THE MASS SPECTROMETRY OF SOME ORGANIC COMPOUNDS

by

Farzanehe Mohammadi-Tabrizi

A thesis submitted to the University of Glasgow
for the degree of Master of Science

March 1964

TABLE OF CONTENTS

		Page
Acknowledgments		
Chapter One	Introduction	1
Chapter Two	Benzanthrones	4
Chapter Three	Ferrocenes	37
Chapter Four	Longifolene derivatives	64
References		96

ACKNOWLEDGMENTS

This work was carried out under the supervision of Dr. R. I. Reed of Glasgow University, to whom the author wishes to express her sincere gratitude for advice and constant encouragement. Thanks are also due to various persons (who are named in the appropriate Chapters) for the provision of the compounds studied; Miss Jean Wilkie for her technical assistance; the International Atomic Energy Agency, Vienna, for a financial grant during the course of the work; Dr. A. A. Azad of the Tehran University Nuclear Centre for enabling me to avail myself of the I.A.E.A. award; Prof. J. M. Robertson for inviting me to study in the Chemistry Department of Glasgow University, and Dr. J. A. Cade of the Cento Institute of Nuclear Science, Tehran, for some help.

A third class of compounds studied was longifolene derivatives of uncertain structure. Here, the occurrence of methyl or isopropyl groups in the molecules was of particular importance, and the presence of abundant ions at $(P-CH_3)$ and $(P-C_3H_7)$ was clearly demonstrated. However, since in such alicyclic hydrocarbons the stability is governed chiefly by stereochemical and conformational factors, it was not possible to make a complete structural analysis from the mass spectral data obtained.

CHAPTER ONE

Introduction

In recent times, mass spectrometry has enjoyed increasingly widespread use in both research work and industry. Many detailed accounts exist (1 to 16) of the theory, construction and operation of mass spectrometers, but the principle on which almost all the instruments depend is quite simple.

Bombardment of a target material with a stream of (50-70eV) electrons, produces positive ions which are accelerated, collimated to a narrow beam by electrodes of different potentials, and finally passed through a mass analyser. The analyser, which can depend on magnetic focussing (1), time of flight measurement (2,3) or radio frequency resonance (4,5), sorts these ions into a spectrum according to their mass-to-charge ratios.

The mass spectrometer is used to measure the ionic mass-to-charge ratio, and also to determine the ionic abundances.

Since the nature of the ions which are formed by electron bombardment is determined by the structure of the target material, the spectrum is unique for each chemical compound so the mass spectrometer is valuable for the analysis of chemical species.

In Thomson's mass spectrograph (6) (1910), the ion beam was passed through electric and magnetic fields, which were parallel and resulted in a separation of ions of different mass-to-charge ratio.

In this way Thomson proved the existence of isotopes of Neon (7).

Aston, in his mass spectrograph, also used electric and magnetic fields applied successively. This produced velocity focussing (8) of the ion beam. Aston was able to obtain accurate atomic weights by an analysis of positive rays, and established the existence of many isotopes among the stable (non-radioactive) elements (9).

In 1919, Dempster (10) made the first mass spectrometer. The method of focusing in his instrument was based on the individual ion beams.

The principle of this instrument was discovered by Classen (11,12). A large number of instruments have been made using this method for focusing the ion beam. In Dempster's instrument, the deflecting angle is 180°, but in the instrument which was developed by Nier (1936-1940) the angle could be 60° or 90°.

Since the single focusing instruments were not capable of giving both velocity and directional focusing, the idea was suggested by Bartky and Dempster of constructing a double-focusing instrument using magnetic and electrostatic analysers (13). Mono-energetic ions are produced by deflection through the electrostatic field, and then traverse the magnetic field which brings them to a focus at the slit. Various designs of such instruments have now been described (14).

Instrumental advances have extended the range of compounds which can be analysed with mass spectrometers. In the conventional mass spectrometer, the sample can be analysed in the vapour phase, so the compounds should have sufficient stability to be heated to a temperature which produces a vapour pressure high enough to give a spectrum.

Various methods have been used for mounting the target material. In the MS2 instrument, which was used to carry out the work described in this thesis, a direct probe was employed. This consisted of a glass probe on which the sample was inserted near to the repeller plate (15,16). This method was useful for mass analysis and determination of molecular weight, but it was not possible to determine and control the sample pressure.

CHAPTER TWO

The mass spectra of some ketones related to benzanthrone

The characteristics of the cracking patterns of aliphatic and some cyclic ketones have been studied by Sharkey, Shultz and Friedel (17) and of selected quinones by Beynon and Williams (18).

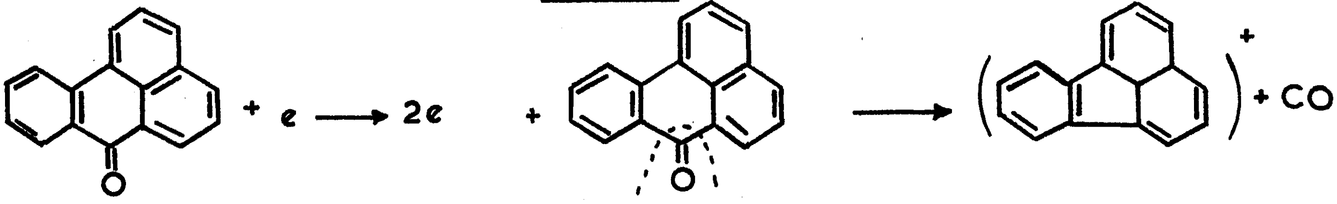
All compounds having a keto group show a tendency to lose a carbonyl group from the molecule, often with re-arrangement.

The present study has been carried out on benzanthrone and some of its derivatives together with a few dihydropleiadenes.

All spectra show the rupture of carbon-carbon bonds in the molecular ion adjacent to a keto group. Finally, they form a stable aromatic hydrocarbon structure.

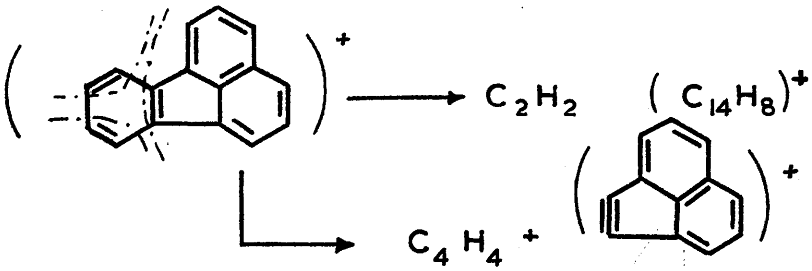
Benzanthrone has its base peak which is also the parent molecular ion at m/e = 230 and an abundant peak at m/e = 202 (82%). This ion comes from the parent ion losing one carbon monoxide with re-arrangement; a metastable peak corresponding to this transition occurs at m/e = 179.5.

Figure 1



After losing the keto group a stable aromatic structure like fluoranthrene, m/e = 202, is formed. Other ions which are significant are P-29 (32%) and P-30 (40%) which are caused by the loss of the elements of a formyl or formaldehyde group respectively. Peaks at m/e = 176 and m/e = 150 arise by the elimination of acetylene, as well as a C_4H_4 group, or two acetylene molecules from the aromatic structure formed by the elimination of the carbonyl group.

Figure 2



In 3-chloro, 3-bromo- and 9-bromo behzanthrones it is not likely that the molecule loses a chlorine or a bromine atom very easily.

There is a metastable ion for the loss of a keto group from the parent ion, in 3-chloro benzanthrone m/e 211 and for the bromine substituted molecule m/e = 254.5.

The rest of the spectrum is similar to that of benzanthrone. The ions at m/e = 201, shows the loss of a carbonyl group and a chlorine or a bromine atom from the respective molecules. The abundant ion at m/e = 200, indicates the loss of carbonyl as well as hydrogen bromide or hydrogen chloride.

3: 9-dibromobenzanthrone shows the same pattern of fragmentation, but there are now two metastable ions corresponding to the following transitions:

$$P + e \longrightarrow P^{+} + 2e$$

$$\quad\quad \hookrightarrow (P{-}CO)^{+} + CO \qquad {}^{m}/_{e} = 334$$

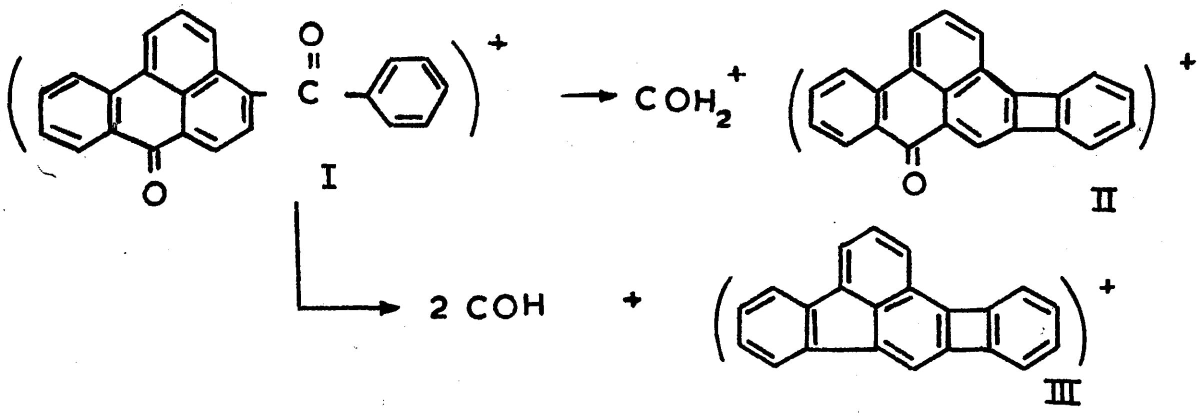
and $$P + e \longrightarrow (P{-}Br)^{+} + Br + 2e$$ where sometimes the charge is on the bromine atom

$$\quad\quad \hookrightarrow [(P{-}Br) - CO]^{+} + CO \qquad {}^{m}/_{e} \quad 253.5$$

There are also doubly charged ions corresponding to all the ions which have been discussed, which shows their great stability.

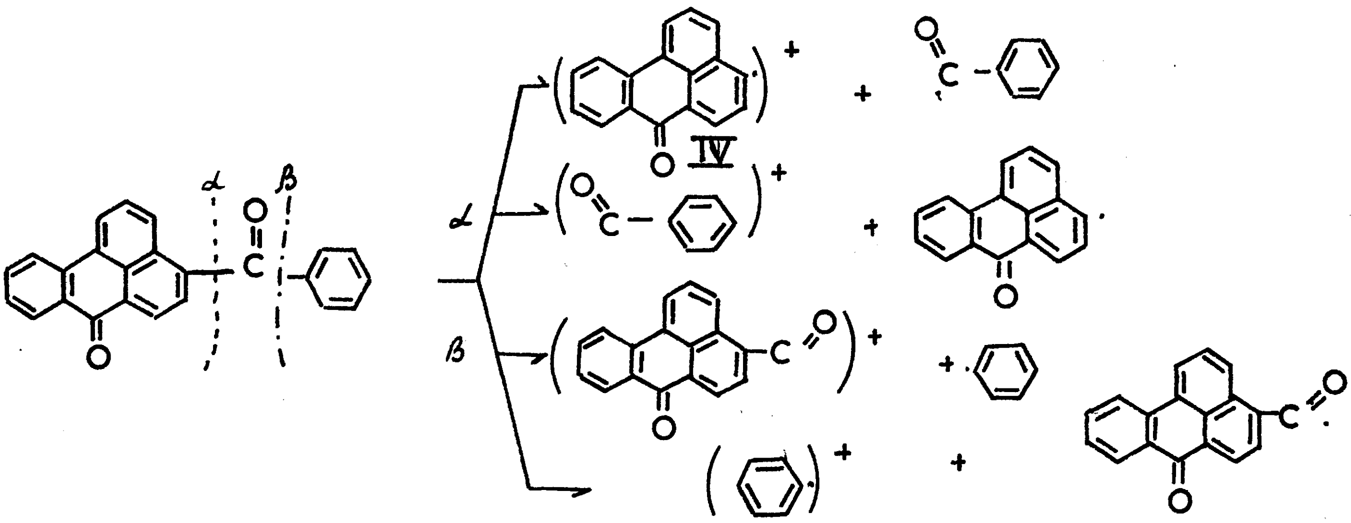
In 4-benzoylmesobenzanthrone we have two keto groups. The loss of the carbonyls can now occur as follows:

Figure 3



The abundances of $(P{-}CO)^{+}$, $(P{-}COH)^{+}$ and $(P{-}H_2CO)^{+}$ are 3%, 10% and 15% of the base peak respectively; which shows that the molecular ions tend to lose a carbonyl group with two hydrogens to form the structure (II) or by losing two formyl groups form a stable aromatic molecule (III). There are doubly charged ions which correspond to all these ions. Meanwhile, molecule (I) can rupture α or β to the carbonyl bond leaving the charge on either fragment.

Figure 4



There are other ions which are less than 10%, e.g. m/e = 51, which is characteristic of fragmentation of a benzene ring and those at m/e = 175, and m/e = 150, which are derived from structure IV by the loss of C_2H_2 and C_4H_4 as well as a carbonyl group.

In 11-hydroxy and 11-methoxybenzanthrone, the characteristics of the cracking patterns of hydroxyl (19) and methoxyl (20) compounds as well as aromatic ketones (21) are observed.

The parent ion in each of them is also the base peak. The (P-28) ion in 11-hydroxybenzanthrone is 22% of the base peak and there is a metastable transition at m/e = 193, corresponding to the loss of a keto group.

$$P^{+} \longrightarrow (P-28)^{+} + CO \qquad {}^{m}/e = 193.0$$

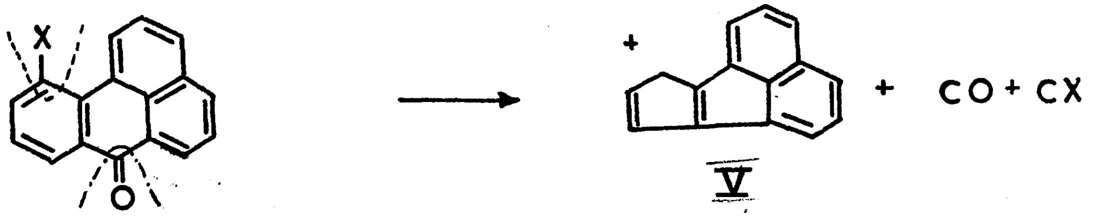
In 11-methoxybenzanthrone, the ion (P-28) is negligible in spite of an abundant $(P\text{-}CH_3)$ (42%). This shows that the molecule tends to lose a methyl radical more readily than to eliminate a carbonyl group, and thus forms the $(P\text{-}CH_3)$ ion which then loses a carbonyl group and gives rise to the metastable ion at m/e = 192.0.

This fragmentation is as follows:

$$\begin{tikzcd}
P^+ \arrow[r] & (P\text{-}CH_3)^+ + CH_3 \arrow[d] \\
 & {[(P\text{-}CH_3) - CO]^+ + CO}
\end{tikzcd}$$

There is a prominent ion at m/e = 189, which arises by the fragmentation of bonds α to the oxygen substituent on carbon (11). The molecule also loses a keto group.

Figure 5



V

This fragment is a stable aromatic ion.

The peak at m/e = 163, corresponds to the loss of twenty-six units from m/e = 189, a fragmentation which may occur in the following way.

