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ELECTRON IMPACT AND MOLECULAR DISSOCIATION—XIII

THE PYRROMYCINONES AND RHODOMYCINONES

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Abstract—The electron induced fragmentation of some pyrromycinones has been examined. The partial structures of some of the less well-studied of these have been proposed. A mass spectrometric method has been employed to determine the relative crowding of ζ-pyrromycinone and a suspected epimer.

IN THE course of some collaborative work with Dr. D. Ollis, the University of Bristol, we have had occasion to examine some pyrromycinones and rhodomycinones. The chemistry of these compounds is discussed elsewhere, but the mass spectra which have many features of interest, are detailed below. Experiments conducted upon the mould metabolites produced by a certain strain of streptomyces yielded four metabolites namely ε-pyrromycinone $C_{22}H_{20}O_9$, ζ-pyrromycinone $C_{22}H_{20}O_8$, η-pyrromycinone $C_{22}H_{16}O_7$ and pyrromycin $C_{30}H_{35}O_{11}$ which were being studied independently by Brockmann[1] and Prelog.[2] Pyrromycin was shown to be composed of ε-pyrromycinone and a nitrogenous sugar. Ollis in collaboration with the above authors showed that ε-pyrromycinone was identical with rutilantinone, a red crystalline aglycone which may be derived from certain metabolites of the mould actinomycete A. 220. Rutilantinone was finally assigned structure (I). η-Pyrromycinone was found to be identical to bisanhydrorutilantinone of structure (II). A structure (III) was proposed for ζ-pyrromycinone. The method of naming these compounds is shown in (IV).

Pyrromycinone and rhodomycinones

The fragmentation patterns of these compounds are recorded in Table 1. The general features are as follows. The parent molecular ion, although abundant, is never the base peak of the spectrum. The remainder of the spectrum falls into two parts, the higher mass range the more useful diagnostic portion which corresponds to the loss of substituents and to fragmentation of the non-aromatic ring, and the lower mass range which corresponds to the fragmentation of the anthraquinone system. Beynon[3] has shown that the 1:4:5:8-tetrahydroxyanthraquinone is even more stable than most of the other isomers under electron impact and fragment ions are of low abundance.

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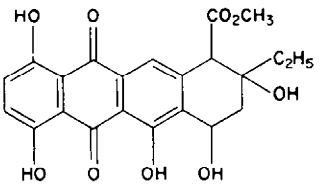
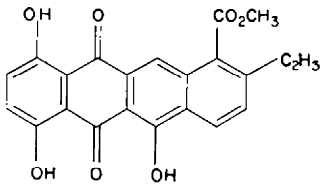
[1] H. Brockmann and W. Lenk, *Chem. Ber.* **92**, 1880 (1959).
[2] L. Ettinger, E. Gäumann, R. Hutter, W. Keller-Schierlein, F. Kradolfer, L. Neipp, V. Prelog, P. Reusser and H. Zähner, *Chem. Ber.*, **92**, 1867 (1959).
[3] J. H. Beynon and A. E. Williams, *Appl. Spec.*, **14**, 156 (1960).



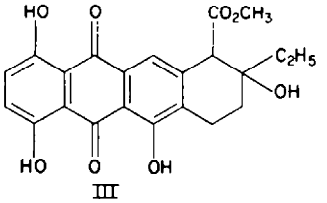
I

ε-pyrromycinone



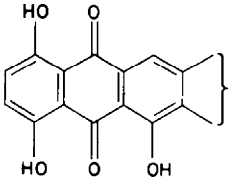
II

η-pyrromycinone



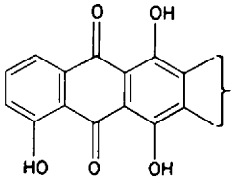
III

ζ-pyrromycinone

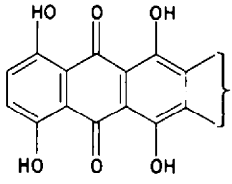


pyrro⁻

IV



rhodo⁻



isorhodo—

As is to be expected the ε and ζ-series have many common fragment ions. These compounds tend to lose molecular water from the unsaturated ring giving rise to the moderately abundant ion $(P - 18)^+$. In ζ-pyrromycinone there is also an abundant ion at $(P - 20)^+$ (55·0%). However, considering the rather drastic experimental conditions necessary to obtain this spectrum it is not possible to be certain that this fragmentation occurs under electron bombardment rather than thermal degradation.

