

Mass Spectrometric Study of 8-Azaxanthine Derivatives

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N-3 and N-9 derivatives of 8-azaxanthine have been studied using electron impact mass spectrometry. Mass-analyzed metastable ion kinetic energy, linked scan at the constant B/E , collision-induced dissociation methods, as well as high-resolution measurements have been used for evaluation of complete fragmentation schemes. Two fragmentation pathways of 8-azaxanthine skeleton begin by the elimination of CH_3NCO or N_2 molecule. The primary elimination of nitrogen molecules is characteristic difference in fragmentation routes of 8-azaxanthines in comparison to purine. Another pathway leads to fragmentation of the N-3 and N-9 substituents.

In our study of purine derivatives we synthesized a series of derivatives of 8-azaxanthines I—XXIV as compounds for evaluation of their pharmacological properties [1]. Because no extended mass spectrometric studies of 8-azaxanthine and its derivatives have been conducted so far, we undertook the investigation of this class of compounds with a view to correlating the findings with those of xanthine series [2—5]. The fragmentation of xanthine derivatives after electron impact involves the fission of pyrimidine ring. The first of pathways is represented by the formation of $[\text{M} - \text{CHO}]^+$ ions after the transfer of hydrogen atom from the methyl group of N-1. The second route of decomposition of molecular ions of xanthine derivatives is characterized by the retro-Diels—Alder reaction to form the $[\text{M} - \text{HNCO}]^+$ or $[\text{M} - \text{CH}_3\text{NCO}]^+$ ion radicals. In the case of some C-6 derivatives [3] the fragmentation of substituents takes place, too.

In the present work 24 derivatives of 8-azaxanthine, possessing various substituents in the

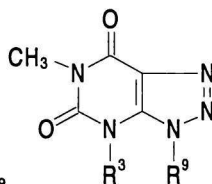
position N-3 and N-9 have been studied by electron impact low- and high-resolution mass spectrometric methods. The fragmentation routes have been confirmed by the metastable transitions study, using the methods of metastable ion kinetic energy (MIKE) measurements, linked scans at the constant B/E , as well as the collision-induced dissociation (CID) of the selected ions.

EXPERIMENTAL

The preparation of model 8-azaxanthines I—XXIV has been described elsewhere [1].

The electron impact mass spectra were obtained with single focussing CH-5 (Varian) and JMS D-100 (Jeol) mass spectrometers using the direct inlet system, 70 eV energy, and ion source temperature of approx. 180 °C. Both the instruments gave qualitatively identical spectra.

The ions were produced also in VG ZAB-2F mass spectrometer, using the same conditions. The ions



	R ³	R ⁹		R ³	R ⁹
I	H	CH ₃	XIII	CH ₂ COCH ₃	CH ₂ Ph
II	CH ₃	CH ₃	XIV	H	C ₂ H ₅
III	CH ₂ Ph	CH ₃	XV	CH ₃	C ₂ H ₅
IV	CH ₂ C≡CH	CH ₃	XVI	H	C ₃ H ₇
V	CH ₂ CH=CH ₂	CH ₃	XVII	CH ₂ COCH ₃	C ₃ H ₇
VI	CH ₂ COCH ₃	CH ₃	XVIII	CH ₃	C ₃ H ₇
VII	CH ₂ (CH ₂) ₃ COCH ₃	CH ₃	XIX	CH ₂ CH=CH ₂	C ₃ H ₇
VIII	H	CH ₂ Ph	XX	CH ₂ C≡CH	C ₃ H ₇
IX	CH ₃	CH ₂ Ph	XXI	H	C ₄ H ₉
X	CH ₂ Ph	CH ₂ Ph	XXII	CH ₃	C ₄ H ₉
XI	CH ₂ C≡CH	CH ₂ Ph	XXIII	CH ₂ C≡CH	C ₄ H ₉
XII	CH ₂ CH=CH ₂	CH ₂ Ph	XXIV	CH ₂ CH=CH ₂	C ₄ H ₉