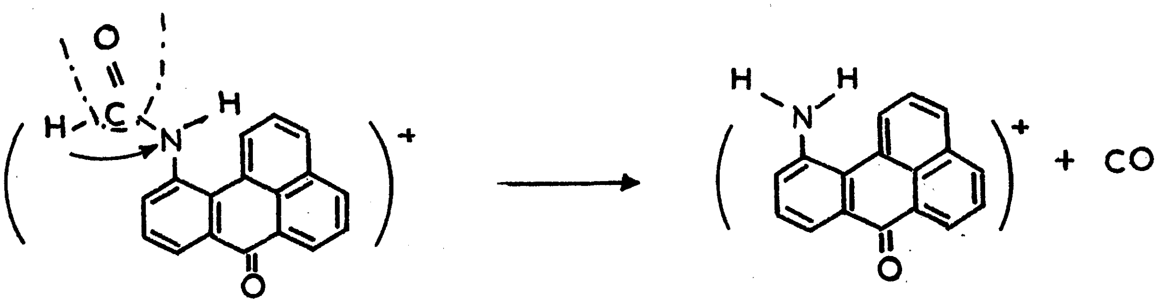
$$(C_{15}H_9)^+ \longrightarrow C_2H_2 + (C_{13}H_7)^+$$

Each of the above mentioned ions gives rise to a peak corresponding to a doubly charged ion, the ion at m/e = 200 corresponds to the loss of the substituent on carbon (11), in addition to the keto group.

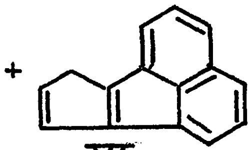
In 11-amino and 11-formylaminobenzanthrone, the parent molecular ion is also the base peak in each case. The loss of the substituent attached to carbon (11) is likely.

Similarity in the electron energy levels of ^{+}O and N may cause the same characteristics in the cracking pattern for nitrogen or oxygen substituted compounds. In these compounds the atom of nitrogen facilitates the elimination of the carbon atom attached to the ring with concomitant re-arrangement and the removal of a thermodynamically stable molecule of hydrogen cyanide or the formation of the isoelectronic ion $H_2{}^{+}CN$.

It seems that in the 11-formyl compound, the cracking pattern may arise in two different ways. Finally, it may lose a keto group attached to the substituent to form a structure similar to 11- aminobenzanthrone and show the same behaviour under electron impact, (22,23) or lose a hydroxyl group. We can interpret these fragmentations as follows:



Giving $H_2{}^{+}CN$ which is quite stable from a thermochemical standpoint and also losing the keto group attached to the molecule to form a stable ion such as:

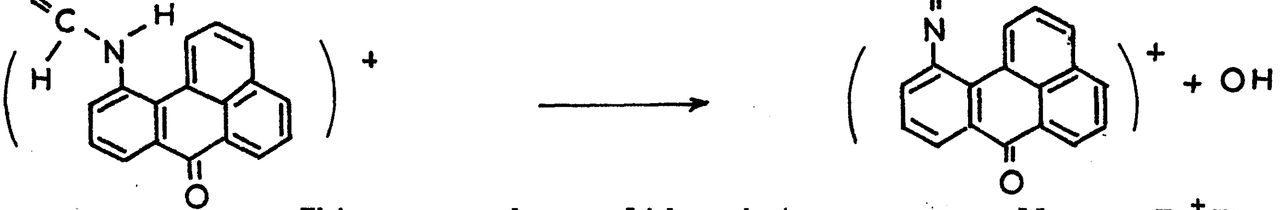


VI

M/e = 189

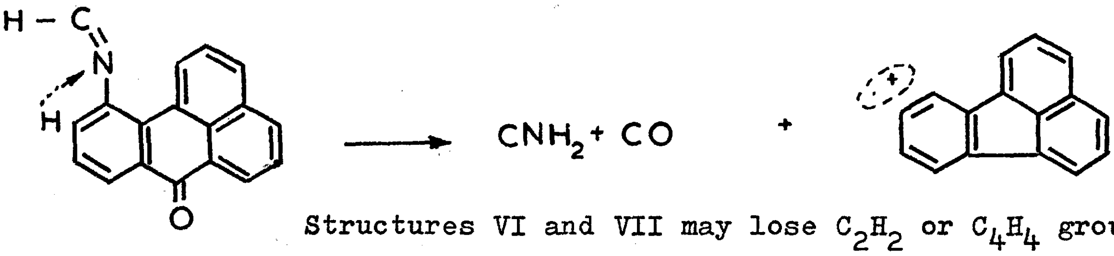
Meanwhile, the 11-formylaminobenzanthrone can lose a hydroxyl group (40%) and form a structure as follows:

Figure 7



This compound may elide a keto group as well as a $H_2{}^{+}CN$ and form an aromatic hydrocarbon of the following type:

Figure 8



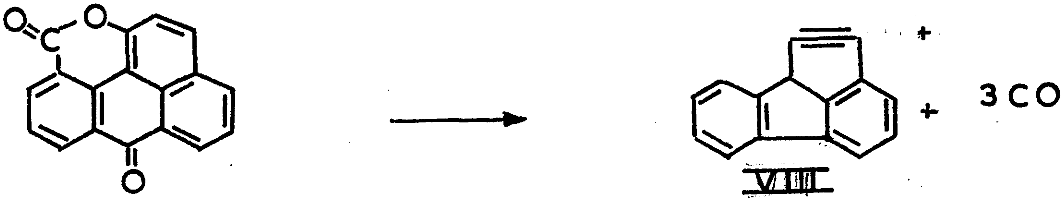
VII

Structures VI and VII may lose C_2H_2 or C_4H_4 groups as do most of the other aromatic hydrocarbon compounds.

In 11:1-benzanthrolactone, the parent molecular ion is very abundant and on losing one of its keto groups, it gives rise to a metastable ion at m/e = 219.0

The loss of a further carbon monoxide is very unlikely, but the ion at m/e = 187 arises by the loss of three carbonyl groups and may form the following structure.

Figure 9



There are doubly charged ions which correspond to all the peaks that have been mentioned above.

Further, there are some peaks of less than 2% abundance which correspond to the loss of acetylene units from structure VIII.

In 9-nitro 1,11- keto and 9-nitro,-11- carboxybenzanthrone, the parent ion is also the base peak. Here the characteristic cracking pattern of a nitro compound (24,25) is apparent P-NO, P-NO_2 and P-CNO_2 are prominent ions which occur in most nitro compounds.

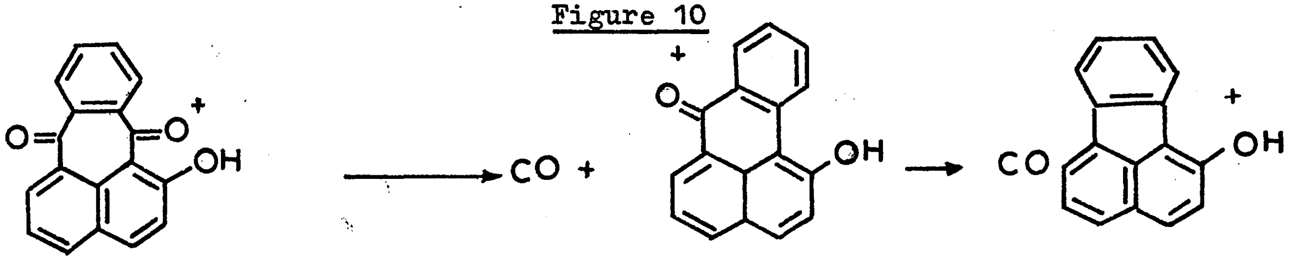
In 9-nitro-1,11-ketobenzanthrone, two ketone groups are eliminated to form a stable aromatic hydrocarbon structure.

In 9-nitro-11-carboxybenzanthrone, there is a peak at P-1 which arises from the loss of the hydrogen of the carboxyl group.

Ions at P-44 and P-45 are characteristic of the cracking pattern of a carboxyl group (26). Additionally, the keto group can be lost and finally form a stable aromatic hydrocarbon structure.

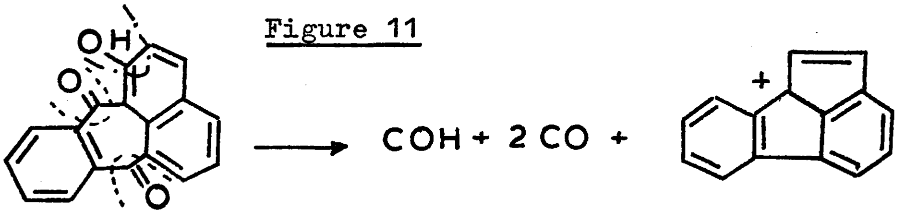
In 1-hydroxy-7,12 dihydropleiadene-7,12 dione, there are two ketone groups attached to the molecule. The parent ion is the base peak and there is the loss of two ketone groups with re-arrangement as follows:

Figure 10



The prominent ion at m/e = 189, corresponds to the loss of two keto groups and CHO from the molecule.

Figure 11



The ion at m/e = 163 may come from this aromatic structure by elimination of acetylene which is of common occurrence in aromatic molecules. Rather abundant ions at half integral masses corresponding to all these have been observed. The possibility of losing a hydroxyl group is not high, but there are ions which correspond to P-OH, P-(OH+CO) and P-(2CO+OH) although their abundances are less than 5%.

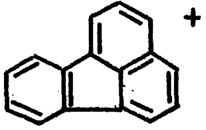
In 1-chloro-7,12 dihydropleiadene-7,12 dione transition for the loss of two ketone groups is as follows:

$$P + e \longrightarrow P^{+} + ze$$

$$\hookrightarrow (P\text{-}CO)^{+} + CO \qquad {}^{m}/e = 240$$

$$\hookrightarrow [(P\text{-}CO) - CO]^{+} + CO \qquad {}^{m}/e = 216$$

The prominent ion at m/e = 200 represents the loss of hydrogen chloride and two carbonyl groups from the parent ion and it may give rise to the structure



IX

There is also the loss of chlorine, and carbon monoxide plus chlorine, from the parent ion. The abundance is less than 20%.

Peaks at m/e = 175 and m/e = 150 are derived from structure IX by the loss of C_2H_2 and C_4H_4 groups respectively. Rather abundant peaks at half mass units correspond to the ions mentioned above.

In 1-methyl-7,12 dihydropleiadene-7-one the P-15 ion is the prominent peak (77%) as we have seen methyl groups attached to such molecules tend to come off very readily. The ion at P-28 (11.9%) which corresponds to the loss of a carbonyl group from the molecule is not very abundant.

A concomitant transition occurs in the following way, with hydrogen migration.

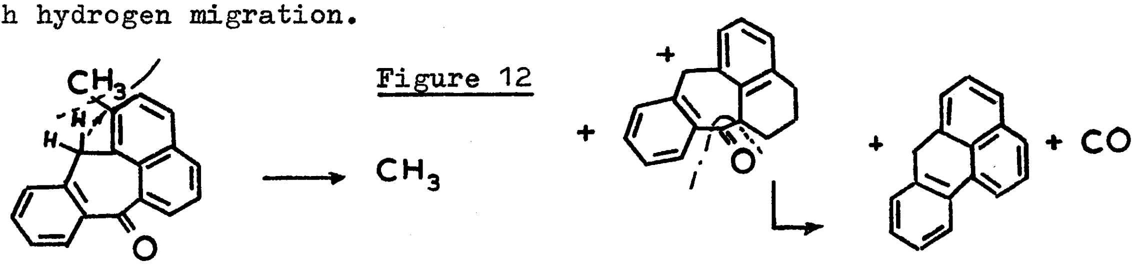


Figure 12

A metastable ion at m/e = 191.0 confirms this rearrangement. Another ion at m/e = 202 may be derived from the loss of ethylene and a carbonyl group from the parent molecule ion. There are doubly charged ions which correspond to these peaks. The presence of an impurity probably of a higher homologue to the extent of about 10% at m/e = 262 will account for the otherwise inexplicable ions at m/e = 224 to 228.

EXPERIMENTAL

All the spectra were obtained on a Metropolitan-Vickers MS2 instrument. An accelerating voltage of 2kV and electron energy of 50ev was used.

For the compounds 11-formylamino, 9-nitro 1,11 keto, 9-nitro 11-carboxy, 11-hydroxy, 4-benzoylmesobenzanthrone, 1-chloro-7,12 dihydropleiadene-7,12-dione and 1-hydroxy-7,12 dihydropleiadene-7,12 dione external heat was applied.

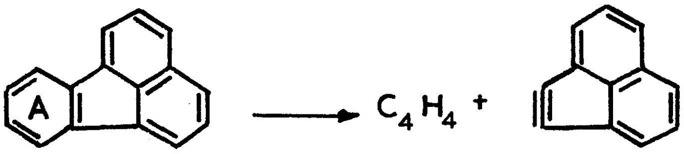
Benzanthrone and its derivatives were provided by Dr. N. Campbell, The University of Edinburgh and the dihydropleiadenes were obtained from Mr. E. Clayton of this department.

DISCUSSION

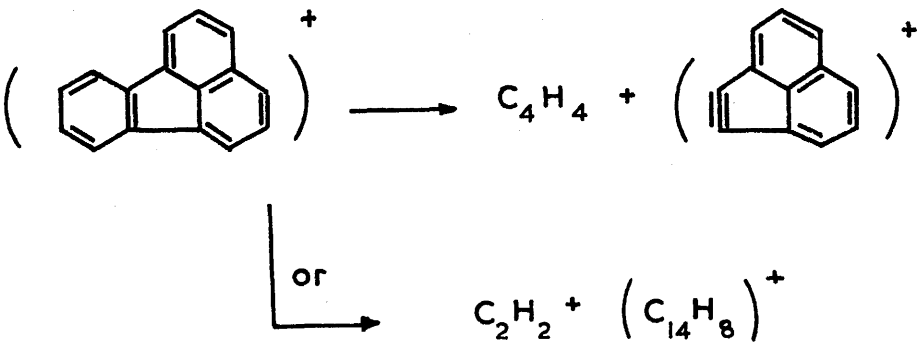
In most aromatic hydrocarbons, one characteristic of their cracking pattern is the loss of one, or more readily two, hydrogen atoms from the parent molecular ion (27). Most of the more abundant ions have a stable structure or they eliminate a stable molecule. So the loss of two hydrogens or in chlorine and bromine derivatives of hydrogen chloride and hydrogen bromide respectively is the more probable.

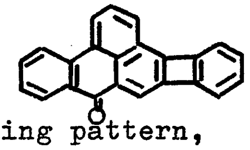
The ions at $m/e = 200$ correspond to the loss of a carbonyl group, as well as one of the substituents (Cl or Br) and a hydrogen. The rest of the molecule may form a triple bond, or extra ring or, preferably, remain with its main structure unaltered but with one or two electrons less in the molecular orbit. This will give rise to a doubly charged ion which has been seen in all spectra.

As the cracking pattern shows, the ions at m/e = 174 and m/e = 150 are derived from ion m/e = 200. The loss of acetylene has been seen in most aromatic hydrocarbons, but it appears that the loss of C_4H_4 is from ring (A) of the molecule.

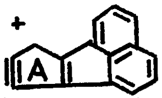
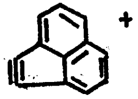


In 4-benzoylmesobenzanthrone, the ion at m/e = 201 is more abundant than ion m/e = 200. This shows that the side chain is not likely to take a further hydrogen atom from the molecule to form a stable structure as with chlorine or bromine. Also in 4-benzoylmesobenzanthrone, the ions at m/e = 175 and m/e = 151 (which are derived from the ion m/e = 201) are more abundant than the ions which occur at m/e = 174 and m/e = 150 in chloro- and bromo- compounds as well as benzanthrone. This indicates that the ions around m/e = 174-176 and 149-151 may be derived from the ions m/e = 200-202 by further fragmentation. It is most probable C_2H_2 and C_4H_4 elide as follows,



In 4-benzoylmesobenzanthrone structure II () is more likely because, as can be seen from the cracking pattern, the stability of the bonds in the α or β positions is less than the stability of the bonds attached to $C_{(7)}$.

