57
206										8·61
207										6·30
208										1·44
209										0·28
210										
211										
212										0·28
213						1·06				0·40
214						1·32				0·53
215			5·14	0·29	0·64	6·59				2·42
216			1·38	1·51	1·29	*100*				7·00
217				0·75	16·91	26·37				4·78
218				0·58	*100*	4·2				2·29
219				2·67	23·07	3·69				1·28
220				0·58	3·22	0·53				2·80
221				0·29						0·93
222										
223										
224										
225·0										Metastable
225										
226										
227										
228										
229			2·07		0·58					0·93
230			90·14		0·58	2·90				3·22
231			23·72	2·20	0·58	3·82				3·75
232			3·45	0·41	0·19	0·79				3·05
233										1·79
234										0·78
235										0·28
236				0·70						0·20
237										
238										
238·9				Metastable						
240										
241										
242					0·23					0·35
243				1·39	0·19	2·11				0·71
244					0·16	0·40				1·79
245					0·32					35·93

TABLE 1 (*Cont.*)

M/e	I	II	III	IV	V	VI	VII	VIII	IX	X
246					0·16					11·68
247										1·79
248										0·78
249										0·98
250										7·98
251										2·39
252										0·47
253										0·15
254										
255						0·79				
256						1·06				
257						0·66				0·25
258						20·83				0·78
259						6·46				2·80
260						1·19				20·85
261										6·93
262				0·58						2·29
263				2·03						1·71
264				52·45						0·73
265				18·16						0·18
266				3·48						
267				0·81						
268				0·12						
269				1·22						
270										
271										
272										
273										
274					6·28					
275					61·85					0·23
276					17·60					1·33
277										5·41
278										27·93
279										7·43
280										0·18
281										
282										
283										
284										
285										
286										
287										
288										
289										
290				0·70						
291				1·91						
292				42·40						
293				17·29						
294				3·48						
295				0·58						

The series is of considerable interest since it provides us with a further opportunity to examine structures which contain a tetrahydropyrrolo(2,3-b)indole system in addition to those already reported.[2]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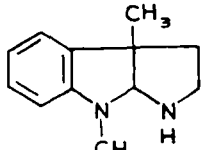
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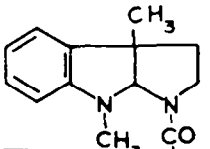
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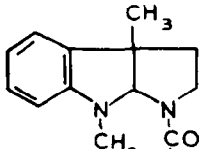
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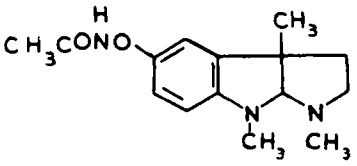
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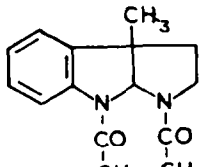
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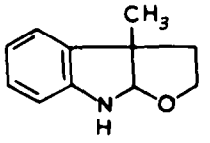
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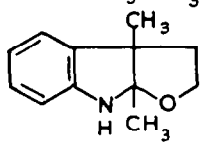
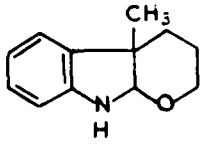
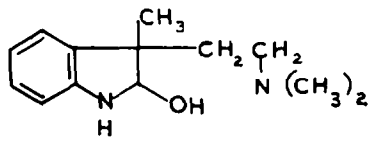

VIII


IX


X

There is a good deal of published evidence[3] in support of the view that the stability of a parent molecular ion depends upon the complexity of the structure and in particular upon the presence of a ternary or quaternary centre. Whilst exceptions are known[4] it is nevertheless generally true that the larger the number of such centres the less abundant is the molecular ion. An examination of the parent ions in the present series is in agreement with this generality. The parent ions of desoxybisnoreseroline (I) and desoxynoreseroline (II) are also the base peaks of their spectra.

[2] E. Clayton, R. T. Reed and J. M. Wilson, *Tetrahedron* **15**, 1449, 1495 (1962).