Table 1. Mass Spectra of 8-Azaxanthine Derivatives I—XII

m/z	Relative intensity/%											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
39	11	4	7	86	44	5	9	8	8	22	44	29
40	24	18	1	24	17	19	7	1	2	1	4	4
41	28	28	3	35	80	10	5	4	4	9	5	36
42	21	30	—	37	37	4	23	1	4	1	3	5
43	29	16	2	24	11	89	100	1	—	1	—	—
51	5	8	5	13	4	4	1	4	7	14	11	9
52	12	8	2	27	16	11	4	2	1	5	7	4
53	100	30	1	35	19	13	11	1	3	2	4	4
54	25	15	4	54	28	24	8	2	—	2	4	4
55	20	11	8	46	24	10	15	1	2	1	—	2
56	28	9	2	11	25	24	10	3	—	3	4	—
57	3	1	—	9	4	7	4	1	1	—	—	1
58	6	4	2	8	9	5	5	6	1	8	2	—
63	—	—	4	3	—	—	—	5	5	14	5	4
64	—	—	4	4	1	—	—	2	1	5	3	2
65	1	1	15	14	1	1	1	22	22	53	28	27
66	6	7	1	33	5	8	5	2	3	5	4	5
67	85	100	9	100	100	32	18	20	12	5	3	5
68	51	7	—	36	24	8	14	—	1	—	1	4
69	7	39	1	11	28	81	11	—	8	1	—	—
70	3	13	—	5	5	4	1	—	—	—	—	—
76	—	—	—	4	—	1	—	—	—	—	—	—
77	1	1	5	5	1	1	—	1	—	3	2	—
78	—	—	1	17	4	1	—	5	4	18	10	4
79	—	1	1	59	15	1	1	3	1	7	1	1
80	6	5	—	32	30	8	6	—	—	—	3	5
81	9	79	4	31	37	100	8	1	22	—	1	3
82	14	75	8	40	60	44	14	—	5	—	1	—
83	8	15	6	19	22	10	9	1	1	—	—	—
89	—	—	4	—	—	—	—	4	5	22	5	7
91	—	—	100	5	—	—	—	100	100	100	100	100
92	—	—	8	1	—	—	—	9	10	38	8	8
93	—	—	—	15	16	—	—	—	—	1	5	—
94	3	2	—	16	4	2	—	1	—	2	—	—
95	2	5	—	25	9	4	—	1	—	1	—	—
96	1	1	—	4	4	4	6	—	—	—	—	—
97	—	—	—	2	3	5	—	—	—	—	—	—
98	2	—	—	1	—	1	7	—	—	—	—	—
104	—	—	6	—	—	—	—	5	3	14	5	30
105	—	—	—	20	1	—	—	1	—	5	4	—
106	—	—	1	29	—	—	—	—	3	11	2	—
107	—	—	—	24	61	—	—	—	—	2	—	1
108	—	—	—	5	23	1	—	—	—	1	—	—
109	—	21	—	7	7	32	8	—	—	1	4	—
110	—	39	—	—	2	19	6	—	—	1	—	—
111	—	4	—	7	7	4	1	—	—	—	—	—
112	—	—	—	1	1	8	1	—	—	—	—	—
116	—	—	4	—	—	—	—	8	4	28	11	4
117	—	—	4	—	—	—	—	6	3	10	1	3
118	—	—	—	—	—	—	—	2	2	3	—	—
119	—	—	—	3	—	—	—	—	—	—	—	—
120	—	—	—	19	—	—	—	—	—	—	—	2
121	—	—	—	4	3	—	—	—	—	—	—	—
122	—	—	—	32	8	—	—	—	—	—	—	—
123	1	—	—	6	8	5	3	—	—	—	1	1
124	2	1	—	—	2	12	4	—	4	9	4	2
128	—	—	3	—	—	—	—	2	9	29	5	2
129	—	—	11	—	—	—	—	4	9	—	3	—
130	—	—	5	—	—	—	—	1	6	1	—	—
131	—	—	—	—	—	—	—	—	—	—	—	—
134	—	—	—	26	—	—	—	—	—	—	—	—
135	—	—	—	62	16	—	—	—	—	—	—	—
136	—	—	—	22	17	—	—	—	—	—	—	—
137	—	—	—	4	68	29	6	—	—	—	—	—
138	—	6	—	—	8	7	1	—	—	4	12	1
142	—	—	—	—	—	—	—	—	—	19	5	—
143	—	—	—	—	—	—	—	6	—	—	3	—
144	—	—	—	—	—	—	—	8	—	—	—	—

Table 1 (Continued)