There is no evidence for ions corresponding to the further break down of the molecule once it has lost the carbonyl group from the benzanthrone skeleton.

In 11-hydroxy-, 11-methoxy-, 11-formyl- and 11-aminobenzanthrone ions at about m/e = 189 have the same origin. In all of them carbon (11) tends to be removed because of the effect of the substituent on it which weakens the bonds. Finally, it forms the stable ion VI (). The ion at m/e = 163 is formed by the elimination of an acetylene group from the ion just discussed. Here it seems also that the ion does not alter its structure by the loss of acetylene. It is more likely that the acetylene comes from part (A) of the molecule because this is already electron deficient. Ions at about m/e = 150 which are present in most compounds discussed and which have an abundance less than 2% of the base peak, may occur by the loss of ring (A) with the formation of the  ion.

A doubly charged ion at m/e = 81.5 which corresponds to the ion m/e = 163 may arise by the loss of acetylene from the ion (VI) taking two electrons from it and leaving the remainder doubly charged.

In the compound 11-aminobenzanthrone, the ion (P-28) may be caused by the loss of a carbonyl or the H_2CN group; also the ions (P-30) and (P-31) which occur in the spectrum of aniline and some amino-compounds by re-arrangement (28) but, unfortunately, the resolving power of our instrument was not high enough to distinguish between these possibilities.

Benzanthrone

m/e	%	m/e	%
74	0.90	164	0.45
75	1.50	173	1.05
76	0.60	174	6.08
77	0.45	175	5.10
87	1.50	176	5.03
88	3.52	177	1.12
98	0.90	179	0.75
99	1.50	180	0.75
99.5	1.20	187	0.45
100	5.30	198	6.10
100.5	3.07	199	11.44
101	9.16	200	40.45
111	0.67	201	32.05
115	2.10	202	82.44
123	0.60	203	33.58
125	0.45	<u>230</u> <u>P</u>	100.00
126	1.05	231	51.14
149	1.65		
150	4.58		
151	2.62		
152	2.62		
153	0.45		
161	0.45		
162	0.60		
163	1.72		

3-chloro benzanthrone

m/e	%	m/e	%	m/e	%
71	0.69	174	5.80	239	4.18
75	0.92	175	4.29	264 P	100.00
81	0.92	176	1.27	265	41.69
83	0.46	197	1.62	266	39.37
87	1.74	198	8.13	267	14.40
91	0.69	199	12.42		
95	0.81	200	40.74		
97	0.69	201	29.03		
98	1.16	202	8.24		
99	1.85	203	1.50		
99.5	1.97	210	1.39		
100	9.05	211	1.50		
100.5	5.45	212	1.62		
101	1.74	213	1.85		
110.5	1.39	214	1.62		
111	0.58	215	1.39		
118	5.22	229	1.62		
119	2.55	230	2.32		
123	0.69	231	1.16		
132	1.97	232	0.58		
133	0.92	234	1.74		
149	1.62	235	3.01		
150	3.01	236	36.93		
151	1.97	237	12.89		
173	1.39	238	13.24		

3-bromo meso benzanthrone

m/e	%	m/e	%	m/e	%
74	1.49	155	2.29	264	5.20
75	1.72	173	1.49	265	2.06
79	0.45	174	7.81	266	1.95
80	1.37	175	5.74	267	0.80
82	1.26	176	1.60	280	19.31
87	3.21	197	2.06	281	8.62
87.5	1.49	198	10.34	282	20.00
95	3.21	199	16.09	283	6.89
98	1.14	200	56.47	308	96.47
99	2.87	201	51.76	309	42.35
99.5	3.44	202	16.89	310	100.00
100	16.09	203	3.44	311	37.64
100.5	12.87	228	0.91		
101	5.40	229	3.79		
114.5	1.83	230	7.12		
115	1.26	231	2.29		
122	0.68	236	1.95		
123	1.03	237	0.68		
126	0.57	238	0.68		
135	0.45	252	0.91		
140	3.44	253	1.37		
141	3.56	254	1.95		
149	2.06	255	2.29		
150	4.71	256	2.52		
151	2.75	257	2.29		
152	0.57	258	2.06		
154	2.06	259	1.37		

9-bromo benzanthrone

m/e	%	m/e	%
87	4.14	202	10.99
87.5	1.65	229	6.42
98	1.65	230	2.90
99	4.14	253	1.03
99.5	5.39	254	1.65
100	21.15	255	2.07
100.5	15.55	256	2.48
101	5.39	257	2.48
114.5	1.86	258	2.07
140	4.97	259	1.45
141	5.39	280	10.16
149	2.69	281	4.14
150	4.97	282	9.95
151	2.90	283	2.09
154	3.94	308 P	100.00
155	4.14	310 P	100.00
173	1.24	311	34.63
174	5.59		
175	4.56		
197	2.48		
198	9.54		
199	14.93		
200	49.99		
201	42.30		

3,9-dibromo benzanthrone

m/e	%	m/e	%	m/e	%
74	2.26	175	1.13	308	5.82
75	1.61	179	1.61	309	1.61
80	2.91	180	3.39	330	0.97
82	2.26	181	1.61	331	1.29
87	3.39	193	1.94	332	1.61
98	2.58	194	3.88	333	1.77
98.5	1.29	195	2.26	334	2.26
99	6.14	197	2.10	335	1.61
99.5	5.82	198	11.32	336	1.29
100	16.17	199	13.26	337	1.29
100.5	6.14	200	44.09	358	3.39
101	1.29	201	12.29	360	6.47
110	0.64	202	2.26	362	3.55
111	0.80	228	2.91	386 P	51.47
122	1.29	229	1.29	388 P	100.00
139	1.77	253	0.80	390 P	55.87
139.5	3.39	254	1.13		
140	2.91	255	1.13		
140.5	3.55	256	0.97		
141	1.61	276	2.42		
149	1.61	277	4.84		
150	2.91	278	4.04		
151	1.29	279	4.85		
153	1.13	280	2.10		
154	1.29	305	3.88		
173	1.13	306	6.14		
174	3.55	307	5.17		

4-benzoylmesobenzanthrone

m/e	%	m/e	%
51	6.24	276	10.41
77	37.49	277	6.94
78	4.16	278	4.16
105	27.77	279	2.08
106	2.77	288	3.47
138	3.47	303	3.81
138.5	2.43	304	15.27
150	2.43	305	10.41
151	2.08	306	3.12
167	5.55	317	3.12
167.5	3.12	332	3.47
174	2.77	333	14.93
175	4.16	334 P	100.00
198	2.77	335	44.99
199	7.29		
200	35.41		
201	47.66		
202	11.80		
229	10.06		
230	4.16		
257	22.22		
258	7.63		
274	4.51		
275	2.77		

11-methoxy benzanthrone

m/e	%	m/e	%	m/e	%
71	0.17	112	0.31	190	10.05
74	0.53	113	0.49	191	1.74
75	0.53	115	0.35	192	0.62
80	0.22	116	0.62	193	0.53
81	0.62	119	0.17	198	1.12
81.5	1.97	121	0.31	199	1.43
82	0.76	122	0.17	200	4.48
83	0.26	122.5	0.44	201	2.55
85	0.22	123	0.49	202	2.37
86	0.53	124	0.17	203	0.80
87	1.16	125	0.22	216	0.85
88	0.67	126	0.22	217	6.28
89	0.53	129	0.40	218	1.97
93	0.53	130	4.30	229	0.80
93.5	2.51	130.5	1.74	230	3.49
94	2.55	131	0.31	231	4.84
94.5	5.74	137	0.49	232	3.05
95	1.74	139	0.53	233	0.98
96	0.17	150	0.94	244	2.24
98	0.44	151	0.62	245	42.21
99	0.62	161	1.16	246	14.57
99.5	0.53	162	1.70	247	2.78
100	2.15	163	6.19	248	0.44
100.5	1.07	164	1.16	257	1.52
101	1.70	174	0.94	258	1.70
101.5	0.62	175	0.62	259	4.03
107	0.40	184	0.44	260 P	100.00
108	0.44	185	1.07	261	29.64
108.5	0.71	186	2.60	262	5.11
109	0.49	187	11.55	263	0.67
110	0.44	188	8.05		
111	0.62	189	45.22		

11 hydroxy benzanthrone

m/e	%	m/e	%	m/e	%
63	1.36	111	0.73	186	2.72
74	0.79	112	0.34	187	14.84
75	0.79	113	0.85	188	12.49
81	0.56	122	0.39	189	55.46
81.5	1.93	123	4.31	190	18.74
82	1.07	123.5	1.93	191	3.12
86	0.79	124	0.39	192	0.51
87	1.59	126	0.45	193	0.79
88	0.56	137	0.96	194	0.90
89	0.62	138	0.45	195	0.90
93	0.45	139	1.19	196	0.56
93.5	2.49	149	0.28	198	0.79
94	4.37	150	1.19	199	0.79
94.5	11.71	151	0.85	200	1.70
95	4.64	152	0.34	201	1.07
96	0.39	161	1.87	202	1.24
97	0.22	162	2.72	205	0.45
98	0.68	163	10.93	216	0.51
99	0.73	164	6.24	217	2.38
100	0.90	165	1.30	218	22.65
109	4.65	174	0.62	219	6.24
109.5	2.10	175	0.45	220	1.07
110	0.79	185	1.02	229	0.73
				230	0.79
				244	1.64
				245	8.80
				246 P	100.00
				247	33.59
				248	6.24

11 amino benzanthrone

m/e	%	m/e	%	m/e	%
71	0.84	139	0.70	216	12.91
81	0.98	150	1.12	217	16.56
81.5	2.10	151	0.84	218	5.61
82	0.98	152	0.56	219	1.12
83	0.70	162	1.12	230	1.12
93.5	2.10	163	4.21	243	5.89
94	3.08	164	2.24	244	17.54
94.5	6.87	165	2.24	245 P	100.00
95	3.22	186	1.40	246	31.57
95.5	3.36	187	6.73		
96	0.56	188	6.45		
100	1.40	189	21.05		
107.5	3.08	190	8.56		
108	1.68	191	1.96		
108.5	4.49	198	0.84		
109	1.68	199	1.12		
111	0.56	200	3.50		
113	0.42	201	1.82		
113.5	2.52	202	0.84		
114	1.12	205	1.54		
122	0.84	212	1.12		
122.5	3.78	213	1.40		
123	1.68	214	7.01		
137	0.56	215	7.01		

11-formyl amino benzanthrone

m/e	%	m/e	%	m/e	%
81.5	7.88	135	2.72	190	20.40
93	5.00	136	2.04	191	4.08
93.5	10.20	136.5	4.66	200	4.08
94	14.96	137	5.44	201	2.72
94.5	21.08	138	2.72	211	3.40
95	14.96	139	3.40	212	4.08
95.5	8.84	148	2.04	213	19.04
96	4.76	149	6.12	214	14.96
99	3.40	150	4.76	215	17.68
99.5	2.04	151	4.08	216	21.08
100	4.76	152	2.72	217	10.20
100.5	2.72	161	3.40	243	10.88
104	7.48	162	5.44	244	25.84
105	4.76	163	12.24	245	58.48
107	5.44	164	6.80	246	30.60
107.5	9.52	165	5.44	254	4.08
108	6.80	166	2.04	255	8.84
108.5	11.56	174	2.72	256	40.80
109	8.84	175	2.72	257	20.40
113	2.72	176	2.72	271	12.24
113.5	6.12	177	2.04	272	13.60
114	5.44	185	2.72	273 P	100.00
121.5	2.04	186	4.08	274	54.40
122	2.72	187	20.40		
122.5	6.80	188	19.04		
123	5.78	189	51.68		

11:1 benzanthrolactone

m/e	%	m/e	%	m/e	%
63	0.96	135.5	0.53	221	0.37
74	0.64	136	3.52	242	0.32
75	0.53	136.5	1.49	243	2.51
81	0.96	137	0.80	244	16.66
86	0.96	138	0.32	245	4.59
87	1.17	161	1.97	246	0.74
93	1.81	162	1.65	272 P	100.00
93.5	6.83	163	0.42	273	34.02
94	8.33	184	0.53	274	5.55
94.5	2.24	185	1.70		
95	0.16	186	6.03		
98	0.64	187	24.30		
99	0.37	188	13.88		
108	2.02	189	2.51		
108.5	0.74	190	0.37		
109	0.26	198	0.48		
110	0.90	199	0.53		
111	0.85	200	0.74		
113	0.26	215	0.74		
122	3.31	216	2.02		
122.5	1.12	217	0.74		
123	0.32	218	0.58		
134	0.37	219	0.69		
135	0.53	220	0.58		

9-nitro-1-carboxybenzanthrone

m/e	%	m/e	%	m/e	%
71	1.41	151	3.30	243	1.88
83	1.41	156	2.83	244	3.77
85	1.88	157	6.36	245	22.64
87	3.06	158	1.88	246	7.07
93.5	3.06	163	2.35	247	1.41
94	3.77	174	3.30	256	3.30
94.5	9.43	175	2.59	259	12.26
95	3.06	176	1.88	260	2.83
97	1.88	177	1.41	261	2.35
98	1.41	185	9.90	269	1.41
99	1.88	186	3.30	271	3.06
99.5	2.12	187	11.32	272	9.43
100	5.66	188	7.78	273	10.84
100.5	1.88	189	9.90	274	4.24
105	2.35	190	2.35	275	7.54
109	2.59	197	2.35	276	1.88
111	2.83	198	8.97	287	5.42
112	4.71	199	18.16	288	6.60
113	2.35	200	35.14	289	16.50
122	3.30	201	19.33	290	4.71
123	5.66	202	4.24	302	5.66
124	2.12	205	2.35	303	2.12
125	2.35	213	2.35	317	12.49
128	2.35	215	1.41	318	37.49
129	5.18	216	3.06	319 P	100.00
136.5	2.12	217	2.12	320	30.66
137	2.35	227	3.30	329	2.83
139	3.30	228	5.66	330	1.65
149	6.13	229	3.06	334	2.35
150	3.77	233	3.30		

9 nitro 1:11 keto benzanthrone

m/e	%	m/e	%	m/e	%
77	4.83	125	1.99	227	10.33
81	1.66	129	2.33	228	2.99
82	0.99	135	1.66	242	1.66
83	1.99	135.5	1.33	243	12.83
84	0.99	136	1.33	244	4.83
85	1.33	137	1.66	245	2.16
86	1.66	139	1.66	246	0.99
87	1.99	149	3.83	255	49.99
93	1.83	158	2.49	256	16.66
93.5	2.83	173	1.99	257	2.99
94	3.16	185	5.99	259	3.99
95	0.99	186	3.99	269	0.99
97	0.66	187	12.66	270	3.99
98	1.83	188	4.33	271	37.49
99	7.33	189	1.33	272	18.83
99.5	6.49	196	1.33	273	4.99
100	2.33	197	5.49	274	0.99
107	1.66	198	27.08	287	4.66
108	1.49	199	45.83	288	1.66
109	1.99	200	10.99	289	0.99
110	2.33	201	2.49	301 P	100.00
111	3.66	202	1.33	302	29.16
112	3.49	203	1.33	303	5.99
113	2.16	212	1.66	317 i	6.66
113.5	2.33	213	1.99	318 i	1.99
119	1.66	214	3.33	328 i	1.33
122	2.99	215	2.99		
123	5.83	216	1.33		
124	1.99	217	0.99		