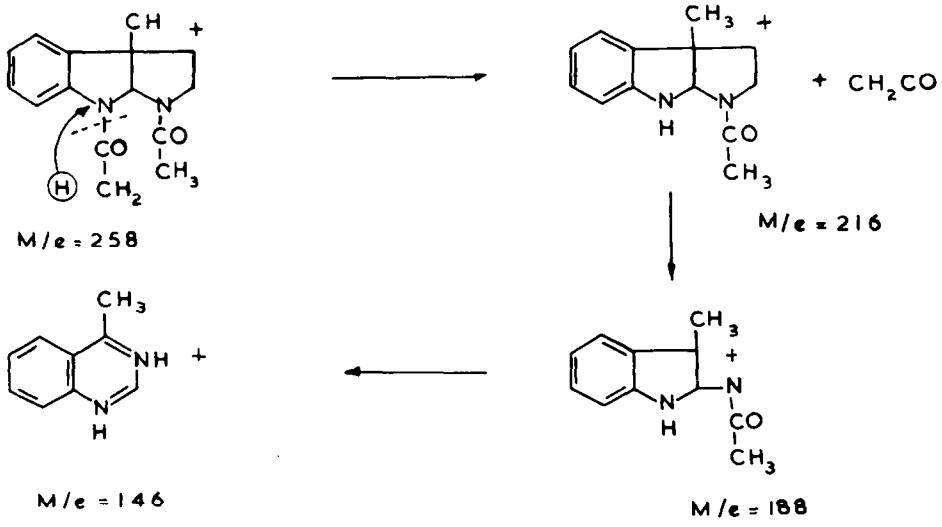
[3] J. H. Beynon, *Mass Spectronomy and its Applications to Organic Chemistry* pp. 297, 330 et seq. Elsevier (1960).

[4] S. S. Friedland, G. H. Lane, R. T. Longman, K. E. Train and M. J. O'Neal, *Analyt. Chem.*, **31**, 169 (1959).

The acetylated (VI) and benzoylated (IV) derivatives which contain at least one extra substituted centre have much less abundant molecular ions. The presence of a side chain also lowers the abundance of the ion as is shown by physostigmine (V) and when the side chain has a further point of branching as in eserethole methine (X) the molecular ion is not very prominent. The replacement of one nitrogen in the eseroline compounds by an oxygen atom to yield molecules (VII and VIII) also lowers the stability of the molecular ion which is no longer the base peak. The most probable reason for this is that, as will be discussed later, the fragments formed from the favoured mode of fission may be thermodynamically stable. This is not so for the nitrogen compounds.

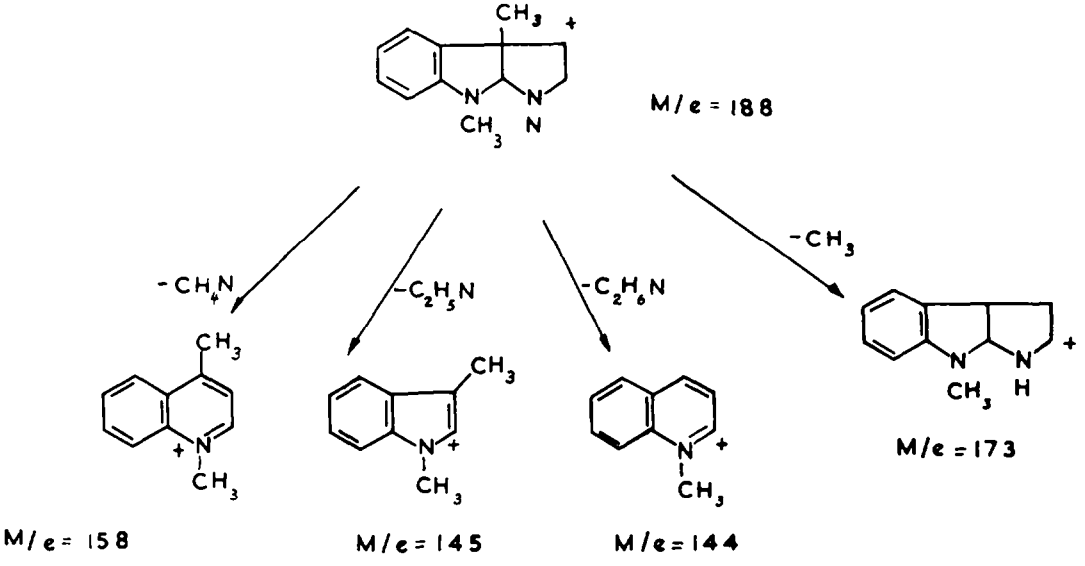
Fragmentation of the acetylated and benzoylated derivatives (III, IV and VI) yields uniformly an ion of mass $(P - 28)^+$. Unfortunately it is not possible to decide whether this comes from the acyl substituent or from part of the ring. There is little available evidence to support the elimination of carbon monoxide from these systems and the alternative hypothesis, namely the elimination of a molecule of ethylene is preferred. There is some evidence to suggest that such eliminations may occur between fully substituted centres and it would be favoured in this instance by the production of two molecular species. The benzoyl compound fragments very much as expected losing the benzoyl group and giving rise to what is considered to be a substituted quinolinium ion at m/e = 158. The two acetyl derivatives show some anomalies which are consistent with the elimination of 28 mass units from the ring. There are as well as the expected abundant quinolium ions at m/e = 158 and m/e = 144 in the spectra of acetyldesoxynoreseroline and diacetyldesoxybisnoreseroline respectively even stronger ions at m/e = 160 and m/e = 146. This fragmentation is thought to occur as below. It is also supported by the spectrum of compound IX which although showing the expected loss of 44 mass-units ($HOCH_2CH_2$) also loses 42 mass units, propylene, leaving the hetero atom attached to the indole.