<i>m/z</i>	Relative intensity/%											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
150	-	-	-	-	5	-	-	-	-	-	-	-
151	-	-	-	-	2	-	1	4	-	-	-	-
152	-	5	-	-	6	18	2	20	-	-	-	-
157	-	-	19	-	-	-	-	-	7	4	6	-
158	-	-	9	-	-	-	-	-	5	3	5	-
162	-	-	-	30	-	-	1	-	-	-	-	-
163	-	-	-	36	-	-	-	-	-	-	-	-
164	-	-	-	17	5	3	-	-	-	-	-	-
165	-	-	-	-	26	1	-	-	2	-	-	-
166	-	-	-	-	4	54	-	-	10	-	-	-
167	-	-	-	-	-	16	-	-	-	-	-	-
171	-	-	-	-	-	-	-	11	-	16	2	1
179	-	-	-	-	1	-	-	7	-	2	-	-
180	2	-	-	-	-	2	1	8	-	-	-	-
181	25	-	-	-	-	-	1	-	-	-	8	-
182	-	-	-	-	-	-	7	-	-	-	4	-
183	-	-	-	-	-	-	-	-	-	-	-	-
184	-	-	-	-	-	-	-	-	-	-	-	4
185	-	-	-	-	-	-	-	-	-	-	-	4
186	-	-	33	-	-	-	-	-	11	-	-	-
190	-	-	8	5	-	-	-	-	1	-	-	-
191	-	-	-	3	-	-	-	-	-	-	-	-
193	-	-	-	-	10	-	-	-	3	-	-	-
194	-	-	-	-	1	8	-	-	-	-	-	-
195	-	14	-	-	-	2	1	-	-	-	-	-
196	-	-	-	-	-	-	-	-	-	-	10	-
197	-	2	-	-	-	-	-	4	-	14	-	3
200	-	-	-	-	-	-	-	4	-	-	-	-
209	-	-	-	-	-	-	-	-	-	7	8	-
210	-	-	-	-	-	21	-	-	-	-	6	-
211	-	-	-	-	-	-	-	-	-	-	-	5
214	-	-	2	-	-	-	6	-	-	-	-	-
215	-	-	-	-	-	-	-	-	3	12	-	-
219	-	-	-	-	-	-	-	-	2	10	-	-
220	-	-	23	-	2	-	-	-	-	-	-	-
221	-	-	2	-	29	-	-	-	-	-	-	-
222	-	-	-	-	-	-	-	-	-	-	-	-
228	-	-	-	-	-	94	2	84	2	42	-	-
233	-	-	-	-	-	-	-	-	-	16	-	-
236	-	-	-	-	-	-	2	-	-	-	-	-
237	-	-	-	-	-	22	-	-	-	-	-	-
238	-	-	-	-	-	6	-	-	-	-	15	-
239	-	-	-	-	-	-	-	-	-	-	9	-
240	-	-	-	-	-	-	-	-	-	-	-	5
242	-	-	9	-	-	-	-	-	70	8	-	-
243	-	-	11	-	-	-	-	-	11	6	-	-
254	-	-	-	-	-	-	-	5	-	-	-	2
256	-	-	-	-	-	-	-	8	-	8	-	-
257	-	-	-	-	-	-	-	-	-	-	-	-
261	-	-	-	-	-	-	-	-	-	13	-	-
262	-	-	-	-	-	-	-	-	-	5	-	-
266	-	-	-	-	-	-	-	-	-	-	13	-
268	-	-	-	-	-	-	-	-	-	-	-	15
269	-	-	-	-	-	-	-	-	-	-	-	8
270	-	-	-	-	-	-	-	-	-	-	-	-
271	-	-	11	-	-	-	-	-	1	-	-	-
279	-	-	-	-	-	-	2	-	6	-	-	-
290	-	-	-	-	-	-	-	-	-	10	-	-
291	-	-	-	-	-	-	-	-	-	3	-	-
294	-	-	-	-	-	-	-	-	-	-	2	-
295	-	-	-	-	-	-	-	-	-	-	4	-
297	-	-	-	-	-	-	-	-	-	-	-	-
318	-	-	-	-	-	-	-	-	-	59	-	-
319	-	-	-	-	-	-	-	-	-	32	-	-
320	-	-	-	-	-	-	-	-	-	7	-	-
347	-	-	-	-	-	-	-	-	-	17	-	-
348	-	-	-	-	-	-	-	-	-	4	-	-