The presence of a carbomethoxyl group in the unsaturated ring gives rise to the abundant ions associated with $(p - OCH_3)^+$, $(P—OCH_3 \cdot H)^+$, $(P—CO_2CH_3)^+$ and $(P—CO_2CH_3 \cdot H)$ which are the common fragments to be expected from the decomposition of esters.[4,5] The main driving force seems to be the progressive aromatization of the unsaturated ring and many ions of the high mass end of the spectrum may be

[4] R. S. Gohlke and F. W. McLafferty, *A.S.T.M.* E-14 Meeting on Mass Spectrometry, San Francisco, 1955.

[5] J. Asselineau, R. Ryhage and E. Stenhagen, *Acta Chem. Scand.*, **11**, 196 (1957).

TABLE 1

ε-Rhodomycinone M.Wt. 428
2 KV, 50 eV, slight heat

M/e	%	M/e	%	M/e	%	M/e	%	M/e	%
40	3·3	103	5·3	237	4·9	325	15·7	377	4·0
41	17·7	104	4·0	247	3·3	330	12·1	378	6·0
42	4·9	105	9·3	265	7·3	331	12·9	379	3·7
43	20·0	107	4·0	268	8·5	332	16·5	380	4·9
44	12·1	109	6·5	269	5·7	333	46·0	381	7·3
53	4·1	111	4·5	270	4·9	334	35·5	392	41·0
54	2·8	115	4·9	275	4·0	335	27·4	393	17·8
55	18·2	119	8·9	277	6·5	336	13·7	394	8·1
56	14·5	120	3·6	293	19·0	337	12·2	410	9·3
57	37·0	121	10·5	294	35·5	338	12·2	411	4·9
59	6·0	128	5·3	295	27·0	339	49·8	412	14·9
65	5·7	131	4·9	296	22·1	340	18·6	413	7·3
67	9·7	139	5·7	297	14·5	345	6·9	428	95.5 P
69	14·5	145	5·3	298	6·1	348	9·7	429	49·2
69·5	4·8	147·5	2·4	303	5·7	349	15·7		
77	7·3	151	4·8	304	6·8	350	23·0		
78	4·0	152	10·9	305	10·9	351	24·1		
79	6·8	163	5·7	306	8·9	352	14·9		
81	11·7	165	7·7	307	8·9	353	11·3		
82	5·3	173	7·3	308	8·5	354	12·2		
83	9·7	180	5·3	309	7·3	359	8·5		
84	4·5	180·5	4·0	310	6·1	360	100·0		
85	6·1	181	6·9	311	9·3	361	38·8		
91	7·3	189	5·7	319	13·7	362	14·9		
92	4·0	200	4·0	320	9·3	363	7·3		
93	6·5	201	5·3	321	31·0	368	36·0		
94	2·4	202	11·3	322	49·1	369	12·5		
95	12·5	203	11·7	323	48·5	370	4·0		
97	6·0	235	4·9	324	22·3	376	6·5		

ζ-Rhodomycinone M.Wt. 412
2 KV, 50 eV

40	1·7	97	18·7	146	6·8	294	10·2	338	6·8
41	18·7	103	7·7	147	8·5	295	48·5	339	8·5
42	3·4	105	17·8	147·5	6·8	296	34·0	340	6·8
43	17·4	107	11·1	149	8·5	297	10·2	349	5·9
44	13·6	109	18·7	151	10·2	298	5·9	350	10·2
45	3·4	110	10·1	152	10·2	303	5·1	351	15·3
55	5·1	111	13·6	153	6·8	304	5·1	352	34·0
56	2·6	115	11·9	161·5	3·4	305	6·8	353	17·0
57	23·8	117	8·5	163	9·4	306	17·8	354	6·8
59	6·8	118	6·8	165	17·0	307	16·2	356	5·1
65	4·3	119	17·9	173	9·4	308	20·4	360	32·5
67	10·2	120	9·4	175	9·4	309	15·3	361	11·9
69	8·5	121	18·7	189	7·7	310	8·5	362	16·8
70	4·0	123	11·9	201	5·1	317	5·1	363	5·9
71	5·1	124	6·8	202	8·5	318	5·1	368	5·1

Table 1 (contd)

ζ-Rhodomycinone M.Wt. 412
2 KV, 50 eV

M/e	%	M/e	%	M/e	%	M/e	%	M/e	%
77	3·4	125	10·2	203	21·0	319	7·7	376	5·1
79	5·1	126	7·7	204	7·7	320	6·8	380	16·5
81	8·5	127	8·5	205	5·1	321	10·2	381	11·2
82	3·4	128	10·2	221	7·7	322	15·3	383	5·1
83	7·7	129	7·7	249	7·6	323	100·0	392	7·7
85	3·4	131	9·4	277	6·8	324	54·5	394	11·1
89	6·8	133	10·2	278	7·7	325	16·2	395	5·1
90	3·4	135	7·7	279	6·8	326	5·1	410	5·1
91	14·5	137	9·4	280	9·4	332	6·8	412	63·8 P
92	6·8	138	6·8	281	9·0	333	13·6	413	24·6
93	11·1	139	11·1	282	9·4	334	44·1	426	4·3 imp
93·5	5·1	140	6·8	283	5·1	335	88·3	428	10·4 imp
95	25·5	141	10·2	291	5·1	336	31·3	429	6·8 imp
96	11·9	145	9·4	293	7·7	337	11·9		