The thermodynamic argument may also be employed for the elimination of forty-two mass units from diacetylbisnordesoxyeseroline (VI) rather than an acetyl radical.



There is no direct evidence as to which acetyl group is involved in the fragmentation, but since the fragmentation pattern of the ion so formed closely resembles that of acetyldesoxynoreseroline, allowing for the mass difference, the above fragmentation is favoured. The neutral product is ketene. A consideration of the ion abundancies in the mass spectra of desoxynoreseroline (I) and acetyldesoxynoreseroline (III) favours the view that the molecular ion of N(b)acetyldesoxybisnoreseroline would be very abundant if not the base peak of the spectrum. The abundance of the ion having one hydrogen less would be about 20 per cent of this. Accordingly, it is to be expected that the fission which gives rise to the more abundant ion as well as the more stable neutral fragment would be the one favoured, namely that stated above. The heat of formation of acetyl ($\Delta H_f = -0{\cdot}437$ eV.) is greater than that of ketene ($\Delta H_f = -0{\cdot}633$ eV.).

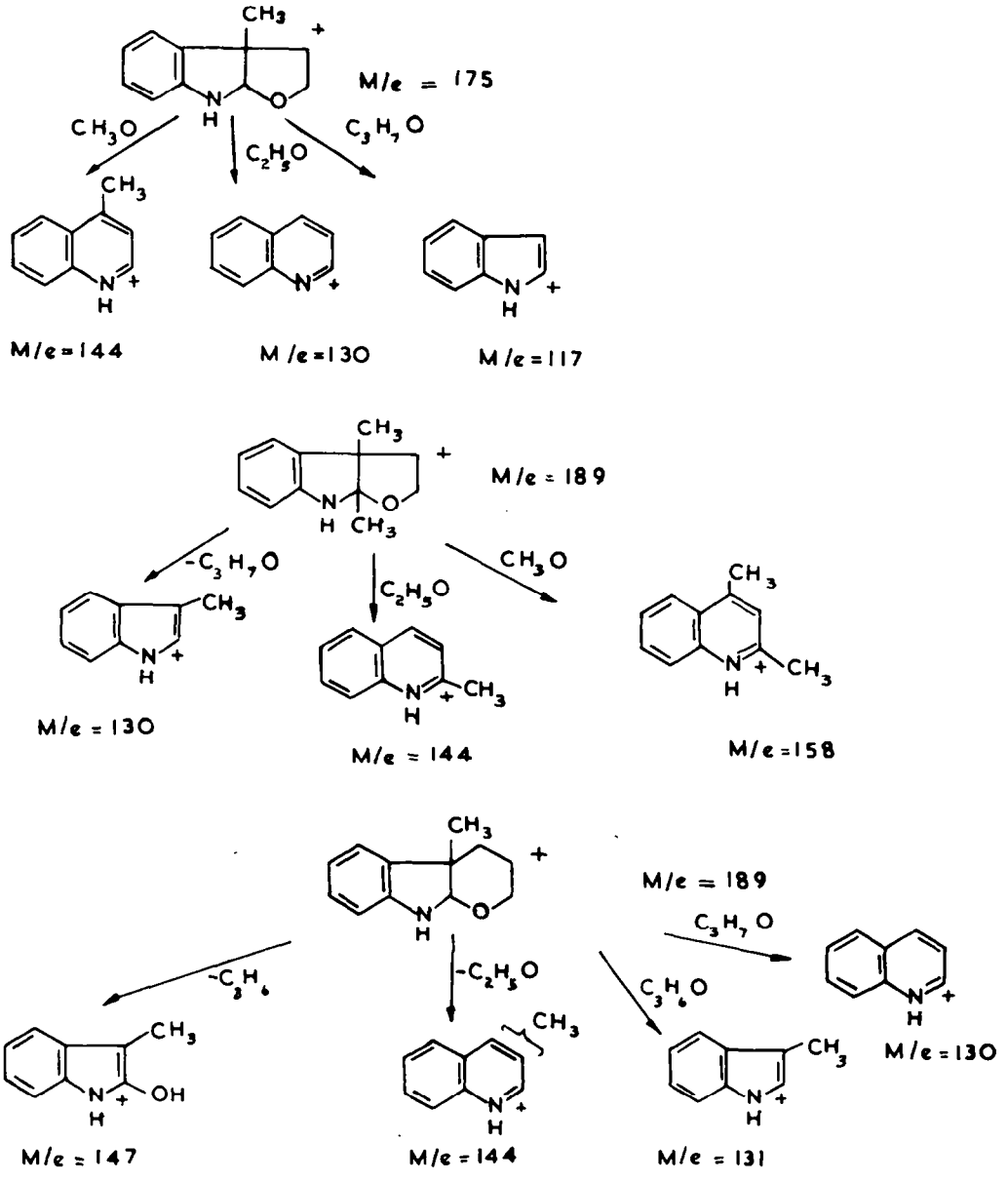
Comparison of the cracking patterns of desoxybisnoreseroline and desoxynoreseroline shows, that allowing for the difference in molecular weight the two closely resemble each other. Both compounds elide CH_2NH_2 and $CH_2CH_2NH_2$ to give abundant fragments, probably with rearrangement to become substituted quinolinium ions. The loss of methyl also occurs and almost certainly represents the elimination of the quaternary methyl group. The suggested fragmentation pattern which is shown for desoxynoreseroline (II) is as follows.