Table 2. Mass Spectra of 8-Azaxanthine Derivatives XIII—XXIV

<i>m/z</i>	Relative intensity/%											
	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV
39	5	18	12	27	19	5	68	66	8	14	50	44
40	2	6	8	28	5	4	11	11	11	11	28	20
41	1	57	14	52	55	18	100	44	12	32	52	48
42	2	6	28	33	7	10	40	21	4	21	10	22
43	22	47	40	42	100	12	59	39	—	1	12	16
51	4	—	—	1	—	—	5	4	—	1	16	18
52	—	—	—	17	21	4	22	12	—	4	18	12
53	1	23	—	21	20	5	24	14	9	13	16	14
54	—	12	—	31	11	13	40	18	10	20	22	20
55	—	56	—	31	14	4	47	19	16	16	26	26
56	3	16	—	56	16	4	22	9	26	10	24	24
57	—	57	—	4	5	—	5	—	10	8	18	18
58	1	8	—	47	4	3	19	6	17	4	4	6
63	1	—	—	—	—	—	—	—	—	—	40	40
64	—	—	—	—	—	—	4	—	—	—	28	26
65	18	—	—	1	—	—	—	8	—	—	32	28
66	—	10	—	9	10	—	10	14	3	5	10	10
67	—	67	77	72	34	12	55	26	44	20	—	14
68	—	20	12	40	21	11	42	21	15	13	—	—
69	—	38	42	11	11	22	18	5	4	28	—	—
70	—	8	—	—	3	—	5	—	6	12	—	—
71	—	29	—	—	—	—	—	—	—	—	—	—
77	—	—	—	—	—	—	5	—	—	—	36	—
78	—	—	—	—	—	—	6	15	—	—	24	12
79	—	—	—	2	—	—	30	8	—	—	32	24
80	2	—	—	4	16	5	32	17	—	8	20	28
81	1	24	100	15	20	84	33	10	6	100	18	42
82	3	11	28	8	6	13	28	13	5	26	16	10
83	—	25	—	20	5	4	7	1	7	9	—	—
91	100	—	—	—	—	—	—	—	—	—	10	—
92	8	—	—	—	—	—	—	13	—	—	14	—
93	—	—	—	—	—	—	13	10	—	—	28	—
94	1	—	—	4	2	1	28	8	—	1	16	—
95	1	—	18	42	6	4	29	1	27	4	—	—
96	—	26	32	8	—	5	5	2	4	8	—	—
98	—	16	—	1	—	—	1	2	—	—	—	—
104	—	—	—	—	—	—	—	—	—	—	28	—
105	1	—	—	—	—	—	11	10	—	—	32	—
106	—	—	—	—	—	—	16	18	—	—	40	—
107	—	—	—	2	1	—	42	7	—	—	20	21
108	—	—	—	1	1	—	26	3	—	—	—	—
109	1	—	—	1	7	5	8	3	—	5	—	—
110	—	10	—	3	4	2	10	—	3	4	—	—
111	—	3	—	4	4	1	6	6	—	—	—	—
112	—	10	—	—	1	—	2	—	—	1	—	—
116	2	—	—	—	—	—	—	—	—	—	—	—
120	—	—	—	—	1	—	2	46	—	—	47	—
121	—	—	—	—	—	—	37	34	—	—	39	—
122	—	—	—	—	—	—	21	13	—	—	—	18
123	1	—	12	5	10	2	1	4	3	2	—	—
124	—	—	20	7	3	1	2	—	1	3	—	3
125	—	—	—	—	—	—	—	—	4	—	—	—
126	—	—	—	—	—	—	—	8	—	—	—	—
129	2	—	—	—	—	—	—	—	—	—	—	—
133	—	—	—	—	—	—	—	11	—	—	—	—
134	—	—	—	—	—	—	5	6	—	—	—	—
135	—	—	—	—	—	—	31	5	—	—	11	20
136	—	—	—	—	—	—	11	1	—	—	—	—
137	—	—	—	—	4	1	—	—	1	2	—	19
138	—	—	—	—	—	4	—	—	—	—	—	—
148	—	—	—	—	—	—	—	8	—	—	—	—
149	—	—	—	—	—	—	11	5	—	—	11	20
150	—	—	—	—	—	—	8	—	—	—	—	11
151	—	—	—	—	—	—	6	—	—	—	—	—
152	—	—	10	6	10	1	8	—	3	1	6	—
153	—	—	14	2	1	—	2	—	8	2	16	—
156	4	—	—	—	—	—	—	—	—	—	—	—