1-methyl-7,12-dihydropleiadene-7-one

m/e	%	m/e	%	m/e	%
39	1.01	86	0.40	106.5	7.68
41	1.05	87	0.97	107	8.43
43	1.05	88	2.64	107.5	21.33
50	0.48	88.5	0.81	108	7.68
51	0.89	89	1.50	109	1.17
55	1.17	89.5	0.69	110	0.60
56	0.48	90	0.56	111	0.97
57	1.09	91	0.48	111.5	1.01
62	0.32	93	0.52	112	3.09
63	1.34	93.5	1.38	112.5	3.65
64	0.36	94	2.11	113	14.13
65	0.32	94.5	7.93	113.5	8.43
67	0.48	95	3.09	114	21.33
69	0.89	96	0.48	114.5	10.16
70	0.48	97	0.65	115	11.90
71	0.65	98	0.56	115.5	3.96
74	0.56	99	0.81	116	1.13
75	1.05	99.5	0.85	117	0.32
76	1.30	100	3.49	118	0.28
77	1.17	100.5	2.84	118.5	0.36
78	0.32	101	7.93	119	0.89
79	0.32	101.5	3.96	119.5	0.85
81	0.73	102	1.46	120	0.85
81.5	0.60	103	0.40	121	4.47
82	0.56	104	0.32	121.5	2.43
83	0.56	105	0.85	122	1.05
84	0.32	105.5	1.05	123	0.52
85	0.40	106	2.60	124	0.32

1-methyl-7,12-dihydropleiadene-7-one

2

m/e	%
125	0.56
126	1.13
127	0.97
127.5	0.69
128	2.03
128.5	1.05
129	2.43
129.5	1.05
130	0.32
131	0.20
133	0.32
134	0.28
135	0.56
135.5	0.40
136	1.87
136.5	0.81
137	0.77
138	0.73
139	2.72
140	0.69
141	0.32
148	0.16
149	0.73
150	2.23
151	2.48
152	3.25
153	0.93
161	0.48
162	0.77
163	2.72
164	1.13
165	1.58
166	0.44
173	0.24
174	1.30
175	1.50
176	1.09
177	0.85
178	0.56
179	0.40
180	1.46
181	0.56
185	0.40
186	1.05
187	3.98
188	2.92
189	6.44
190	2.35
191	1.05
192	0.93
193	0.77
194	0.48
198	1.09
199	2.23
200	6.69
201	6.44
202	11.15
203	3.96
213	17.70
214	14.58
215	63.51
216	21.87
224	4.96
225	7.93
226	19.21
227	16.61
228	23.81
229	28.77
230	11.90
243	77.08
244	26.04
257	22.91
258 P	100.00
259	23.95

1 chloro 7,12 dihydropleiadene 7,12-dions

m/e	%	m/e	%	m/e	%
50	7.44	98	5.95	120	1.15
51	5.78	99	14.21	121	0.99
55	1.65	99.5	15.21	122	2.81
62	2.31	100	58.33	123	5.45
63	4.96	100.5	27.08	124	2.97
74	8.92	101	7.44	125	7.60
75	14.05	101.5	1.81	126	3.80
76	7.71	105	6.44	131.5	1.48
77	3.47	105.5	3.30	132	6.94
80	1.15	106	3.63	132.5	3.14
82	1.15	106.5	2.14	133	3.30
82.5	0.99	107	0.66	133.5	0.99
83	0.82	107.5	0.66	134	0.99
85	0.99	108	0.82	135	1.32
86	3.47	109	2.48	137	1.32
86.5	2.31	110	2.48	138	0.82
87	13.22	111	2.97	139	0.66
87.5	5.78	112	0.99	145.5	0.99
88	2.97	113	1.81	146	1.15
89	0.66	114	3.80	146.5	0.66
92	0.99	114.5	5.95	147	1.15
93	1.32	115	2.31	148	1.15
93.5	1.98	117	2.31	149	4.62
94	2.48	117.5	4.96	150	8.59
94.5	4.13	118	37.49	151	5.62
95	2.31	118.5	14.21	152	0.99
96	0.99	119	13.88	160	4.29
97	1.32	119.5	4.79	161	2.97

1 chloro 7,12 dihydropleiadene 7,12-dions

2

m/e	%	m/e	%	m/e	%
162	3.63	228	2.14	268	1.65
163	3.14	229	12.07	290	1.32
164	0.66	230	4.29	291	21.99
173	3.80	231	0.82	292 P	100.00
174	14.05	234	3.30	293	37.49
175	10.58	235	10.25	294	35.41
176	2.48	236	68.74	295	10.91
197	4.46	237	24.80	296	2.31
198	16.86	238	27.11		
199	31.24	239	9.92		
200	95.83	240	4.29		
201	60.41	241	2.97		
202	13.22	242	1.65		
203	2.64	243	2.14		
209	1.98	244	1.32		
210	3.30	257	19.51		
211	4.46	258	7.77		
212	4.13	259	1.81		
213	4.62	263	9.25		
214	2.97	264	81.24		
215	2.64	265	28.10		
216	1.65	266	29.16		
227	0.82	267	9.25		

1 hydroxy 7,12 dihydropleiadene 7,12-dions

m/e	%	m/e	%	m/e	%
39	2.86	87	3.14	112	0.81
41	5.46	88	2.18	113	4.64
42	1.50	89	1.36	114	2.86
43	3.82	91	3.14	115	1.91
50	1.50	92	0.68	117	1.09
51	2.32	93	2.73	118	0.95
53	1.91	93.5	2.73	119	1.91
55	7.65	94	6.55	120	0.95
56	1.36	94.5	15.71	121	1.36
57	1.50	95	8.87	122	1.22
62	1.36	96	1.36	122.5	1.09
63	3.82	97	2.18	123	6.01
65	1.36	98	1.50	123.5	1.77
67	2.45	99	1.50	124	1.09
69	3.14	100	2.32	125	0.81
75	2.18	100.5	0.81	126	0.81
76	2.04	101	0.81	131	1.09
77	4.23	103	0.54	132	0.54
78	0.68	104	0.68	133	1.91
79	2.18	105	3.00	134	0.81
80	0.81	106	1.09	135	1.22
81	3.27	107	2.04	136	0.81
81.5	2.86	108	1.09	136.5	0.81
82	2.73	109	10.51	137	2.04
83	1.36	109.5	3.27	138	1.36
85	0.68	110	2.04	139	2.32
86	1.63	111	1.50	145	0.95

1 hydroxy 7,12 dihydropleiadene 7,12 dions

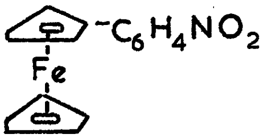
2

m/e	%	m/e	%	m/e	%
146	0.54	195	0.81	274 P	100.00
147	1.09	198	1.36	275	30.32
148	1.36	199	1.63	276	6.01
149	1.09	200	4.09	277	1.09
150	2.32	201	3.00		
151	1.22	202	1.36		
152	0.68	203	0.81		
159	0.81	216	1.22		
160	0.54	217	6.96		
161	2.18	218	26.22		
162	3.00	219	7.65		
163	11.20	220	2.59		
164	3.96	221	1.77		
165	0.95	222	1.77		
173	0.81	223	1.50		
174	1.63	224	0.81		
175	1.36	229	2.32		
176	1.63	230	1.36		
185	1.36	232	2.04		
186	3.82	244	1.91		
187	16.12	245	14.48		
188	15.57	246	88.52		
189	59.83	247	24.59		
190	18.98	248	4.64		
191	3.27	249	1.09		
192	0.81	257	1.77		
193	0.81	258	0.54		
194	1.09	273	24.59		

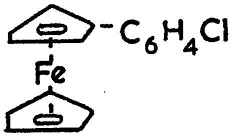
CHAPTER THREE

The Mass Spectra of some Ferrocenes

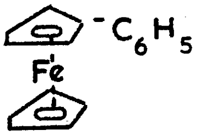
Previous studies in this class of compounds have been mainly concerned with the electron-impact measurements of ionization potential (29) and with some mass spectra of the simple cyclopentadienyls (30). One or two isolated reports of such spectra (68) have been made and the present communication extends the investigation to a wider range of substituted cyclopentadienyl iron compounds. The structure of the compounds studied are given below:



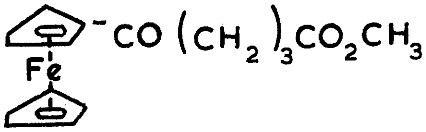
1



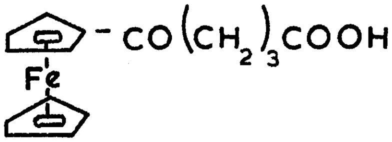
2



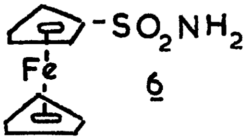
3



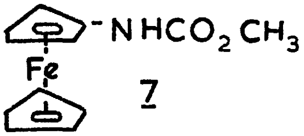
4



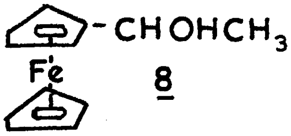
5



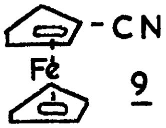
6



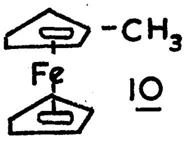
7



8



9



10

The known stability and 'aromatic' character of ferrocene compounds is quite consistent with the present observation that the most abundant ion, the base peak, is also the parent molecular ion. This ion is much more abundant than any other ion in the spectrum, a feature which is also found in the spectra of aromatic hydrocarbons.

It is usually considered that the further oxidized ferrocene which has a ferric ion atom is unstable and decomposes in solution. Since the ionization of the process ferrous to ferric is very much less than any other plausible electron removal in the molecule (69,70), it is reasonable to suppose that the electron removed in the reaction:

$$Fe(C_5H_5)_2 + e — Fe(C_5H_5)_2{+} + 2e$$

comes from the iron atom. It must be inferred from this that the time which elapses between ionization and collection of the ion, about 1 x 10^{-6} sec., is too short for the break-up of the ferrocinium ion.

Consideration of the structure of a ferrocene suggests that the molecular ion might fragment by the loss of one ring from the structure or, less probably, by the loss of the iron. An examination of the present spectra shows little evidence for the loss of fifty-six mass units corresponding to the iron or, except in one instance, of the removal of sixty units. In the exceptional case, the appropriate mass could be obtained from the attached side chain $-CO-(CH_2)_3CO_2H$.

Analysis of a large number of aromatic compounds possessing an alkyl side-chain (52) has shown a preferred point of fission at the benzylic carbon-carbon bond (49). This phenomenon has been examined in considerable detail by Meyerson and his collaborators (50,52,53) who have provided a rational explanation for this and related observations. These authors suggest that the driving-force for such bond-fission is the formation of tropylium ion, a thermodynamically stable product.

An examination of the present spectra shows that such an effect does not operate in the ferrocenes. Fragmentations that occur do so in accordance with the usually recognized weak bonds in the ions. In particular the methyl cyclopentadienyl iron ion does not show a facile loss of hydrogen atom as is the case with the toluene ion. Thus it seems that on the present, rather limited evidence, there is no similarity in the modes of fission of the ferrocenes and corresponding aromatic compounds.

These analyses were made using a Metropolitan-Vickers MS2 mass spectrometer in the usual way.

We wish to acknowledge with thanks the kind provision of the ferrocene compounds by Professor P. L. Pauson of the Royal College of Science and Technology, Glasgow.

CHAPTER THREE

The mass spectra of some ferrocenes

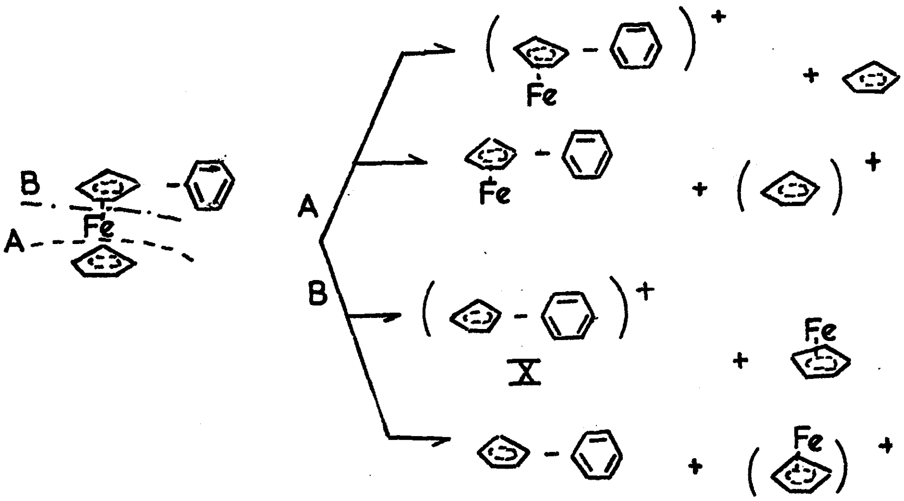
Previous studies in this class of compounds have been mainly concerned with electron impact measurements of ionization potential (29) and with some mass spectra of the simple cyclopentadienyls (30, 31, 32).

The present studies have been carried out to examine the characteristic cracking patterns of ferrocene and some of its derivatives. In all spectra except one the molecular ion is the most abundant, the base peak. This evidence shows that this class of metallo-organic compounds has high stability arising from the conjugation of the cyclopentadiene rings through the iron atom.

Ferrocene has the base peak and the molecular ion at m/e $=$ 186, the prominent peaks in the ferrocene spectrum being at m/e $=$ 121 and m/e $=$ 56 and arising from the bond fission of iron to the ring (C_5H_5). The ion at m/e $=$ 121 may split in two different ways and give rise to $C_3H_3Fe^+$ (m/e $=$ 95) and C_2HFe^+ (m/e $=$ 81) ions; their abundance is less than 10% of the base peak. The ion at (P-2) corresponds to an isotope of the iron atom. The molecular ion also gives rise to a doubly charged ion at m/e $=$ 93.

In phenylferrocene there is evidence of the loss of a cyclopentadiene ring (C_5H_5), or of C_5H_5Fe which gives the following ions:

Figure 13

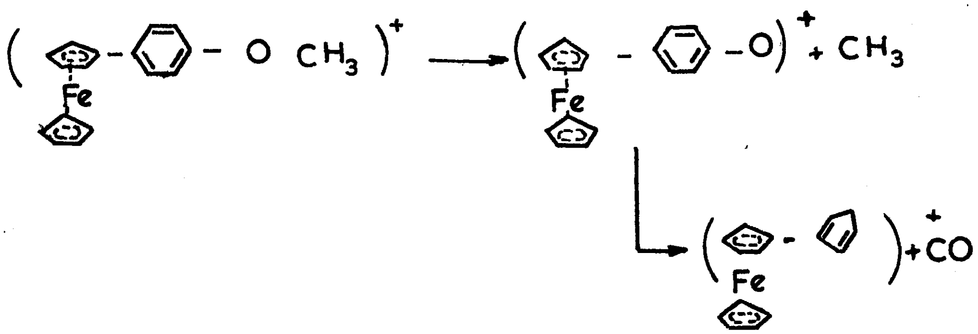


Compound X is an aromatic one and there is the loss of acetylene group from the molecule to form an ion at m/e = 115. The rest are the ions which have been seen in the ferrocene spectra.

In m-chlorophenylferrocene there is the possibility of losing the chloro substituent; also p-nitrophenylferrocene shows a tendency to lose 'O', NO, NO_2 and CNO_2 groups from the molecular ion which is one of the characteristics of the cracking pattern of nitro compounds (25,26). The rest of the spectrum is similar to that of phenylferrocene, although the molecule may lose C_5H_5 or C_5H_5Fe. It also elides the substituent on the benzene ring together with one hydrogen atom. The ion m/e = 140 arises from this fragmentation and there is a further possibility of the loss of an acetylene molecule from the ion to yield a new ion less than 5% of the base peak.