These molecules may be conveniently compared with the tetrahydrofuro[2,3-b] indoles and hexahydropyrano[2,3-b]indoles which as already mentioned are less stable. From the mass spectra it is apparent that all these molecules lose thirty-one, forty-five and fifty-eight or -nine mass units rather readily. The ions $(P - 31)^+$, $(P - 45)^+$ and $(P - 58)^+$ are the base peaks for compounds VII, VIII and IX respectively.

By analogy with the compounds just discussed, it is thought that the fragmentation proceeds as shown on the following page.

The variations within these compounds provide a further argument for assigning at least the most abundant ion in any group upon the basis of the thermodynamical



stability of the products. In both tetrahydro[2,3-b]indoles the elimination of the fragment CH_3O occurs, with great facility to leave an ion which can rearrange to give a substituted quinolinium ion. A similar ion cannot be obtained from compound IX by this process; the loss of thirty-one mass units does not occur. Equally the loss of C_2H_5O from compound VIII can yield a quinolinium ion by rearrangement and this ion is the base peak of the spectrum. Compounds VIII and IX can form a similar ion by the loss of C_2H_5O and C_3H_7O respectively.

A consideration of all these five compounds yields a further interesting observation, namely the relative ease with which the eserine derivatives lose a single hydrogen from

the parent molecular ion. In general, because of the basicity of many nitrogen containing systems under electron impact it is not practicable to discuss this loss as there is always the possibility that the $(P - 1)^+$ ion observed represents the facile loss of molecular hydrogen from the $(P + 1)^+$ ion-formed by an ion molecule reaction.

In comparison with the oxygen containing compounds, however, we see that whereas the $(P + 1)^+$ ions are all of a comparable magnitude the $(P - 1)^+$ ions are distinctly more abundant in the purely nitrogen containing compounds. Such an observation would be consistent with the hypothesis that the parent molecular ion may rearrange and with the elimination of a single hydrogen atom, form a thermodynamically stable "onium" ion.

Acetylation of the nitrogen inhibits the formation of the "onium" ion and the loss of a single hydrogen is no longer pronounced. The oxonium ions formed in compounds VII, VIII and IX are not thermodynamically as stable as ammonium compounds and consequently there is no ion of great abundance in these spectra which correspond to the loss of a single hydrogen atom.

A further occurrence is the loss of methyl. This is much more pronounced in compound VIII than in either VII or IX which may be correlated with the presence of a second methyl group and its effect on the molecular ion. Compound IX shows the loss of methyl clearly followed by the elimination of four hydrogen atoms with the resulting aromatization of the pyran ring.