ε-Isorhodomycinone M.Wt. 444
2 KV, 50 eV
(Spectrum very weak even under drastic conditions)

M/e	%	M/e	%	M/e	%	M/e	%	M/e	%
40	21·6	95	33·1	295	17·9	353	14·0	428	52·1
41	30·0	96	14·0	296	18·0	354	7·7	429	20·5
42	29·2	97	7·7	297	12·7	355	20·5	444	42·0 P
43	46·1	98	14·0	309	22·6	360	8·9	445	19·2
44	45·0	105	2·5	310	30·5	366	11·4		
45	16·6	107	29·2	311	46·0	367	15·4		
53	16·6	109	59·0	312	29·2	368	25·1		
55	95·0	111	40·8	313	15·3	369	14·0		
56	34·6	119	53·5	319	12·7	370	7·7		
57	91·0	123	44·5	320	10·1	376	100·0		
65	28·0	185	30·0	321	16·6	377	46·1		
66	10·1	186	15·3	322	19·9	378	40·8		
67	71·5	189	23·0	323	21·6	384	17·9		
68	14·0	191	16·6	324	25·6	385	7·7		
69	97·0	203	17·9	325	10·1	392	16·6		
70	20·5	312	19·2	334	23·0	393	7·7		
71	41·0	217	15·3	335	25·6	394	12·7		
77	20·5	218	16·6	336	15·3	395	7·7		
79	17·9	219	25·6	337	39·5	396	17·9		
81	34·6	235	48·5	338	43·2	408	24·2		
82	67·5	236	22·6	339	68·6	409	10·2		
83	40·9	237	15·3	340	34·5	410	11·4		
84	19·2	256	19·2	349	94·5	411	5·1		
85	41·0	277	20·5	350	71·5	412	16·6		
91	5·0	293	14·0	351	75·0	426	10·1		
94	10·1	294	12·8	352	29·2	427	7·7		

TABLE 1 (contd)

ζ-Isorhodomycinone M.Wt. 428
2 KV, 50 eV

M/e	%	M/e	%	M/e	%	M/e	%	M/e	%
41	24·5	111	9·4	201	3·6	309	13·8	355	6·0
43	18·0	115	79·5	202	7·2	310	8·4	356	7·2
44	13·2	119	11·3	203	25·2	311	14·4	359	2·0
55	21·5	121	13·9	204	6·0	312	8·4	360	10·2
56	4·2	123	7·8	205	3·6	319	6·0	361	6·0
57	36·0	125	6·0	219	5·4	320	5·4	362	16·8
67	10·2	128	5·4	221	5·4	321	9·6	363	6·6
69	18·6	129	3·6	249	6·0	322	20·5	364	2·4
70	4·8	131	5·4	250	2·4	323	100·0	368	9·6
71	10·8	133	6·0	267	3·6	324	60·1	369	6·6
77	4·8	137	6·6	268	3·0	325	22·1	376	5·4
79	4·8	139	7·2	277	3·6	326	7·2	377	2·4
81	1·4	141	6·0	278	3·6	332	4·8	378	6·0
82	3·6	145	6·6	279	6·6	333	10·8	379	4·8
83	8·4	147	6·0	280	8·4	334	32·5	380	16·8
85	2·4	147·5	5·4	281	9·6	335	84·5	381	11·4
91	9·6	149	6·0	282	6·6	336	32·5	382	4·8
92	4·2	150	4·2	283	3·6	337	13·2	394	9·6
93	7·3	151	7·2	285	4·8	338	7·2	395	4·2
95	18·6	152	6·6	293	6·6	339	24·6	396	7·8
96	7·8	163	6·6	294	15·6	340	15·6	397	3·6
97	12·6	165	12·0	295	46·2	347	3·6	410	6·0
98	4·2	166	5·4	296	31·2	348	4·2	411	21·6
103	3·6	168	4·8	297	13·2	349	6·6	412	70·5
104	3·6	173	7·2	298	5·4	350	15·6	413	28·1
105	10·8	175	7·8	305	4·8	351	44·5	424	2·4
107	7·2	176	5·4	306	13·8	352	21·6	426	1·8
109	13·2	189	6·6	307	13·2	353	8·4	428	21·2 P
110	6·0	191	5·4	308	18·0	354	8·4	429	9·6

interpreted as resulting from the elimination of substituents on this ring without an accompanying ring breaking. The ions in the following table are all abundant.