In p-anisylferrocene the loss of methyl and methoxyl groups from the molecular ion is accompanied by the metastable ions at m/e = 263 and m/e = 224 respectively.

Figure 14

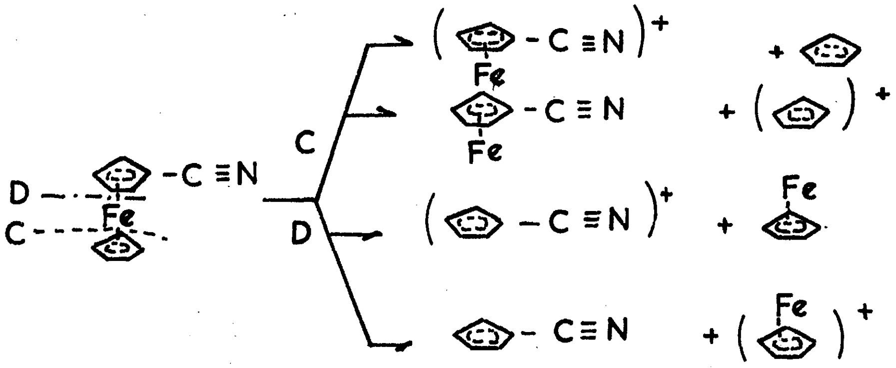


Additionally, the following metastable transitions were observed:

m/e	Process
143	171^+ .... 156^+ + CH_3
107	156^+ .... 128^+ + CO

The rest of the spectrum is similar to m-chloro or p-nitro phenylferrocene. In cyanoferrocene there is the evidence of the loss of a hydrogen cyanide molecule. Fissions may also occur in the following ways:

Figure 15



There is, moreover, the possibility of fission at 'C' and 'D' bond positions simultaneously to give the iron atom ion at m/e = 56. Further, the (C_5H_5Fe) fragment may split in two different ways and give rise to the ions (FeC_3H_3) at m/e = 95 and (C_2HFe) m/e = 81.

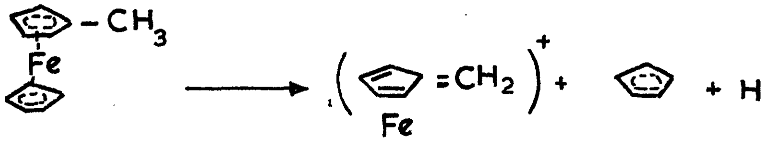
In ferrocene methyl glutarylate and ferrocene glutarylic acid the parent ion is also the base peak. These compounds give the same products as acids (33,34,27) and esters (35,36) under electron impact. In the spectrum of ferrocene glutarylic acid ions (P-17), (P-44) and (P-46) are observed which correspond to the loss of hydroxyl, carbon dioxide and CO_2H_2 groups by rearrangements (37). The ion at m/e = 240 represents the loss of acetic acid from the molecular ion. In the ferrocene methyl glutarylate compound a methoxyl group is elided from the molecular ion (38). Further fragmentations in these two compounds occur with single hydrogen transfer. Formation of rearranged ions in this class of compounds has already been investigated (39,40,41,42,43).

The fragmentation occurs at the α , β , or γ bond relative to the carboxyl group with a concomitant single hydrogen transfer. There is the possibility of losing the entire side chain and leaving a ferrocene radical ion. The evidence of breakdown at the metal bond with cyclopentadiene ring (C_5H_5) is shown by the presence of m/e = 121 and m/e = 56 ions. In acetamidoferrocene the possibility of formation of ($P-OCH_3$) ion at m/e = 228 is high. The possibility of fission α to a nitrogen bond has been observed in most amide compounds (44,45). The (P-OCH_3) ion may elide cyclopentadiene (C_5H_5 and one hydrogen attached to the nitrogen atom) to form an ion at m/e = 162. The rest of the spectra is similar to the ions which have already been discussed in this class of compounds.

In methylferrocene the base peak is the parent molecular ion. Another prominent peak is (P-66). The spectrum indicates that this ion has resulted from the loss of a cyclopentadienyl ring plus one hydrogen atom of the methyl group.

We would expect the iron-methylcyclopentadiene ion to lose a proton readily, yielding $C_6H_6Fe^+$ which would be resonance stabilised. Whether this has the same skeleton as the original material:

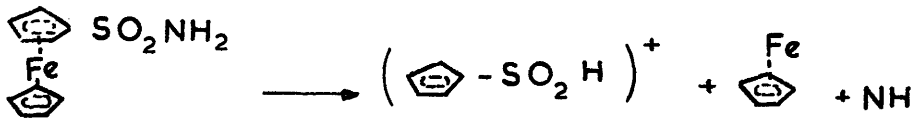
Figure 16



or whether it re-arranges to a six-membered ring is uncertain. It depends on whether or not the nucleophilic power of the residual delocalised π electron system is sufficient to retain the iron atom to form an ion m/e = 134. The ions at m/e = 121, 79 and 56 arise by the fission of single bonds between the iron and cyclopentadiene rings.

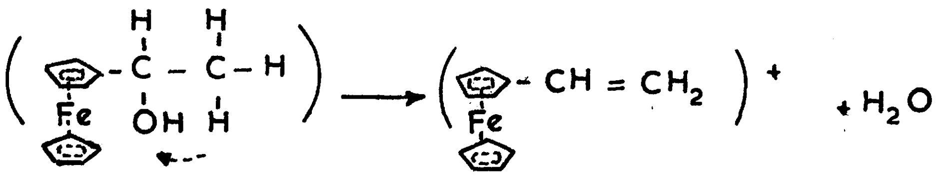
Elements containing sulphur compounds have been little studied (46,47). In sulfamidoferrocene the parent molecular ion is the base peak. There is a tendency for fission of the side chain, the charge residing on either fragment. The prominent peak at m/e = 121 corresponds to the fission of a single metallic bond to the cyclopentadiene ring. There is an ion at m/e = 128 which may arise from the breakdown of the metallic bond and the elimination of an imino group from the side chain by re-arrangements to form the following ion:

Figure 17



Ions at m/e = 121 and 56 have the same origin as reported for ferrocene. In α -hydroxyethylferrocene the molecular ion may lose water to form a stable structure (48) as follows:

Figure 18



The molecule may break down by loss of the side chain to give a ferrocene radical or ferrocene ion with a single hydrogen shift.

The molecular ion or (P-18) ion may elide cyclopentadiene to yield ions at m/e = 165 and m/e = 147 respectively. Fission at the metallo-organic bond is quite probable to yield the fragment ions at m/e = 121, 110, 65 and 56.

The ion at m/e = 138, which is a prominent peak, may result from a re-arrangement process. There is a doubly charged ion at m/e = 68 corresponding to the above mentioned ion.

EXPERIMENTAL

These analyses were carried out by a Metropolitan-Vickers MS2 mass spectrometer modified for high mass work. Only the spectrum of anisylferrocene was obtained from the MS9 mass spectrometer. The samples were provided by Professor P. L. Pauson of the Royal College of Science and Technology, Glasgow, to whom we are indebted for his interest in this work.

DISCUSSION

The stability and aromatic character of ferrocene compounds are quite obvious from the observation of the characteristics of their cracking-patterns. As with aromatic compounds, the molecular ion in this class of metallo-organic compounds was also the base peak. It seems the electron which is lost to form the molecular ion comes from the iron atom. The time which elapses between ionization and collection of the ion is about 1.10^{-6} sec. which is too short to allow the ferrocene molecule to decompose. Analyses of some aromatic compounds possessing an alkyl side chain (49) has shown a fission at the benzylic carbon-carbon bond. This evidence has been examined in great detail by Meyerson and his collaborators (50,51,52,53). They have suggested that the driving-force for such bond-fission is the formation of a tropylium ion, which is more stable from the thermodynamic stand point. In all ferrocene derivatives, however, there is no evidence of this kind of bond fission. Only in methylferrocene the loss of a single hydrogen atom in addition to a cyclopentadienyl ring from the molecular ion may occur because the resulting quinonoid structure is more stable than the methylcyclopentadienyl group.

Ferrocene

m/e	%	m/e	%
39	6.4	95	9.0
41	2.6	96	1.0
43	2.3	103	1.1
54	2.6	105	1.3
55	2.3	115	1.0
56	40.9	119	3.8
57	3.6	120	1.3
63	1.0	121	40.5
65	2.3	122	3.8
67	1.0	127	1.1
69	1.5	128	3.4
70	1.0	129	3.5
71	1.3	133	1.0
77	1.3	134	1.4
81	7.9	182	1.0
82	1.9	184	9.3
83	1.3	185	3.0
92	1.0	186 p	100.0
93	8.8	187	26.3
93.5	1.8	188	2.9
94	6.6		

Phenyl ferrocene

m/e	%	m/e	%
55	2.5	139	2.7
56	16.9	141	13.4
57	2.5	197	7.6
81	3.6	260	2.8
95	3.6	261	6.2
115	10.7	262 p	100.0
121	15.2	263	30.3
131	3.6	264	5.3

m-chloro phenyl ferrocene

m/e	%	m/e	%
56	8.0	178	2.6
89	1.8	189	2.5
91	2.0	190	1.7
95	2.2	195	2.0
113	2.0	201	1.8
114	1.5	202	12.2
115	2.8	203	11.1
121	14.5	204	6.0
138	1.7	205	4.0
139	30.1	260	3.1
140	10.8	261	3.8
148	2.5	262	2.0
149	2.9	294	12.0
175	4.9	<u>296</u> p	100.0
176	2.2	298	44.6
177	2.6		

P-nitro phenyl ferrocene

m/e	%	m/e	%	m/e	%
55	1.1	138	1.3	195	2.2
56	19.9	139	18.5	200	0.9
57	1.8	140	5.5	201	1.7
81	4.2	141	1.7	202	6.5
82	0.9	144	1.0	203	10.4
83	1.0	145	1.2	204	4.6
89	1.7	151	0.8	205	11.7
94	2.2	152	1.6	206	3.0
95	2.6	153	1.4	207	0.8
102	1.2	153.5	2.0	209	1.2
109	0.8	154	1.4	210	0.8
113	1.3	155	0.6	211	0.9
114	1.3	156	3.8	212	0.7
115	2.6	157	2.0	249	3.2
119	2.0	158	1.2	250	1.3
120	0.8	165	2.6	259	7.2
121	20.5	166	0.9	260	13.6
122	2.0	170	1.6	261	56.8
126	0.8	171	1.1	262	19.4
127	1.7	176	1.5	274	1.7
128	3.1	177	1.4	277	17.2
129	0.8	178	3.3	278	5.8
130	0.7	179	2.4	291	2.3
131	1.1	183	1.4	292	0.8
132	0.9	189	3.5	305	8.8
133	1.1	190	2.4	<u>307</u> p	100.0
137	0.6	191	1.4	308	32.9

Anisyl ferrocene

m/e	%	m/e	%	m/e	%
50	0.4	81	1.8	123	0.2
51	0.6	82	0.3	125	0.8
52	0.3	83	0.1	126	1.7
53	0.2	84	0.3	127	2.2
54	0.9	87	0.2	128	4.5
54.1	0.1	88	0.1	129	0.7
55	0.4	89	0.8	130	0.2
56	10.4	90	0.1	131	0.5
56.2	0.5	91	0.4	132	0.5
57	0.7	92	0.1	133	0.3
57.1	0.3	93	0.4	134	0.2
58	0.3	94	1.2	138	0.2
62	0.2	95	1.6	139	1.7
63	0.8	101	0.3	140	0.5
63.9	0.2	102	1.9	141	0.6
64	0.2	103	0.4	142	0.2
65	0.6	105	0.5	144	0.2
66	0.4	106	0.3	145	0.9
67	0.2	106.9	0.3	145.5	0.2
68	0.1	107	0.3	146	5.4
69	0.3	113	0.3	146.5	1.3
70	0.1	114	0.2	147	0.2
71	0.1	115	1.2	151	0.2
74	0.3	116	0.2	152	0.5
75	0.5	118	0.3	153	0.3
76	0.5	119	2.0	154	0.1
77	0.9	120	0.4	155	0.4
78	0.6	121	24.5	156	1.2
79	0.2	122	2.2	157	1.2

Anisyl ferrocene (continued)

m/e	%	m/e	%	m/e	%
158	2.0	194	0.1	250	1.2
159	0.2	195	0.2	251	0.2
163	0.2	196	0.1	260	0.5
164	0.2	197	0.2	261	0.3
165	0.9	202	0.6	262	0.5
166	0.4	203	0.6	263	1.0
167	0.2	204	0.3	264	0.4
168	0.1	205	0.3	275	1.4
169	0.2	209	0.2	276	0.4
170	0.3	210	0.2	277	15.3
171	3.2	211	0.6	278	3.6
172	0.6	212	0.9	279	0.5
176	0.2	213	0.2	290	6.8
177	0.2	219	0.2	291	1.9
178	0.4	221	0.2	292 p	100.0
179	0.2	223	0.2	293	19.8
181	0.1	224	0.2	294	3.1
182	0.3	225	0.2	295	0.3
183	0.3	227	0.2		
184	0.3	233	0.2		
185	0.2	234	0.1		
186	0.2	235	0.1		
189	0.8	245	0.1		
190	0.5	246	0.1		
191	0.9	247	0.7		
192	0.3	248	1.0		
193	0.2	249	5.0		

Cyano ferrocene

m/e	%	m/e	%
56	54.2	115.5	2.0
57	4.3	120	2.0
63	4.0	121	74.6
64	3.3	122	7.5
65	3.0	128	3.0
69	2.5	146	2.5
81	5.8	184	4.5
82	2.5	209	6.8
90	6.0	210	3.8
91	2.5	211 p	100.0
93	2.5	212	22.9
94	5.3	213	3.0
95	8.0		
115	1.5		

Ferrocene methyl glutarate

m/e	%	m/e	%	m/e	%
55	1.4	133	2.5	213	8.6
56	11.1	134	1.8	214	2.9
57	0.9	135	5.2	215	1.8
59	1.1	145	2.9	217	13.9
65	0.9	149	1.8	218	3.2
67	1.8	159	2.9	219	0.9
78	2.5	161	2.7	228	4.1
87	1.4	163	1.8	229	1.3
92	1.8	171	0.7	231	2.5
93	0.9	173	0.7	240	3.2
94	1.1	175	1.1	241	1.3
98	1.3	183	1.1	249	4.3
106.5	3.9	184	2.0	250	1.1
107	1.5	185	9.3	281	1.1
121	22.3	186	10.7	282	2.1
122	4.6	187	3.2	283	12.5
123	1.4	189	10.2	284	3.9
125	1.8	190	2.1	285	0.9
127	1.8	199	5.7	312	8.6
128	3.9	200	1.1	314 p	100.0
129	9.5	211	0.9	315	64.9
130	1.6	212	1.1		

Ferrocene glutarate

m/e	%	m/e	%	m/e	%
55	15.0	134	8.0	198	3.0
56	36.0	135	8.1	199	9.6
57	28.3	137	3.1	200	4.5
63	2.0	138	8.1	201	2.8
65	28.0	139	5.0	211	4.5
66	28.3	142	2.0	212	9.3
67	10.6	145	4.5	213	41.4
69	5.6	149	3.5	214	11.9
71	6.6	151	2.0	215	6.1
73	3.5	152	4.0	217	23.2
81	5.6	153	2.0	218	5.1
83	5.7	155	4.7	219	2.3
85	2.0	156	11.1	229	29.3
91	15.0	157	15.6	230	7.4
95	4.5	159	5.0	240	16.7
97	3.0	163	2.3	241	6.6
105	8.5	165	7.1	252	3.0
106	12.5	166	3.6	254	15.2
107	5.2	167	4.0	256	30.8
111	2.0	168	3.8	257	9.0
112	13.1	169	4.5	258	2.0
115	2.0	181	4.3	269	4.3
120	5.0	182	5.1	270	2.0
121	42.9	183	28.5	276	12.1
122	3.0	184	83.3	283	7.1
125	2.0	185	60.0	284	3.3
128	8.1	186	43.3	285	3.8
129	24.7	187	10.6	298	8.6
130	2.0	188	3.5	300 p	100.0
131	2.0	189	13.6		
133	7.8	190	3.3		