Table 2 (Continued)

<i>m/z</i>	Relative intensity/%											
	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV
157	3	—	—	—	—	—	—	—	—	—	—	—
161	—	—	—	—	—	—	—	4	—	—	—	—
162	—	—	—	—	—	—	1	5	—	—	—	—
163	—	—	—	—	—	—	8	4	—	—	—	—
164	—	—	6	—	—	—	8	1	—	—	—	—
165	—	—	—	—	—	—	9	—	—	—	—	10
166	—	—	7	—	3	3	—	2	6	4	—	—
167	—	—	—	—	—	2	1	1	22	2	—	—
168	—	—	—	—	—	—	—	—	—	—	10	—
171	—	—	—	—	—	—	1	—	—	—	—	—
177	—	—	—	—	—	—	1	23	—	—	—	—
179	—	—	—	—	—	—	24	2	—	—	—	14
180	—	100	—	100	4	14	6	—	100	9	—	—
181	—	8	35	37	—	—	—	—	18	7	—	—
185	3	—	—	—	—	—	—	—	—	—	—	6
186	—	—	—	—	—	—	—	—	—	—	6	—
191	—	—	—	—	—	—	—	2	—	—	7	—
192	—	—	—	—	—	—	100	3	—	1	100	—
193	—	—	—	—	—	—	28	—	—	—	17	31
194	—	—	29	—	2	100	4	—	4	76	—	—
195	—	35	—	—	—	10	1	—	3	8	—	—
205	—	—	—	—	—	—	—	100	—	—	100	—
206	—	—	—	—	—	—	12	10	—	—	17	—
207	—	—	—	—	—	—	52	—	—	—	—	24
208	—	—	—	2	—	—	7	2	—	1	—	—
209	—	—	26	41	4	—	—	—	—	2	—	—
213	3	—	—	—	—	—	—	—	—	—	—	—
218	—	—	—	—	—	—	—	3	—	—	—	—
219	—	—	—	—	—	—	—	—	—	—	9	—
220	—	—	—	—	—	—	17	—	—	—	—	21
221	—	—	—	—	—	—	6	—	—	—	—	6
222	—	—	—	—	2	—	—	—	—	—	—	—
223	—	—	—	—	—	12	—	—	9	—	—	—
228	8	—	—	—	—	—	—	—	—	—	—	—
232	—	—	—	—	—	—	—	—	—	—	8	—
234	—	—	—	—	—	—	—	—	—	—	—	12
236	—	—	—	—	7	—	—	—	—	—	—	—
237	—	—	—	—	—	—	—	—	—	9	—	—
246	—	—	—	—	—	—	—	1	—	—	6	—
247	—	—	—	—	—	—	—	4	—	—	—	—
248	—	—	—	—	—	—	—	4	—	—	—	5
249	—	—	—	—	—	—	24	—	—	—	—	—
250	—	—	—	—	4	—	4	—	—	—	—	—
256	5	—	—	—	—	—	—	—	—	—	—	—
261	—	—	—	—	—	—	—	—	—	—	14	—
263	—	—	—	—	—	—	—	—	—	—	—	30
264	—	—	—	—	—	—	—	—	—	—	—	6
265	—	—	—	—	2	—	—	—	—	—	—	—
270	3	—	—	—	—	—	—	—	—	—	—	—
284	6	—	—	—	—	—	—	—	—	—	—	—
285	4	—	—	—	—	—	—	—	—	—	—	—
298	2	—	—	—	—	—	—	—	—	—	—	—
313	1	—	—	—	—	—	—	—	—	—	—	—

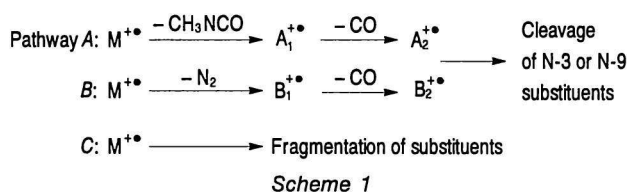
under study were focussed magnetically into the second field-free region of the instrument, and the MIKE or *B/E* linked scans were recorded by scanning of the deflection voltage of the electrostatic analyzer or by the linked electrostatic and magnetic field of the instrument. The CID spectra were obtained by the same technique like MIKE, while helium was introduced as the reaction gas into the collision chamber of the second field-free region of the VG ZAB-2F instrument, until the peak intensity

of the parent peak was reduced to approx. 50 %. The exact mass measurements have been accomplished with MAT 900 (Finnigan) instrument in the application laboratory of the firm in Bremen, Germany.