The main difference between the series arises from the presence of two hydroxyls in the unsaturated ring of the ε-series and the loss of two molecules of water will aromatize it. The ε-series is characterized by an abundant $(P-36)^+$ ion in agreement with this. The corresponding ion is absent from the spectrum of ζ-pyrromycinone as also is the ion $(P-68)^+$ which is the peak in both the ε-rhodomycinones.

When ζ-pyrromycinone is heated a keto-ester and an anhydro-compound are formed.[6] Since the molecular weight of the keto ester is 412, it is isomeric with ζ-pyrromycinone and the fragmentation pattern is shown in Table 3. The ion $(P-31)^+$ indicates that there is a methoxyl or a hydroxymethyl group present and since there is no chemical evidence for the latter, a methoxyl must be present. An abundant ion $(P-29)^+$, which does not appear in the spectra of other pyrro- or rhodomycinones, indicates that there must be a free carbonyl group. Since one common form of

[6] W. D. Ollis. Personal communication.

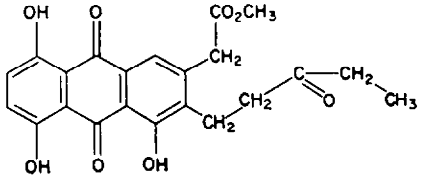
TABLE 2

ζ-Pyrromycinone M.Wt. 412
2 KV, 50 eV

M/e	%	M/e	%	M/e	%	M/e	%	M/e	%
41	11·0	105	43·9	145	13·8	307	26·3	378	12·5
43	15·1	106	15·0	147	13·8	308	25·0	379	7·5
44	12·1	107	25·0	147·5	13·5	309	20·0	380	27·5
55	27·5	108	17·5	148	13·8	319	13·8	381	12·5
56	20·1	109	47·5	149	44·0	320	10·0	382	7·5
57	35·2	110	23·8	152	17·5	321	15·0	383	10·0
59	13·5	111	35·0	163	13·7	322	11·3	392	55·1
67	10·1	112	17·5	165	27·5	323	82·5	393	22·5
69	13·4	113	13·8	166	17·5	324	41·2	394	43·8
71	6·4	115	27·5	167	15·0	325	12·5	395	12·5
77	13·1	117	15·0	179	13·5	332	12·5	396	7·5
79	7·5	119	40·0	180	12·5	333	17·5	412	82·5 P
81	7·5	121	20·0	221	12·5	334	42·5	413	32·5
82	6·5	122	12·5	235	13·7	335	100·0		
83	6·5	123	32·5	249	12·5	336	38·8		
84	7·5	124	17·5	277	15·0	337	15·0		
85	5·2	125	23·6	278	10·0	338	8·8		
91	4·6	126	15·0	279	11·3	351	10·0		
92	5·5	127	17·5	280	20·0	355	13·7		
93	28·7	128	22·5	281	21·2	356	40·0		
94	25·0	129	22·5	282	10·0	357	13·8		
95	72·5	131	20·0	283	10·0	360	10·0		
96	37·5	133	25·0	294	15·0	361	13·8		
97	55·0	135	20·0	295	86·5	362	17·5		
98	25·0	137	25·0	296	41·2	363	10·0		
99	17·5	138	15·0	297	16·3	365	12·5		
103	12·5	139	20·0	305	11·2	376	5·0		
104	12·5	141	20·0	306	26·3	377	12·5		

fragmentation of a ketone[7] is by the sundering of the bond next to the keto group the formation of the abundant ions M/e = 56, 57 suggest that the molecule contains the grouping —CO·CH_2·CH_3.

The abundant ions $(P - 88)^+$ and $(P - 89)^+$ probably result from the combined loss of $HOCH_3$ and —CO·CH_2·CH_3 or of OCH_3 and OCH·CH_2·CH_3. Assuming that the —CO_2Me group has not changed its position in the formation of the keto ester, a tentative structure (V) may be written[7]. It may be observed in addition that



Keto-ester V

[7] R. A. Friedel, A. G. Sharkey and J. L. Shultz, *Anal. Chem.*, **28**, 934 (1956).