Methyl ferrocene

m/e	%	m/e	%
55	4.4	119	2.5
56	62.1	120	1.2
57	9.8	121	21.7
77	3.4	122	5.9
78	2.0	132	3.4
79	4.4	133	1.5
81	6.4	134	41.4
82	2.2	135	6.4
83	2.5	139	2.2
91	2.0	141	2.9
93	1.7	156	2.2
94	3.9	157	2.9
95	5.7	198	8.7
100	2.7	199	15.0
112	3.2	200 p	100.0
115	2.5	201	22.2

Sulfamidoferrocene

m/e	%	m/e	%
56	10.5	128	8.3
68	5.0	129	6.5
72	6.5	137	24.9
80	9.5	184	6.5
81	5.5	185	6.5
83	4.1	263	8.3
94	3.2	265 p	100.0
119	1.5	266	26.7
121	18.4	267	10.1

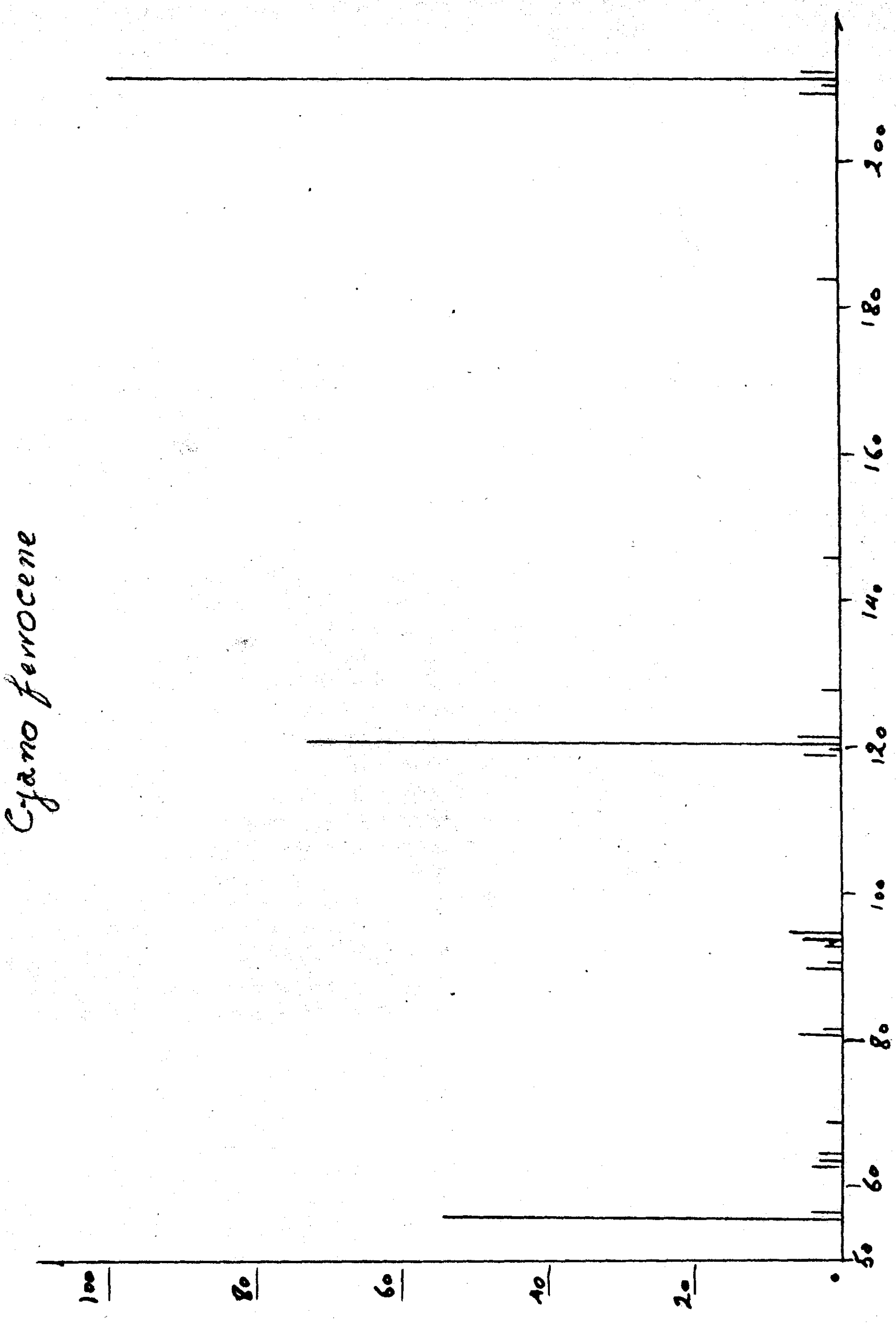
α-hydroxy ethyl ferrocene

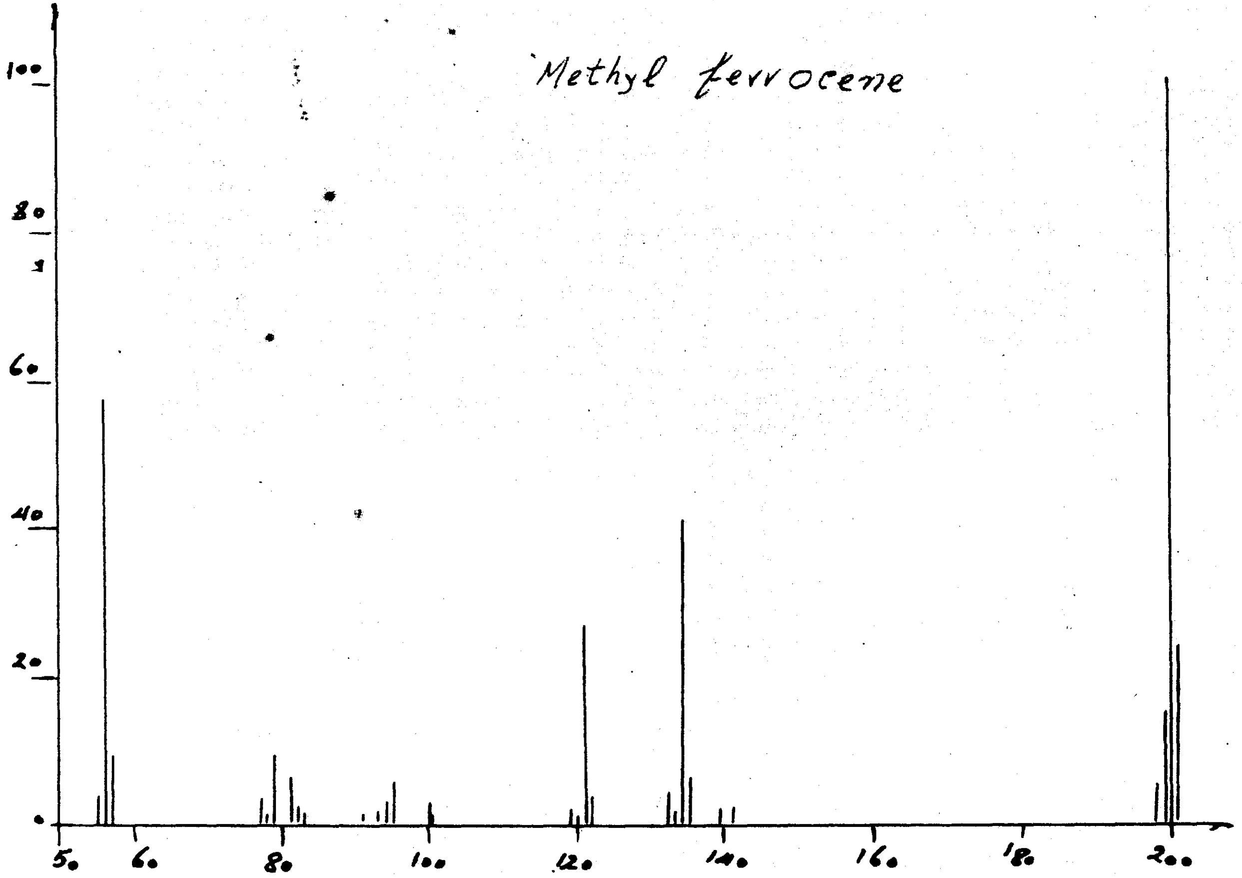
m/e	%	m/e	%	m/e	%
56	19.5	91	14.3	137	3.7
57	17.7	92	8.7	138	81.8
59	5.9	93	5.2	139	8.5
60	5.2	94	8.5	145	8.5
65	5.5	95	13.3	147	38.4
66	3.3	96	6.3	148	5.5
67	7.4	97	9.6	149	10.3
68	3.7	98	4.4	163	4.4
68.5	1.8	99	3.7	165	12.5
69	13.3	105	5.5	185	11.8
70	5.9	109	7.4	186	11.1
71	10.7	110	4.1	187	4.1
73	12.2	111	6.3	212	29.9
74	4.4	119	6.3	213	9.6
77	4.4	120	6.3	214	4.1
78	4.4	121	28.1	228	25.1
79	4.4	122	5.2	229	6.6
81	5.2	123	5.9	230 p	100.0
82	7.7	125	3.7	231	22.2
83	9.6	128	4.4	232	3.3
84	4.4	129	7.4		
85	6.6	136	7.0		

Acetamidoferrocene

m/e	%	m/e	%
55	1.9	135	2.7
56	41.6	136	3.7
57	6.8	152	1.7
59	1.8	158	1.1
65	1.8	160	2.0
69	1.4	162	26.2
79	1.4	163	4.6
80	3.3	168	0.8
81	5.6	171	1.1
82	3.3	172	4.8
83	2.2	173	1.8
93	1.4	185	1.7
94	3.8	186	0.9
95	8.0	193	0.8
96	1.2	195	12.5
107	2.3	196	2.6
108	2.7	199	1.2
109	2.1	200	3.7
119	3.5	201	3.0
120	1.9	202	6.7
121	39.3	203	2.6
122	11.5	204	0.8
123	1.5	226	7.5
128	2.5	228	100.0
129	1.5	229	30.3
131	1.2	257	5.5
132	1.4	259 p	72.0
133	14.0	260	28.3
134	9.2		

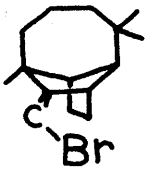
Cyano ferrocene





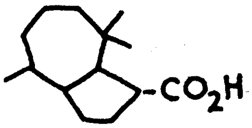
Methyl ferrocene

G.O.1



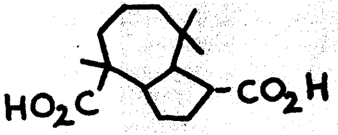
ω-bromolongifolene.

G.O.2



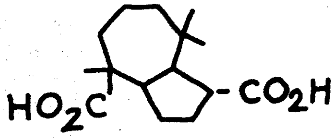
C acid.

G.O.3



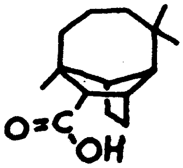
β-longiforic acid.

G.O.4



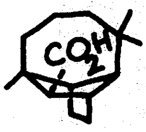
α-longiforic acid.

G.O.5



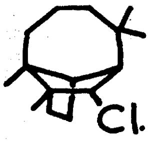
Isolongifolic acid.

G.O.6



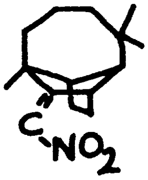
Longifolic acid.

G.O.7



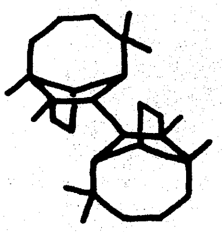
Longibornyl chloride

G.O.9



Nitrolongifolene

G.O.10



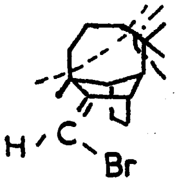
Dilongibornyl

FIG.19

CHAPTER FOUR

The mass spectra of some longifolene derivatives

The compounds investigated were prepared by Professor G. Ourisson (54) and the main objective was to establish the existence of common structural regularities such as the incidence of the isopropyl group. The structural formulae appearing in Figure 19 are those suggested by Professor Ourisson and his collaborators. An analysis of the spectra of ω-nitrolongifolene and ω-bromolongifolene shows the loss of a methyl group or the C_3H_7 radical from the parent molecular ion. It has been shown that there is a tendency for fragmentation to occur at highly branched positions in this class of compound (55,56,57,58). The loss of a methyl group is quite reasonable as there are three methyl groups attached to a quaternary centre at carbon (4). The ion at $(P-C_3H_7)$ may arise by fission of the (8,7 and 1,8) carbon-carbon bonds or the (1,8 and 3,4) bonds with a hydrogen re-arrangement.



A cracking pattern characteristic of nitro compounds (24,25) was also observed with ω-nitrolongifolene. Remarkably, the (P-OH) ion was 66% of the base peak. This ion has only previously been reported for nitro compounds in the case of o-nitranaline (59). The bromine atom was eliminated very easily from ω-bromolongifolene and, therefore, very little information on the manner of fragmentation in the parent molecule was provided by the characteristic spectrum of bromine containing compounds. The ions around m/e = 105-109 and m/e = 91-95 which were prominent peaks in the spectra arose solely from hydrocarbon fragments. The congested structure of the molecules and the interaction effects of the rings make a detailed interpretation rather difficult.

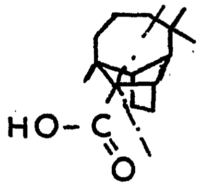
In the spectra of longifolic and isolongifolic acids, there is some evidence for the ions ($P-CH_3$) and ($P-C_3H_7$) which shows that methyl and isopropyl groups probably existed in the parent molecules. The spectrum of longifolic acid obtained with a double-focusing machine (MS9) shows metastable ions corresponding to the following transitions.

$$P^+ \text{———} (P-15)^+ + CH_3 \qquad m/e = 206.9$$

$$[(P-15)-18]^+ + H_2O \qquad m/e = 186.46$$

$$P^+ \text{———} (P-18)^+ + H_2O \qquad m/e = 201.37$$

The existence of the carboxyl group (60) in the spectra and its cracking pattern is also evident. The most abundant ion in the spectra given by longifolic and isolongifolic acids and ω-bromolongifolene is at m/e = 109. A typical fragmentation may, therefore, be written.

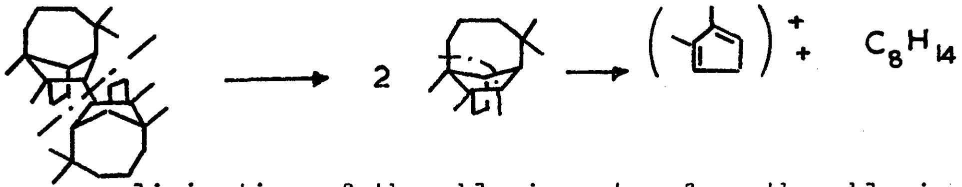


$$\longrightarrow \quad C_8^+H_3 + \text{Residue.}$$

The other ions around m/e = 95, 81 and 67 probably arise from the further fission of the carbon-carbon bonds ($C_{8,9}$ and $C_{8,10}$) while breaking of the $C_{8,7}$ bond yields the m/e = 109 ion. There is an ion at m/e = 44 in the spectrum of longifolic acid which was not observed in isolongifolic acid. This ion corresponds to carbon dioxide which is one of the characteristic features of the cracking patterns of acid anhydrides (61). In dilongibornyl the most abundant peak is $\overset{+}{P}/2$, which indicates that the molecule ruptures very easily at the $C_{6,14}$ carbon-carbon bond. The loss of methyl and C_3H_7 groups from the parent molecular ion is also probable, as it possesses four methyl groups attached to quaternary centres and two gem-dimethyl groups.