RESULTS AND DISCUSSION

The 70 eV conventional EI mass spectra of 8-azaxanthine derivatives I—XXIV are presented in Tables 1 and 2. The fragmentation of compounds

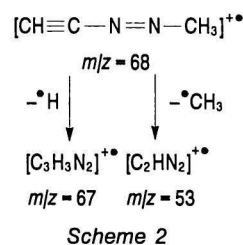
of this type begins either on the 8-azaxanthine skeleton or on the N-3 or N-9 substituents. The disintegration of 8-azaxanthine skeleton follows two modes. The pathway *A* is characterized by the retro-Diels—Alder reaction, leading to $[M - \text{CH}_3\text{NCO}]^{+\bullet}$ ion radicals. The second mode (*B*) begins with the elimination of the N_2 molecule from the 1,2,3-triazole cycle of the 8-azaxanthine skeleton. These findings resemble the data of published spectra of 8-azaxanthine and 1-methyl-8-azaxanthine [6, 7]. The fragmentation of $[M - \text{CH}_3\text{NCO}]^{+\bullet}$ and $[M - \text{N}_2]^{+\bullet}$ ion radicals proceeds by the elimination of CO molecule and is followed by splitting off of hydrogen atom or some radical from N-3 or N-9 substituents. The third (*C*) mode is dependent on the structure of these substituents and begins by their fragmentation. All fragmentation steps have been confirmed by MIKE, *B/E* or CID measurements. The common fragmentation features are depicted in Scheme 1.



The m/z values of the *A* and *B* type fragments of the compounds *I*—*XXIV* are summarized in Table 3.

The *C* fragments, as well as fragments of deeper destruction will be discussed individually, according to the structure of N-3 and N-9 substituents.

The spectrum of N-9 methyl derivative *I* contains the intensive peaks of ions, produced by deep destruction, at $m/z = 68$, 67, and 53, the proposed structure and elemental composition of which is introduced in Scheme 2.



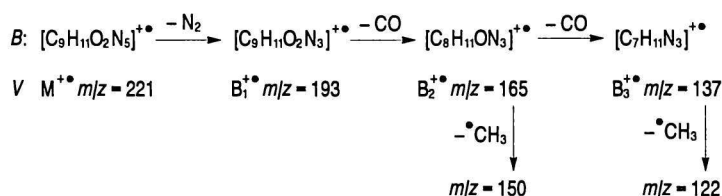
In the spectrum of N-3 and N-9 dimethyl derivative *II* are similarly very intensive peaks of the ions with $m/z = 82$, 81, and 67. The spectra of *N*-benzyl derivatives *III*, *VIII*—*XIII* contain the base peak of tropylium ions at $m/z = 91$, produced by splitting off of benzyl group. The spectra of substances, possessing $\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$ or $\text{N}-\text{CH}_2-\text{C}\equiv\text{CH}$ grouping (*IV*, *V*, *XI*, *XII*, *XIX*, *XX*, *XXIII*, and *XXIV*) contain analogically very intense peaks of ions with $m/z = 41$ or 39.

The role of high-resolution measurements in the EI mass spectrometric study of 8-azaxanthine derivatives is demonstrated on the *B* series of the fragmentation of the compounds *V* in Scheme 3.

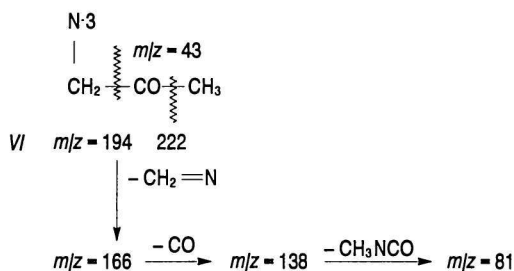
The presence of CH_2COCH_3 substituent on N-3 (compound *VI*) is the reason for *C*-type fragmentation according to Scheme 4.