TABLE 3

Ketone derived from ζ-pyrromycinone 2 KV, 50 eV				M.Wt. 412	
M/e	%	M/e	%	M/e	%
40	1·3	235	3·7	335	10·7
41	13·8	239	3·7	339	3·7
42	3·9	249	4·4	352	3·7
44	8·8	253	5·0	353	4·4
51	6·3	255	5·0	354	6·3
53	3·7	265	2·5	355	28·4
54	2·5	267	5·7	356	74·1
55	8·2	277	4·4	357	22·6
56	5·0	278	3·9	358	6·3
57	17·6	279	4·4	365	6·9
59	3·7	280	3·9	376	3·7
67	8·8	281	14·5	380	7·5
69	13·8	282	8·2	381	11·3
71	9·4	283	9·5	382	3·7
81	9·5	284	4·4	383	6·3
83	8·8	293	3·9	393	2·5
85	5·7	294	6·3	394	13·2
91	5·0	295	42·7	395	5·1
95	9·4	296	22·5	412	100·0 P
96	5·7	297	10·1	413	15·5
97	7·5	298	4·4		
105	5·7	306	3·9		
109	6·3	307	4·4		
110	3·7	308	3·9		
119	5·0	309	12·6		
123	3·7	310	5·0		
149	3·7	321	8·2		
165	4·4	322	5·0		
197	3·7	323	26·5		
207	5·1	324	16·4		
221	3·7	325	5·7		
225	3·2	334	5·1		

the present fragmentation pattern closely resembles those obtained with tetra-cyclic systems containing an anthraquinone which supports the view that the thermal isomerization has destroyed the unsaturated ring. Other rhodomycinones have been reported from cultures of *Streptomyces purpurascens* which are distinguished by Greek letters.[8] Amongst these are β, γ and δ-rhodomycinone. Mass spectrometric analysis shows the first of these to have a parent molecular ion M/e = 386 with a fragmentation pattern as follows (Table 4).

Since there are no abundant ions corresponding to $(P - 31)^+$, $(P - 59)^+$ nor $(P - 60)^+$ it is concluded that a $-CO_2Me$ is not present in the molecule. The abundant ion $(P - 36)^+$ as well as a moderately abundant $(P - 18)^+$ confirms the presence in the molecule of two hydroxyl groups with hydrogen atoms in the proximity. The general

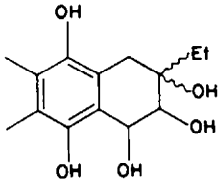
[8] H. Brockmann and B. Franck, *Chem. Ber.*, **88**, 1792 (1955).

TABLE 4

	β-Rhodomycinone			Unknown 2 KV, 50 eV		M.Wt. (found) 386			
M/e	%	M/e	%	M/e	%	M/e	%	M/e	%
40	12·5	94	6·6	139	9·6	265	5·4	319	21·6
41	10·0	94·5	3·3	141	5·4	270	10·0	320	10·0
43	25·0	95	23·4	145	6·7	276	2·5	321	7·9
44	23·3	96	11·2	145·5	2·5	277	5·0	322	8·3
45	11·9	97	22·9	147	5·0	278	4·6	323	7·5
53	6·7	98	6·7	149	7·1	279	6·3	333	4·2
54	5·4	99	5·8	151	9·6	280	4·2	332	7·5
55	42·9	102·5	1·7	152	9·2	281	4·6	333	8·4
56	15·8	105	8·8	153	7·9	282	5·4	334	100·0
57	52·2	107	6·7	155	15·8	283	12·0	335	59·9
60	5·6	108	6·3	154·5	3·3	284	10·4	336	16·7
63	4·5	108·5	2·5	163	7·5	285	7·5	337	20·0
65	5·8	109	15·8	165	9·6	286	7·5	349	5·8
67	17·9	110	7·5	167	8·3	291	8·8	350	70·1
68	7·9	111	17·1	173	7·5	292	5·0	351	25·8
69	36·1	112	8·3	174	4·6	293	8·4	352	12·1
70	13·3	115	6·7	175	8·8	294	16·7	365	5·4
71	22·1	117	4·2	176	6·7	295	14·6	367	2·5
72	5·4	119	8·3	177	5·8	296	35·5	368	22·1
77	9·6	120	5·4	178	5·0	297	15·8	369	7·5
78	4·2	121	13·8	179	6·3	298	1·0	370	8·3
79	9·6	123	11·2	181	6·3	303	2·5	384	2·5
80	4·6	124	5·8	187	4·8	304	4·2	386	3·8 P
81	24·1	125	12·1	189	9·1	305	6·3	387	1·7
82	11·7	126	6·3	191	4·2	306	6·3		
83	25·0	127	7·5	202	7·1	307	9·6		
84	8·4	128	5·8	203	7·5	310	5·4		
85	16·2	129	5·0	205	5·4	311	33·4		
86	5·4	131	4·2	207	5·0	312	32·5		
89	5·4	133	5·0	221	5·4	313	15·0		
91	9·3	135	5·0	237	4·6	314	34·1		
92	5·0	137	8·8	249	4·2	315	11·2		
93	9·3	138	5·4	257	4·2	318	6·7		