In longibornylchloride and dilongibornyl the ion at m/e = 95 is more abundant than the ion at m/e = 106.

We may interpret this to mean that fission occurs in the following way: the substituents on carbon (6) in these two compounds elide very easily so the bonds attached to this carbon atom are weakened and fragmentation results as follows:



The easy elimination of the chlorine atom from the chlorinated molecule again means that the trace isotope in the spectrum is of little assistance in interpreting the parent structure.

Ions at m/e = 225, 205 and 189 respectively indicate the loss of methyl, chlorine and methyl plus chlorine fragments from the molecular ion.

DISCUSSION

The salient features of the spectra of isolongifolic, longifolic acids and longibornyl chloride were the prominent (P-15) ion in all of them and the $(P-C_3H_7)$ ion in isolongifolic and longifolic acid which was more than 23% of the most abundant ion.

There is also evidence of these ions in the spectra given by ω-nitrolongifolene and ω-bromolongifolene, but they are not nearly so abundant. Since we are dealing with alicyclic hydrocarbon compounds we can assume that the stability is decided chiefly by stereochemical and comformational factors (62,63). Therefore, we should not infer that these fragments are of less importance in the related parent compounds, even if they appear less prominent in the spectra.

In the carbon (14) acid there is a carboxyl group attached to carbon (12). The parent ion abundance is not more than 7% of the most abundant ion which is at $m/e = 95$. The molecular ion loses H_2O, HCO and CO_2H groups to form a stable ion. The loss of methyl and C_3H_7 groups may indicate the presence of methyl and isopropyl groups attached to a ring. Here also the $(P-C_3H_7)$ ion may arise from the successive bond fission of $C_{7,1}$ and $C_{3,4}$ to account for the peak at $m/e = 181$.

In α-longiforic and β-longiforic acid there are no ions corresponding to the parent molecules as it has been shown that compounds which contain two carboxyl groups are thermally unstable and usually decompose before giving a vapour pressure sufficient for a spectrum to be produced (64,65). Such compounds must be converted into their methyl or ethyl esters for successful examination either by mass spectrometry or vapour-phase chromatography.

The spectra of α-longiforic and β-longiforic acids show that the cis compound is less stable than the trans isomer. Mohler and his co-workers have also studied some compounds exhibiting cis and trans isomerism (66) and the results considered together with those from other kinds of isomeric compounds show that the less crowded molecule usually has greater stability under electron impact (66,67,63).

From our spectra we can only infer that compound G.O.4. is a much more crowded molecule than G.O.3. and that whatever the disposition of the hydrogen atoms on C_5 and C_6, the carboxyl group on C_4 interferes with a methyl group on C_7 in compound G.O.4.

EXPERIMENTAL

The spectra of longifolic acid, α-longiforic and β-longiforic acid were obtained with an A.E.I. type MS9 double-focusing mass spectrometer. An accelerating voltage of 8kV and an electron energy of 70eV were used.

The other compounds were examined with a Metropolitan-Vickers MS2 instrument.

G.O.

m/e	%	m/e	%	m/e	%	m/e	%
36	6.4	70	0.4	115	0.1	167	0.1
37	21.6	71	0.3	117	0.1	175	0.1
38	26.3	73	0.1	119	0.3	176	0.1
39	50.0	74	0.1	120	0.3	177	0.2
40	13.9	77	0.4	121	0.4	179	1.6
41	16.5	78	0.2	122	0.2	180	0.4
42	100.0	79	0.5	123	0.4	181	0.1
43		80	0.3	124	0.2	189	0.2
44	34.6	81	1.0	125	0.2	191	0.1
45	4.1	82	0.4	128	0.1	193	0.1
46	0.2	83	0.5	129	0.1	194	0.8
48	0.1	84	0.2	131	0.2	195	0.2
50	0.2	85	0.2	132	0.1	198	0.2
51	0.3	91	0.7	133	0.2	199	0.3
52	1.9	92	0.2	135	0.2	200	0.4
53	6.9	93	0.4	136	0.3	201	0.3
54	0.7	94	0.3	137	0.4	202	0.5
55	6.7	95	0.8	138	0.1	203	0.2
56	0.7	96	0.3	145	0.1	204	0.2
57		97	0.3	147	0.1	207	0.1
58		98	0.2	149	0.2	249	0.1
59	18.5	99	0.1	151	0.2	262	0.1
60	1.6	101	0.1	152	0.1		
63	0.1	105	0.4	154	0.1		
64	0.3	106	0.1	157	0.1		
65	0.3	107	0.7	159	0.1		
66	0.2	108	0.3	161	0.2		
67	0.8	109	0.6	163	0.1		
68	0.3	110	0.3	165	0.2		
69	1.0	111	0.3	166	0.1		

G.O.1. ω-bromolongifolene $C_{15}H_{23}Br$ M.W.282

m/e	%	m/e	%	m/e	%	m/e	%
29	5.5	97	7.1	143	1.3	193	4.2
39	3.5	98	1.1	144	2.2	194	23.0
40	0.9	103	4.2	145	11.3	195	6.4
41	33.2	104	10.4	146	8.4	196	1.5
42	2.4	105	67.3	147	36.1	197	2.0
43	15.9	106	19.5	148	7.3	198	3.1
53	7.1	107	46.6	149	2.4	199	3.8
54	1.8	108	17.9	150	1.3	200	4.0
55	48.2	109	100.0	157	1.8	201	7.7
56	5.5	110	14.2	158	2.2	202	11.9
57	9.3	111	3.5	159	11.5	203	87.6
65	5.8	112	1.1	160	7.7	204	22.1
66	3.5	113	1.1	161	19.7	205	3.3
67	34.5	115	4.2	162	4.9	211	2.9
68	4.4	116	4.0	163	2.7	212	3.3
69	12.4	117	15.7	164	3.5	213	4.4
70	4.2	118	11.3	165	15.5	214	3.2
71	4.6	119	42.3	166	5.1	215	1.8
77	14.8	120	12.8	167	0.9	225	1.3
78	6.0	121	40.6	169	1.3	226	0.7
79	31.9	122	7.5	170	1.5	227	1.3
80	9.3	123	11.9	171	4.4	228	0.4
81	41.2	124	2.2	172	8.0	239	3.8
82	22.8	128	1.8	173	9.7	240	1.3
83	14.4	129	2.2	174	8.6	241	3.8
84	1.3	130	3.5	175	10.4	242	1.1
85	0.7	131	15.0	176	2.2	243	0.4
89	1.1	132	12.4	183	2.4	267	2.9
90	6.6	133	34.1	184	2.0	268	1.1
91	50.0	134	12.6	185	5.8	269	2.7
92	15.9	135	13.3	186	5.0	270	0.7
93	57.8	136	3.5	187	14.2	282 p	11.9
94	13.1	137	2.2	188	6.0	283	4.4
95	59.5	139	0.9	189	3.5	284	11.1
96	8.8	142	0.9	192	2.2	285	3.1

C_{14} acid

G.O.2. $C_{14}H_{24}O_2$ M.W. 224

m/e	%	m/e	%	m/e	%	m/e	%
55	17.8	95	100.0	132	0.6	167	3.6
56	15.6	96	16.9	133	2.9	168	9.1
57	1.9	97	6.8	134	2.3	169	3.9
60	1.9	98	0.6	135	16.6	173	1.9
65	0.6	99	1.0	136	10.1	175	1.9
66	2.6	105	4.2	137	28.9	177	1.9
67	28.9	106	2.3	138	5.5	178	7.1
68	5.8	107	38.0	139	14.3	179	10.1
69	40.3	108	18.8	140	46.1	180	3.9
70	7.8	109	64.3	142	8.4	181	14.9
71	6.8	110	12.0	143	2.9	182	4.2
73	9.1	111	19.5	145	2.9	191	7.5
77	2.3	112	6.8	149	2.6	194	3.2
78	0.6	113	5.2	150	2.6	195	2.6
79	12.7	114	7.1	151	2.3	203	5.8
80	3.2	115	1.0	152	11.7	204	1.9
81	26.3	117	0.3	153	14.6	206	4.9
82	33.8	119	2.6	154	13.3	207	1.6
83	14.9	120	2.6	155	9.1	208	1.6
84	2.9	121	29.9	156	2.6	209	10.7
85	0.3	122	15.6	159	1.3	210	2.6
86	2.3	123	26.6	161	3.2	219	0.6
87	1.3	124	4.5	162	3.9	224 p	7.1
91	5.2	125	5.2	163	34.4	225	2.6
92	2.3	126	1.9	164	7.8		
93	29.2	127	1.9	165	3.2		
94	16.2	131	1.0	166	1.3		

β-longiforic acid

G.O.3. $C_{15}H_{24}O_4$ M.W. 268

m/e	%	m/e	%	m/e	%
36	0.1	71	1.6	107	18.7
38	0.6	72	0.3	108	10.3
39	10.7	73	0.7	109	16.4
40	21.8	74	0.4	110	5.4
41	27.4	75	0.2	111	1.9
42	3.0	77	0.7	112	0.5
43	8.7	78	1.8	113	0.3
44	100.0	79	12.0	115	0.8
45	2.5	80	3.1	116	0.3
46	1.0	81	16.2	117	1.0
48	0.5	82	13.4	118	1.0
50	0.7	83	4.9	119	4.1
51	2.0	84	1.0	120	2.7
52	1.1	85	0.8	121	7.4
53	6.9	86	0.2	122	5.1
54	2.1	87	1.1	123	3.0
55	19.0	89	0.3	124	1.3
56	2.8	91	8.4	125	0.5
57	2.7	92	2.3	126	0.2
58	0.9	93	15.2	127	0.2
59	0.8	94	9.5	128	0.5
60	0.7	95	11.6	129	0.5
63	0.8	96	4.4	130	0.2
64	1.3	97	2.3	131	2.3
65	3.9	98	0.7	132	1.7
66	3.5	99	0.3	133	4.1
67	20.1	103	0.7	134	2.5
68	5.7	104	0.5	135	9.1
69	11.6	105	5.7	136	2.5
70	3.9	106	3.4	137	3.3

β-longiforic acid (continued)

G.O.3. $C_{15}H_{24}O_4$

m/e	%	m/e	%	m/e	%
138	2.1	165	0.5	205	0.3
139	2.8	166	0.8	206	3.7
140	1.3	167	0.2	207	1.6
141	0.3	168	0.5	208	0.2
142	0.2	173	0.5	219	0.2
143	0.2	174	1.0	220	0.2
144	0.2	175	5.7	221	0.2
145	11.0	176	1.0	222	0.5
146	2.0	177	1.2	223	0.2
147	8.4	178	1.3	230	0.4
148	2.0	179	2.1	234	0.2
149	2.3	180	0.5	235	0.2
150	1.8	181	0.2	236	0.2
151	1.0	188	1.3	262	0.3
152	0.5	189	1.0	263	0.1
153	0.5	190	0.3		
154	0.2	191	3.8		
155	0.2	192	0.7		
156	0.4	193	0.2		
157	0.3	194	0.2		
159	1.6	195	0.2		
160	1.1	196	0.2		
161	2.8	201	0.2		
162	0.8	202	0.2		
163	6.6	203	0.5		
164	1.3	204	0.4		

α-longiforic acid

G.O.4. $C_{15}H_{24}O_4$ M.W. 268

m/e	%	m/e	%	m/e	%
36	5.5	71	1.6	115	0.2
37	22.2	72	0.2	117	0.3
38	27.4	73	0.5	119	0.7
39	50.6	77	0.9	120	0.8
40	11.9	78	0.5	121	0.8
41	18.1	79	1.1	122	0.5
42	100.0	80	0.5	123	0.7
43		81	2.1	124	0.5
44	38.3	82	1.4	125	0.3
45	3.5	83	1.4	126	0.2
46	0.3	84	0.7	128	0.2
50	0.5	85	0.9	129	0.3
51	0.3	86	0.2	131	0.3
52	1.5	91	1.4	132	0.2
53	5.5	92	0.5	133	0.6
54	0.7	93	1.1	134	0.3
55	5.9	94	0.7	135	0.6
56	1.8	95	2.1	136	0.5
57	16.8	96	0.8	137	0.7
58		97	1.0	138	0.5
59	19.9	98	0.5	139	0.2
60	1.6	105	0.9	140	0.2
63	0.2	106	0.5	141	0.2
64	0.5	107	2.5	143	0.3
65	0.7	108	0.8	145	0.3
66	0.5	109	2.1	147	0.5
67	1.8	110	0.7	148	0.3
68	0.7	111	0.7	149	0.5
69	2.5	112	0.2	150	0.2
70	1.1	113	0.2	151	0.6

α-longiforic acid (continued)

G.O.4. $C_{15}H_{24}O_4$ M.W. 268

m/e	%	m/e	%
152	0.3	192	0.2
153	0.2	193	0.5
159	0.2	201	0.2
161	0.3	202	0.3
163	0.3	203	0.8
165	0.3	204	0.3
166	0.5	205	0.2
167	0.2	218	0.3
168	0.2	219	0.2
173	0.2	221	0.9
175	0.5	222	0.2
176	0.5	236	0.5
177	0.5	262	0.7
179	0.2	263	0.2
180	0.3		
181	0.2		
187	0.2		
189	0.5		
190	0.3		
191	0.3		

Isolongifolic acid

G.O.5. $C_{15}H_{24}O_2$ M.W. 236

m/e	%	m/e	%	m/e	%
39	10.7	86	4.6	117	4.1
40	1.8	87	2.5	118	2.0
41	53.0	89	1.8	119	10.2
42	3.3	89.5	1.5	120	7.1
43	22.3	91	33.0	121	20.1
45	1.0	92	6.6	122	8.1
51	2.5	93	36.8	123	16.2
53	14.7	94	16.2	124	22.6
54	2.0	95	64.7	125	12.2
55	38.3	96	10.7	126	6.6
56	6.9	97	4.1	127	1.8
57	1.8	99	2.8	128	0.5
65	7.9	100	4.3	129	1.0
66	9.9	103	4.1	131	2.8
67	40.9	104	2.5	132	2.3
68	6.3	105	20.8	133	12.9
69	26.9	106	8.1	134	3.8
73	1.3	107	33.5	135	13.5
75	0.5	108	18.8	136	13.2
77	26.4	109	100.0	137	34.0
78	8.1	110	23.6	138	25.4
79	40.1	111	9.9	139	9.1
80	11.2	112	3.0	140	2.8
81	46.4	113	5.6	141	0.5
82	30.7	114	1.5	145	1.3
83	8.6	115	3.3	147	9.4
85	1.3	116	1.5	148	2.3

Isolongifolic acid (continued)

G.O.5. $C_{15}H_{24}O_2$ M.W. 236

m/e	%	m/e	%	m/e	%
149	9.1	179	4.6	237	8.6
150	5.8	180	12.2	238	1.5
151	27.9	181	2.3		
152	10.7	189	2.0		
153	7.6	190	2.3		
154	3.0	191	3.6		
159	2.3	192	1.3		
161	7.6	193	22.8		
162	2.0	194	4.6		
163	3.0	195	4.1		
164	2.3	203	6.1		
165	14.7	204	1.5		
166	10.7	205	1.8		
167	9.1	206	2.8		
168	10.2	207	6.9		
169	3.8	208	5.3		
170	2.8	218	6.6		
171	3.8	219	8.4		
172	1.8	220	6.6		
173	2.0	221	87.4		
174	2.0	222	21.3		
175	15.0	223	4.1		
176	21.1	234	3.3		
177	11.7	235	2.5		
178	2.5	236 p	29.4		