Table 3. m/z Values and Relative Intensities of *A*- and *B*-Type Ions of 8-Azaxanthine Derivatives *I*—*XXIV*

Compound	m/z (%)				
	M	A_1	A_2	B_1	B_2
<i>I</i>	181(25)	124(2)	96(1)	—	—
<i>II</i>	195(14)	138(6)	110(39)	167(2)	—
<i>III</i>	271(11)	214(2)	186(8)	243(11)	—
<i>IV</i>	219(23)	162(30)	134(26)	191(2)	163(36)
<i>V</i>	221(29)	164(4)	136(17)	193(10)	165(26)
<i>VI</i>	237(22)	180(2)	152(18)	209(21)	181(26)
<i>VII</i>	279(2)	222(2)	—	—	—
<i>VIII</i>	257(17)	200(10)	—	—	—
<i>IX</i>	271(6)	214(2)	186(1)	243(11)	215(2)
<i>X</i>	347(17)	290(10)	262(5)	319(22)	291(3)
<i>XI</i>	295(4)	238(15)	210(5)	267(2)	239(9)
<i>XII</i>	297(4)	240(5)	—	269(8)	—
<i>XIII</i>	313(1)	256(5)	228(8)	285(4)	—
<i>XIV</i>	195(35)	—	110(10)	—	—
<i>XV</i>	209(26)	152(10)	124(20)	181(35)	153(14)
<i>XVI</i>	209(41)	152(6)	124(7)	181(31)	153(14)
<i>XVII</i>	265(2)	—	180(4)	237(2)	209(4)
<i>XVIII</i>	223(9)	166(3)	138(4)	195(10)	167(2)
<i>XIX</i>	249(24)	192(100)	164(8)	221(6)	193(28)
<i>XX</i>	247(4)	—	162(5)	—	—
<i>XXI</i>	223(9)	166(6)	—	195(3)	167(22)
<i>XXII</i>	237(9)	180(9)	—	209(2)	181(7)
<i>XXIII</i>	261(14)	—	—	—	—
<i>XXIV</i>	263(30)	—	—	—	—

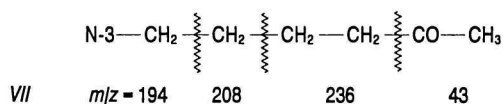


Scheme 3

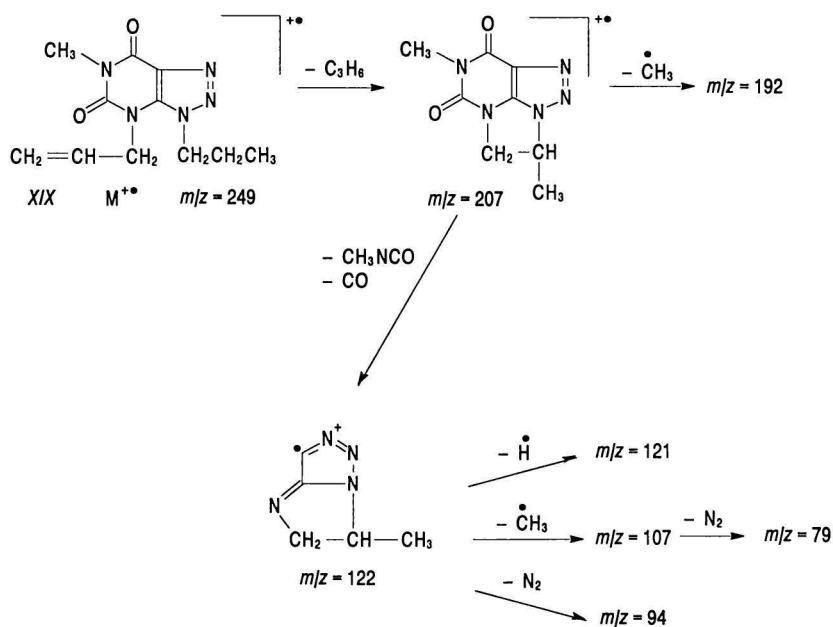


Scheme 4

The presence of the six-membered $\text{CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CO---CH}_3$ N-3 substituent in the compound VII gives rise to the production of the following C-type fragments (Scheme 5).