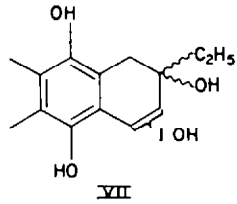
similarity of the remainder of the cracking pattern with that of known rhodomycinones places this molecule as a rhodomycinone also. The second series of ions given by this compound corresponding to $(P - 72)^+$, $(P - 73)^+$, $(P - 90)^+$ and $(P - 103)^+$ provide evidence for the fragmentation of the unsaturated ring system. Treatment of β-rhodomycinone with hydriodic acid[9] yields a compound which, on oxidation and analysis of the product, gave β-rhodomycinone as $C_{20}H_{16-18}O_8$ or $C_{23}H_{20-22}O_9$. The molecular weight of 386, determined in this work, gives a true formula of $C_{20}H_{18}O_8$. Further the $(P - 51)^+$, $(P - 52)^+$, $(P - 53)^+$ and $(P - 36)^+$ ions in the mass spectrum correspond to aromatization of the non-aromatic ring and loss of a further hydroxyl from this ring indicate that the two hydroxyl groups are attached to different carbon atoms. This evidence taken collectively allows a partial structure to be

[9] H. Brockmann and P. Boldt, *Naturwiss.*, **44**, 616 (1957).



VI

β-rhodomycinone ?



VII

γ-rhodomycinone ?

proposed for this molecule. If fragmentation occurred adjacent to a quarternary centre C_9 to yield the abundant ions $(P - 71)^+$ and $(P - 72)^+$ one must infer that C_{10} carried no substituent as assumed above. The further compound γ-rhodomycinone has also been examined, the fragmentation pattern being listed in with others (Table 5). Employing the same arguments as for the β isomer one concludes that the present

TABLE 5

γ-Rhodomycinone Unknown M.Wt. (found) 370
2 KV, 50 eV, slight heat

M/e	%	M/e	%	M/e	%	M/e	%
40	17·1	97	13·2	175	7·3	311	6·8
41	16·6	102·5	1·8	176	6·7	318	8·5
42	8·1	105	9·5	189	7·3	319	13·4
43	33·1	108·5	1·8	202	8·5	320	7·3
44	35·2	109	11·0	203	14·0	321	8·5
53	9·3	111	10·4	213	6·2	322	6·2
55	32·4	112	7·9	241	6·2	323	18·9
56	15·3	113	21·4	242	4·8	324	12·9
57	29·3	115	7·9	255	11·6	325	6·7
65	7·3	119	10·3	268	8·5	332	4·3
67	14·0	121	15·2	270	100·0	333	6·1
68	7·9	123	9·1	271	29·9	334	45·1
69	30·5	125	8·5	272	6·7	335	27·5
70	11·6	127	7·9	282	9·4	336	39·5
71	13·6	128	7·7	283	7·3	337	15·2
72	9·3	129	6·0	285	13·4	338	6·7
77	9·8	135·5	1·8	286	7·3	339	3·1
79	7·3	139	10·4	291	7·9	341	3·6
81	15·2	144·5	1·2	294	9·8	342	2·4
82	7·3	145	7·2	295	55·1	350	15·2
83	16·4	146	6·7	296	35·4	351	7·9
85	11·6	147·5	3·1	297	17·1	352	33·6
90·5	2·4	152	7·9	299	16·4	354	12·8
91	9·8	155	18·3	300	4·8	355	11·6
93	8·5	159·5	2·4	303	5·5	368	3·6
94	6·7	165	9·5	306	8·5	369	3·6
94·5	3·6	168	7·3	307	26·7	370	51·8 P
95	16·5	173	7·9	308	11·0	371	18·3
96	9·3	174	6·7	309	8·1	372	7·9

TABLE 5 (contd)