As previously mentioned the parent molecular ion of diacetylbisnordesoxyeseroline readily loses ketene and is considered to yield the molecular ion of acetylbisnordesoxyeseroline. Assuming this to be the case and further supposing that the fragment ions of lower mass derive from this ion and not the original parent molecular ion, one may compare this cracking pattern with that of another acetyl derivative. The abundant ions of the acetylbisnor derivative arranged in descending order of abundance are m/e = 216 (100%), 188 (90·9%), 146 (88·9%), 43 (72·5%), 130 (40·00%), 144 (35·75%), 69 (30·2%) and 131 (25·47%). A similar array of ions from acetylnordesoxyeseroline is as follows m/e = 144 (100%), 230 (90·14%), 202 (44·76%), 158 (42·76%), 145 (35·93%), 43 (32·25%) and 159 (28·10%). It will be seen that although the abundances of the ions differ somewhat, the general fragmentation sequences are the same and are probably as in diagram III.

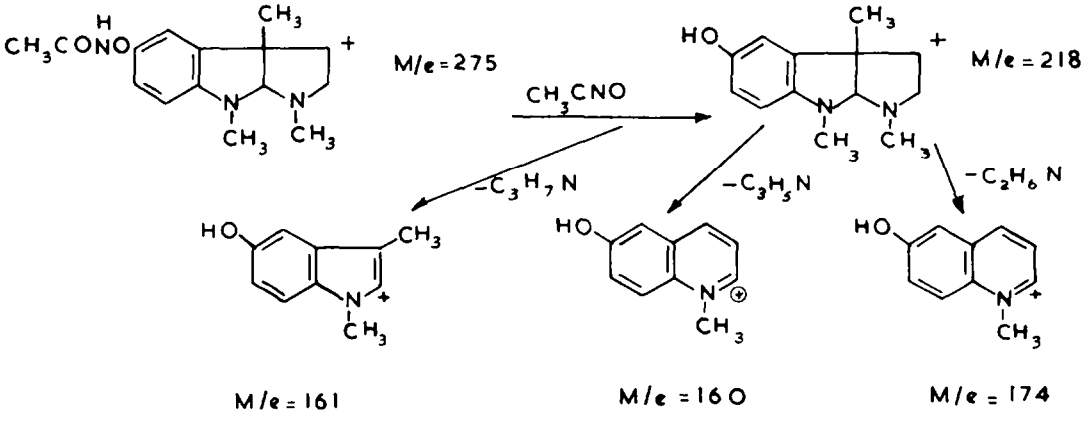
Again, where it is possible and a facile rearrangement exists, a molecular ion has been drawn. The remaining fragment ion m/e = 43 certainly refers to the acetyl ion. The similarity in the fragmentation processes lead us to suppose that the two compounds discussed differ only in the presence of an $N\text{-}CH_3$ in the second. This is in accordance with the conclusion already reached.

Benzoyldesoxynoreseroline (IV) has also been examined and the abundant ions in the cracking-pattern are as follows. The ions in descending order occur at m/e = 105 (100%), 264 (52·45%), 144 (51·5%), 292 (42·40%), 159 (27·45%), 77 (27·74%), 69 (23·52%) and 158 (23·34%).

The fragmentation pattern thus closely resembles that of the corresponding acetyl derivative except for the absence of the acetyl ion and the presence of an abundant ion m/e = 105, the base peak of the spectrum. This is the benzoyl ion from which part at least of the phenyl ion m/e = 77 is derived. The similarity in fragment ions supports the correctness of the assumption that the acyl group is eliminated as ketene and does not undergo a step wise degradation. The benzoyl group cannot leave one hydrogen by a rearrangement process and this provides a ready explanation for the absence of fragment ions m/e = 146 and 145 which were present in the acetyl derivatives.

In addition to the spectrum of benzoyldesoxynoreseroline (IV) in which the presence of the ion m/e = 77 may be easily explained, other compounds, in particular I, II, VII, VIII and IX also show unusually large abundances of this ion and often an even more abundant m/e = 91 ($C_7H_7^+$). Since these are common to all five molecules it is probable that they derive from the aromatic part of the molecule whereby with the breaking of two bonds and a hydrogen rearrangement a phenyl ion would be obtained. The ion m/e = 91 which is considered to be the tropylium ion could be formed also from these molecules as they all have a carbon atom directly attached to the benzenoid system. It is significant that the two compounds studied, physostigmine and eserethole methine, which have a further substituent upon the aromatic centre do not show ions at m/e = 77 and 91. Since these two compounds differ from those already discussed by possessing side-chains and differ from each other in the complexity of the cyclic system, they are best discussed separately.