Scheme 5



Scheme 6

The fragmentation of the ions at $m/z = 194$ was described in the case of substance VI (Scheme 4).

The presence of two N-benzyl groups (compound X) in the position N-3 and N-9 reflects the produc-

tion of $[M - N_2 - \cdot\text{CHPh}]^+$ ions at $m/z = 228$ in the series C.

β -Splitting of ethyl group in the position N-9 (compounds XIV and XV) leads to the formation of $[M - \cdot\text{CH}_3]^+$, $m/z = 180$ (XVI), $m/z = 194$ (XV) and similarly $[M - \cdot\text{C}_3\text{H}_7]^+$, $m/z = 180$ (XXI) and 194 (XXII) species. The C series fragmentation of compounds XVII (N-3— CH_2COCH_3 and N-9— $\text{CH}_2\text{---CH}_2\text{---CH}_3$) mirrors β -splittings on both N atoms, giving rise to the atoms with $m/z = 222$ or 236.

Interesting rearrangement processes have been observed after the study of EI mass spectra of the compounds XIX and XX (in lesser extent also XXIII and XXIV, possessing the unsaturated $\text{CH}_2\text{---CH=CH}_2$ or $\text{CH}_2\text{---C}\equiv\text{CH}$ substituents on N-3 together with propyl (or butyl) groups on N-9). The elimination of olefin is followed by the destruction of the pyrimidine ring. The fragmentation ends by the splitting off of methyl radical and N_2 molecule. The fragmentation of this type is introduced as example in Scheme 6 with the compound XIX.

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Translated by V. Kovacik

Determination of Linkage Position in Per-O-methylated Xylooligosaccharides by MIKE and CID Mass Spectra of Ammonia and Methylamine Cluster Ions

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The linkage types 1→2, 1→3, and 1→4 of D-xylobioses can be distinguished based on the unimolecular decomposition spectra (MIKE) of the cluster $[M + NH_4]^+$ ions or by collision-induced dissociation (CID) mass spectra of $[M + CH_3NH_3]^+$ ions of per-O-methylated compounds. The MIKE spectra of $[M + NH_4]^+$ and $[M + CH_3NH_3]^+$ adducts allow the determination of linkage positions between the xylose residues in per-O-methylated D-xylotrioses. The branching point of the branched trisaccharides can be deduced from these mass spectra, too.

D-Xylans and (4-O-methyl-D-glucurono)xylans are components of industrially important plants [1]. With the aim to use mass spectrometric technique for structure elucidation of oligosaccharides related to D-xylans, we have studied per-O-methylated oligosaccharides [2, 3]. As a result, the sequential analysis of oligosaccharides by electron impact (EI) mass spectrometry has been described [3]. In continuation of our studies directed to the mass spectrometric analysis of xylooligosaccharides we have examined the gas-phase reactions of per-O-methylated D-xylotriose with several protonated reagents by chemical ionization (CI) mass spectrometry [4]. Under these conditions the ammonium ions produced from ammonia and amines yield abundant cluster ions with per-O-methylated oligosaccharides. Nowadays, CID and fast atom bombardment tandem mass spectrometry (FAB MS/MS) have been used successfully at the study of per-O-methylated oligosaccharides [5–7]. Common fragmentation process in low energy CID FAB MS/MS cleaves the

internal glycosidic bonds to possess oxonium ions [5]. The high energy CID FAB MS/MS has been used for the study of alkali metal cationized and per-O-methylated higher oligosaccharides by *Fournet et al.* [6, 7]. As a result, many linkage positions in one compound may be determined by the presence or absence of specific fragment ions that arise from the cleavage of two ring bonds. Here we discuss the results of an investigation by CI of per-O-methylated D-xylan type oligosaccharides I–VIII, using ammonia and methylamine as a reaction gas. MIKE and CID mass spectrometry were used to study the fragmentation of these cluster ions.

Compounds investigated:

I Methyl per-O-methyl-(O-β-D-xylopyranosyl-(1→2)-β-D-xylopyranoside)

(Symbol a→2b)

II Methyl per-O-methyl-(O-β-D-xylopyranosyl-(1→3)-β-D-xylopyranoside)

(Symbol a→3b)