γ-Rhodomycinone Unknown M.Wt. (found) 428
2 KV, 50 eV, slight heat

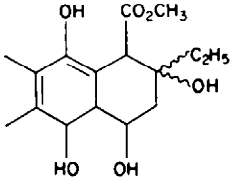
M/e	%	M/e	%	M/e	%	M/e	%	M/e	%	M/e	%
40	4·6	102·5	2·8	135	6·5	231	7·5	330	5·6	382	7·0
41	9·4	103	6·5	136	5·1	261	7·9	331	9·4	392	21·0
42	5·6	105	10·3	137	12·2	268	7·5	332	13·1	393	13·1
43	11·2	107	10·3	138	7·9	269	7·0	333	31·6	394	8·9
44	10·3	108	7·5	139	18·2	270	7·5	334	34·5	395	5·6
45	3·8	109	8·4	140	7·5	289	6·1	335	20·5	396	5·6
55	10·3	110	6·5	141	8·4	290	5·2	336	14·1	408	3·3
56	6·1	110·5	2·8	144·5	1·4	291	6·5	337	10·8	409	3·8
57	19·7	111	9·4	146	4·2	292	4·7	338	10·8	410	9·8
59	4·7	112	6·5	146·5	1·8	293	16·4	339	17·3	411	5·6
60	3·8	113	11·2	147	4·2	294	35·0	340	11·2	412	7·9
67	4·6	114	7·0	147·5	1·9	295	24·3	345	16·8	426	7·0
68	2·8	114·5	2·8	148	1·8	296	18·7	346	9·4	427	6·5
69	17·7	115	17·2	148·5	1·9	297	10·7	347	6·5	428	30·4P
70	7·5	116	5·6	149	6·5	298	7·5	348	7·0	429	17·8
71	14·0	117	5·5	150	6·5	303	5·6	349	12·2		
77	10·3	119	11·2	151	11·2	304	5·6	350	20·6		
79	11·2	120·5	3·8	152	14·0	305	6·5	351	48·6		
81	15·9	123	8·9	155	8·4	306	7·5	352	29·0		
83	16·8	124	5·6	163	9·8	307	9·4	353	16·8		
84	3·8	125	13·1	164	7·5	308	6·4	354	15·1		
85	6·5	126	9·4	165	13·1	309	9·4	359	15·0		
91	10·3	127	14·0	166	6·6	310	7·5	360	100·0		
92	3·7	128	11·7	176	6·5	311	14·1	361	51·2		
93	6·4	129	8·4	177·5	3·3	317	2·8	362	28·1		
93·5	2·8	129·5	2·8	180	6·5	318	11·2	363	15·9		
94	5·6	130	3·7	180·5	3·7	319	9·4	368	12·6		
94·5	3·7	130·5	2·3	181	5·1	320	7·0	369	6·5		
95	15·9	131	7·5	183·5	1·8	321	10·3	370	6·1		
96	9·4	131·5	2·8	188·5	2·8	322	27·1	376	7·0		
97	14·0	132	2·8	189	8·9	323	28·9	377	4·8		
100·5	1·9	132·5	0·9	202	6·5	324	21·5	378	5·6		
101	7·5	133	4·7	205	6·4	325	11·2	380	10·3		
102	6·5	133	3·8	221	6·5	326	5·6	381	7·5		

compound has no carbomethoxyl group, has two hydroxyl groups in the non-aromatic part of the structure, no substituent on C_{10} and, finally, the quaternary centre found in other rhodomycinones is here present also. In general the cracking pattern of this compound is more closely related to that of β- than ε-rhodomycinone. Accordingly a partial structure of the following form is proposed (VII).

TABLE 6

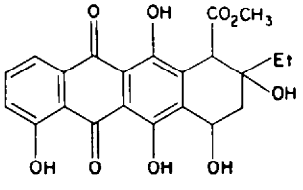
Racemate of ζ-pyrromycinone at C_{10} and C_9 M.Wt. 412

M/e	%	M/e	%	M/e	%	M/e	%	M/e	%	M/e	%
41	2·8	127	2·4	192	1·3	265	1·9	318	2·8	360	1·5
43	3·1	128	2·6	193	1·3	266	1·9	319	4·6	361	2·4
44	2·6	129	1·7	197	2·4	267	2·6	320	6·3	362	5·7
55	3·9	133·5	1·1	205	1·5	268	2·2	321	9·6	363	9·3
56	2·2	137	3·1	211	1·7	269	3·3	322	17·4	364	4·4
57	9·8	139	2·8	220	1·5	270	2·8	323	36·0	365	9·6
59	3·7	140·5	2·6	221	3·3	277	3·9	324	20·5	366	3·7
67	1·7	147·5	5·2	222	1·7	278	4·2	325	9·6	367	1·9
69	2·6	148	3·1	223	1·9	279	7·8	327	2·2	376	3·9
71	1·7	150	1·5	224	1·9	280	9·4	328	1·8	377	5·7
77	1.7	151	2·8	225	4·8	281	5·8	329	1·5	378	3·9
79	1.7	152	2·6	237	1·9	282	4·4	333	36·5	379	4·0
81	1·9	153	2·4	239	1·9	283	2·1	334	100·0	380	10·6
82	1·3	154	1·7	248	2·2	289	2·1	335	37·0	381	9·3
82·5	0·7	155	2·2	259	3·0	290	1·9	336	9·8	382	4·8
83	1·7	169	1·9	250	2·2	291	2·4	337	3·9	383	8·5
84	1·7	161·5	1·3	251	2·4	292	4·4	338	3·9	384	3·5
93·5	0·7	163	2·1	252	3·7	293	6·1	340	4·4	391	1·7
94·5	4·4	164	1·7	253	3·3	294	29·5	348	3·5	392	2·8
95	1·9	165	4·1	254	1·9	295	34·4	349	4·8	393	0·9
97	1·5	166	1·7	255	2·1	296	17·4	350	7·8	394	36·5
103	1·5	167	1·9	256	1·3	297	3·9	351	10·9	395	15·2
105	1·5	168	1·7	261	1·5	303	2·2	352	8·3	408	1·9
107	1·7	169	1·3	263	1·5	304	3·1	353	4·6	409	1·5
108	1·8	171	1·5	265	1·9	305	3·1	354	5·0	412	49·1P
109	1·7	175	1·7	266	1·9	306	14·8	355	9·8	413	25·2
110·5	0·9	176	2·2	267	2·6	307	13·9	356	19·4		
115	3·9	179	1·5	268	2·2	308	11·5	357	12·3		
116	1·5	181	1·8	261	3·3	309	9·3	358	2·1		
119	1·9	189	1·8	263	1·5	317	2·2	359	1·3		