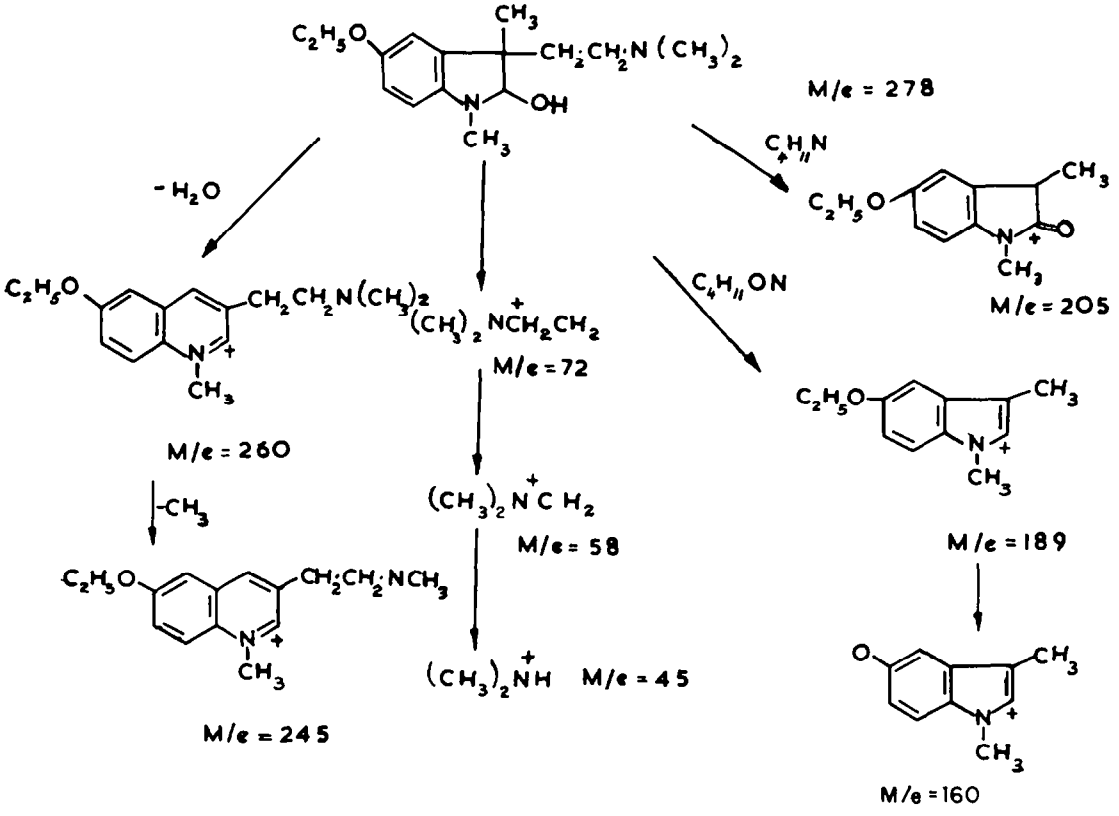
Physostigmine gives rise to the following series of ions, m/e = 275, (61·85%), 219 (23·07%), 218 (100%), 174 (44·95%), 161 (36·65%) and 160 (40·70%) of which m/e = 275 corresponds to the parent molecular ion and 218 is the base peak. The fragmentation pattern is consistent with well established modes of fission and is shown in the following diagram.



The loss of the methyl isocyanate group is a facile process and yields the hydroxy derivative which ion is also the base peak of the spectrum. The remainder of the breakdown follows the now established pattern.

Eserethole methine gives rise to the following series of ions m/e = 278 (27·93%), 260 (20·85%), 245 (35·93%), 205 (23·57%), 189 (33·77%), 160 (40·52%), 58 (100%), and 45 (23·85%) of which m/e = 278 and 58 are the parent molecular ion and the base

peak respectively. The fragmentation probably occurs as follows, in which the proposed scissions are consistent with the breakdown of known molecular ions. There is some evidence for the loss of molecular water from substituted phenols which are of course, well known to elide carbon monoxide and formyl radicals. Again where possible the fragment ion has been written as a molecular ion, favoured from thermodynamic considerations.



EXPERIMENTAL

The measurements were made with a Metropolitan-Vickers Ltd. M.S.2. Mass Spectrometer, the spectra being recorded on a N.E.P. 1050 Ultraviolet Recorder. The samples were inserted in to the ion-chamber by the technique which has already been adequately described.

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