VIII

δ - rhodomycinone ?



IX

ε - rhodomycinone

δ-Rhodomycinone has the cracking pattern shown in Table 5. The abundant ion $(P - 36)^+$ is again present corresponding to two hydroxyl groups in the non-aromatic part of the molecule. On the other hand the presence of an abundant ion $(P - 60)^+$ is consistent with the presence of a carbomethoxyl group in this compound. The base peak $(P - 68)^+$ which also occurs in other rhodomycinones also supports the idea that this is a rhodomycinone. Again a partial structure may be proposed. This

partial structure has to be joined to the 1:4:5-trihydroxyanthraquinone which makes up the rest of the molecule. Joining these fragments in the following way and assuming the distribution of groups shown it will be seen that δ- could be stereoisomeric with ε-rhodomycinone. The cracking patterns certainly resemble each other closely but as they are not identical there is probably some difference in the stereochemistry of the substituents.

ζ-Pyrromycinone and its isomer

A compound which is thought to be the isomer of ζ-pyrromycinone at atoms C_9 and C_{10} has been isolated by Ollis.[6] The marked similarity of the cracking patterns of these two compounds are in agreement with this view. There are, however, some differences in ion abundance as is shown by comparing the following table and the spectrum in Table 2. As has already been mentioned the pyrromycinone spectra are rather simple to analyse as the phenolic anthraquinone system is scarcely fragmented by electron impact. Accordingly the abundant ions mostly refer to dissociations in the non-aromatic portion. Assuming that these two compounds are epimers one may examine them from the point of molecular crowding by the method of Biemann and Seibl.[10] Expressing the abundance of the parent molecular ion $(\overset{+}{P})$ and of $(P - 17)^+$ as a percentage of the total ion current (ΣI) in each case one has

TABLE 7

Compound	Ratio $\overset{+}{(P)}/(P-17)^+$	Ratio $\overset{+}{(P)}/(P-18)^+$
ζ-Pyrromycinone	6·60	1·88
Isomer	3·12	1·30

Now the more crowded epimer should be less stable and thus give rise to more abundant fragment ions. In consequence this epimer would have the smaller value of $\overset{+}{P}/\Sigma I$.

It has, however, been pointed out by Johnsen[11] that this method has certain experimental difficulties. The value of ΣI depends upon the abundance of every ion in the spectrum and in order to arrive at a true value it is essential that the pressure of the sample under examination remain the same. Fluctuations in temperature in the sample system will obviously result in variations in pressure of the sample and this problem may well be important when our technique of placing the sample on a probe in the proximity of the electron beam is employed. Accordingly the method of Johnsen has been employed in which the ratio of the abundance of the appropriate fragment ions are compared. If the two ions are close together in mass and are scanned sufficiently rapidly, the ratio should be independent of pressure variations which will be rather slower.

Provided that one of the ions considered is the parent molecular ion, the more crowded epimer which will have the less abundant parent ion and the more abundant fragment leading to a smaller value of the ratio. In the present example it is clear that the ratio is smaller for the isomer which implies that ζ-pyrromycinone is the more stable and the less crowded epimer.

[10] K. Biemann and J. Seibl, *J. Amer. Chem. Soc.*, **81**, 3149 (1959).
[11] S E. J. Johnsen, *Anal. Chem.*, **19**, 305 (1947).

EXPERIMENTAL

These spectra were obtained using a Metropolitan Vickers Ltd. M.S.2. mass spectrometer in conjunction with a N.E.P. Ultra-Violet Recorder. The sample insertion method has already been described.[12] The compounds were used as supplied.

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[12] Part IX of this series. Tetrahedron **19**, (1963).