Longifolic acid

G.O.6. $C_{15}H_{24}O_2$ M.W. 236

m/e	%	m/e	%	m/e	%
36	5.2	71	7.8	99	4.4
38	1.9	72	1.5	100	4.8
39	25.9	73	3.7	101	1.5
40	6.3	74	1.1	102	0.7
41	85.9	75	0.7	103	3.7
42	10.0	76	0.7	104	2.2
43	34.8	77	23.3	105	19.3
44	94.1	78	7.4	106	7.4
45	5.2	79	34.1	107	37.0
46	1.1	80	10.4	108	20.0
50	1.5	81	57.0	109	100.0
51	5.9	82	48.5	110	31.1
52	3.3	83	20.0	111	10.0
53	20.7	84	4.1	112	2.2
54	5.2	85	7.4	113	5.2
55	54.8	86	5.2	114	1.5
56	14.8	87	3.7	115	3.7
57	17.8	88	0.7	116	1.5
58	5.2	89	1.5	117	3.7
59	2.2	89.5	0.7	118	1.5
60	2.6	90	0.7	119	12.6
63	2.2	91	29.6	120	9.3
64	1.5	92	6.7	121	21.5
65	11.1	93	33.0	122	8.9
66	11.9	94	21.1	123	17.8
67	46.7	95	83.3	124	19.6
68	11.1	96	16.3	125	12.6
69	49.6	97	8.5	126	8.5
70	8.1	98	3.0	127	3.7

Longifolic acid (continued)

G.O.6. $C_{15}H_{24}O_2$ M.W. 236

m/e	%	m/e	%	m/e	%
128	2.2	159	2.2	193	23.0
129	2.2	160	1.1	194	4.4
130	1.1	161	7.4	195	4.1
131	3.3	162	2.2	196	0.7
132	1.5	163	3.7	201	0.7
133	11.1	164	2.2	202	1.1
134	5.2	165	14.8	203	7.0
135	16.7	166	11.5	204	2.2
136	15.2	167	8.9	205	1.1
137	38.5	168	10.4	206	0.7
138	29.3	169	3.0	207	3.7
139	6.7	170	1.5	208	2.6
140	3.0	171	3.0	209	0.7
141	1.9	172	0.7	217	0.7
143	1.5	173	1.5	218	7.0
145	2.6	174	0.7	219	3.0
146	1.1	175	12.6	220	0.7
147	10.0	176	14.4	221	77.0
148	3.3	177	11.9	222	12.6
149	10.7	178	3.0	223	1.5
150	3.7	179	5.2	224	0.7
151	25.9	180	12.6	234	2.6
152	8.1	181	3.0	235	0.7
153	3.0	182	0.7	236 p	28.9
154	1.5	185	0.7	237	5.2
155	0.7	189	3.0	238	0.7
156	1.1	190	3.7	262	2.6
157	1.1	191	4.4		
158	0.7	192	2.6		

Longibornyl chloride

G.O.7. $C_{15}H_{25}Cl$ M.W. 240

m/e	%	m/e	%	m/e	%
36	5.1	81	68.3	119	45.7
37	1.7	82	86.3	120	17.9
38	3.4	83	22.2	121	70.0
39	13.2	84	3.0	122	23.1
40	11.1	85	3.0	123	32.1
41	61.5	89	6.0	124	12.0
42	6.0	91	41.9	125	3.0
43	23.5	92	14.1	127	4.3
51	3.4	93	51.7	128	6.0
52	2.1	94	25.2	129	7.7
53	18.8	<u>95</u>	100.0	130	4.3
54	3.4	96	21.4	131	5.6
55	50.9	97	8.5	132	3.4
56	8.5	102	1.7	133	23.1
57	11.5	103	12.8	134	18.8
63	2.6	104	5.1	135	47.0
65	10.3	105	37.6	136	22.2
66	4.3	106	13.7	137	9.4
67	31.6	107	47.9	138	2.6
68	7.7	108	23.5	141	6.0
69	49.6	109	59.8	142	3.0
70	6.0	110	12.0	143	6.4
71	6.0	111	6.0	144	2.1
75	4.7	113	3.4	145	3.8
77	27.8	115	8.9	146	2.1
78	7.7	116	5.1	147	14.5
79	37.6	117	7.7	148	15.8
80	9.4	118	6.0	149	33.3

Longibornyl chloride (continued)

G.O.7. $C_{15}H_{25}Cl$ M.W. 240

m/e	%	m/e	%	m/e	%
150	7.3	176	6.8	211	5.1
151	2.1	177	15.4	212	3.8
152	3.0	178	3.8	213	4.7
155	15.4	183	3.8	223	4.3
156	6.0	184	17.5	224	6.0
157	7.7	185	4.7	225	76.7
158	3.8	186	6.4	226	23.1
159	1.7	187	3.0	227	28.2
160	3.4	189	34.2	228	7.7
161	20.9	190	9.0	238	3.0
162	8.5	191	5.1	239	3.4
163	14.5	197	7.7	240 p	50.0
164	3.4	198	3.0	241	16.7
169	6.0	199	3.0	242	17.9
170	9.0	202	4.3	243	6.0
171	9.8	203	6.8		
172	14.1	204	44.4		
173	5.1	205	76.7		
174	5.1	206	20.5		
175	5.6	207	3.4		

ω-nitrolongifolene

G.O.9. $C_{15}H_{23}NO_2$ M.W. 249

m/e	%	m/e	%	m/e	%
39	24.1	80	24.1	112	8.8
40	7.0	81	70.2	113	3.5
41	100.0	82	29.8	114	6.1
42	10.5	83	28.9	115	18.9
43	72.8	84	9.0	116	14.0
44	5.3	85	7.0	117	28.9
45	3.1	86	3.9	118	21.9
51	8.8	89	4.4	119	50.9
52	6.1	90	10.5	120	30.7
53	31.6	91	89.5	121	46.1
54	9.6	92	26.3	122	31.6
55	94.7	93	66.7	123	33.3
56	15.4	94	29.6	124	21.9
57	16.2	95	53.5	125	11.4
58	3.1	96	28.1	126	5.7
59	3.5	97	18.4	127	5.7
63	4.4	98	10.1	128	10.5
65	28.5	99	4.4	129	12.7
66	13.2	100	2.6	130	13.2
67	59.2	101	1.8	131	35.5
68	13.6	102	3.9	132	23.7
69	65.4	103	14.0	133	43.0
70	12.3	104	16.7	134	25.4
71	10.1	105	70.6	135	33.8
72	3.9	106	31.6	136	25.4
75	2.6	107	65.5	137	20.6
76	6.1	108	32.5	138	14.0
77	60.1	109	80.3	139	7.0
78	21.5	110	32.5	140	3.5
79	66.7	111	14.0	141	3.5

ω-nitrolongifolene (continued)

G.0.9. $C_{15}H_{23}NO_2$ M.W. 249

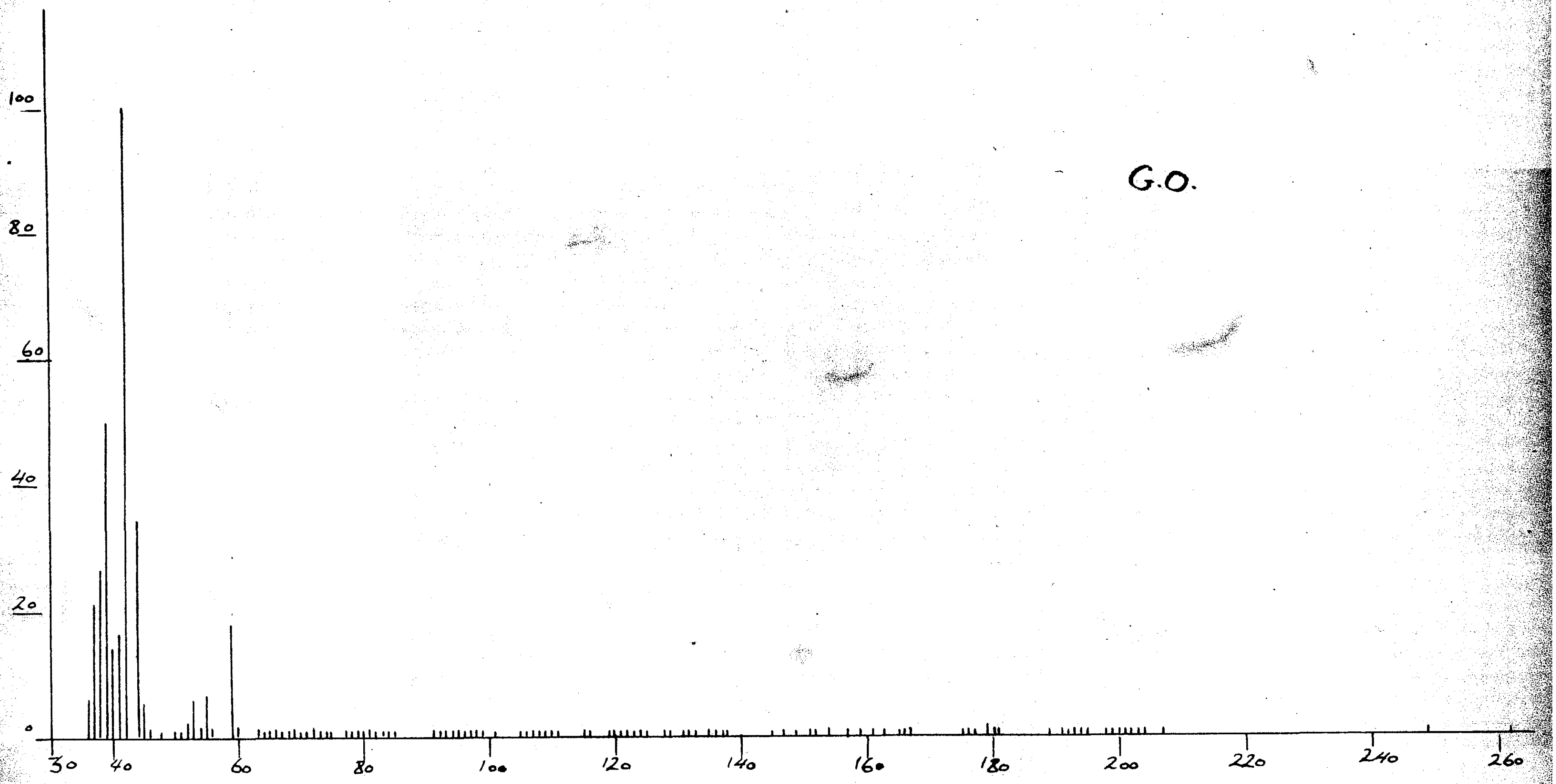
m/e	%	m/e	%	m/e	%
142	4.4	172	9.6	205	10.5
143	10.5	173	22.8	206	15.8
144	12.7	174	18.0	207	5.7
145	26.8	175	22.8	208	2.2
146	24.6	176	16.7	214	7.5
147	40.4	177	11.4	215	6.6
148	23.2	178	12.7	216	6.6
149	20.6	179	6.1	217	5.7
150	20.2	180	3.5	218	4.4
151	9.6	184	3.9	219	12.3
152	9.6	185	6.1	220	23.7
153	6.1	186	8.3	221	7.9
154	2.6	187	24.1	230	5.3
155	3.5	188	16.2	231	7.0
156	3.5	189	10.5	232	66.7
157	8.8	190	14.0	233	15.8
158	10.5	191	8.8	234	12.3
159	31.6	192	6.1	235	3.5
160	18.9	193	3.1	249 p	9.2
161	30.7	194	3.1	250	5.3
162	19.7	197	2.2		
163	19.7	198	2.6		
164	18.9	199	8.3		
165	14.9	200	8.8		
166	7.0	201	35.5		
167	2.6	202	22.4		
170	2.6	203	38.6		
171	7.5	204	22.8		

G.O.10. **Dilongibornyl** $C_{30}H_{50}$ M.W. 410

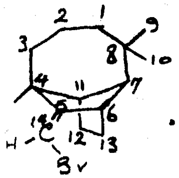
m/e	%	m/e	%	m/e	%
39	1.2	103	0.6	141	0.6
40	0.3	104	1.1	141.5	0.5
41	10.5	105	11.3	142	1.0
42	0.7	106	5.6	142.5	0.4
43	9.3	107	26.9	143	0.9
44	0.4	108	10.7	144	0.6
53	2.2	109	37.8	145	2.9
55	21.1	110	5.3	146	1.5
56	1.0	111	4.2	147	6.9
57	6.4	112	0.5	148	5.9
63	0.4	113	0.4	149	32.3
65	1.0	114	0.3	150	6.9
66	0.7	115	0.8	151	2.7
67	11.9	116	0.6	152	0.6
68	2.0	117	0.2	154	0.2
69	31.2	118	1.5	155	1.3
70	2.1	119	10.4	155.5	1.0
71	2.3	120	6.1	156	0.4
77	4.2	121	27.2	157	0.5
78	1.5	122	13.9	158	0.5
79	12.3	123	24.3	159	2.3
80	3.7	124	3.6	160	1.4
81	31.0	125	1.5	161	7.2
82	8.1	127	0.4	162	4.5
83	9.7	128	0.9	163	12.3
84	0.8	129	1.4	164	3.7
85	0.2	130	0.7	165	1.7
91	9.5	131	2.7	166	0.4
92	4.1	132	1.5	169	0.7
93	22.4	133	8.3	169.5	0.5
94	11.3	134	7.5	170	0.4
95	53.5	135	21.9	171	0.5
96	8.8	136	10.7	172	0.3
97	6.1	137	8.0	173	2.3
98	0.7	139	0.2	174	1.4

G.O.10. <u>Dilongibornyl (continued)</u> $C_{30}H_{50}$ M.W. 410

m/e	%	m/e	%	m/e	%
175	6.1	219	4.1	286	1.0
176	4.6	220	0.9	287	1.0
177	16.3	227	0.3	288	0.4
178	5.2	228	0.4	297	0.4
179	3.3	229	1.8	298	0.4
180	0.7	230	2.2	299	0.8
183	0.3	231	7.7	300	1.3
183.5	0.2	232	4.8	301	0.7
184	0.2	233	1.2	302	0.3
185	0.4	234	0.2	311	0.3
187	1.3	241	0.2	312	0.3
188	0.9	242	0.3	313	1.5
189	5.3	243	1.1	314	1.3
190	4.4	244	0.8	315	0.5
191	8.0	245	2.7	316	0.2
192	10.7	246	1.2	325	2.5
193	2.7	247	0.3	326	1.3
194	0.3	255	0.3	327	1.1
198	1.4	256	0.3	328	1.9
198.5	0.8	257	1.3	329	1.3
199	0.3	258	1.1	338	0.3
201	1.1	259	0.9	339	0.7
202	1.6	260	1.0	340	0.6
203	10.7	261	0.4	341	0.9
204	18.4	269	0.3	342	0.5
<u>205</u>	100.0	270	0.6	353	0.3
206	24.5	271	1.9	354	0.9
207	4.2	272	1.4	355	0.4
208	0.8	273	4.8	367	2.2
213	0.3	274	2.4	368	0.9
214	0.3	275	1.4	379	0.9
215	1.4	276	0.4	380	1.1
216	1.3	283	0.3	385	12.5
217	6.7	284	0.4	396	5.9
218	5.9	285	2.1	410 p	32.5
				411	18.9



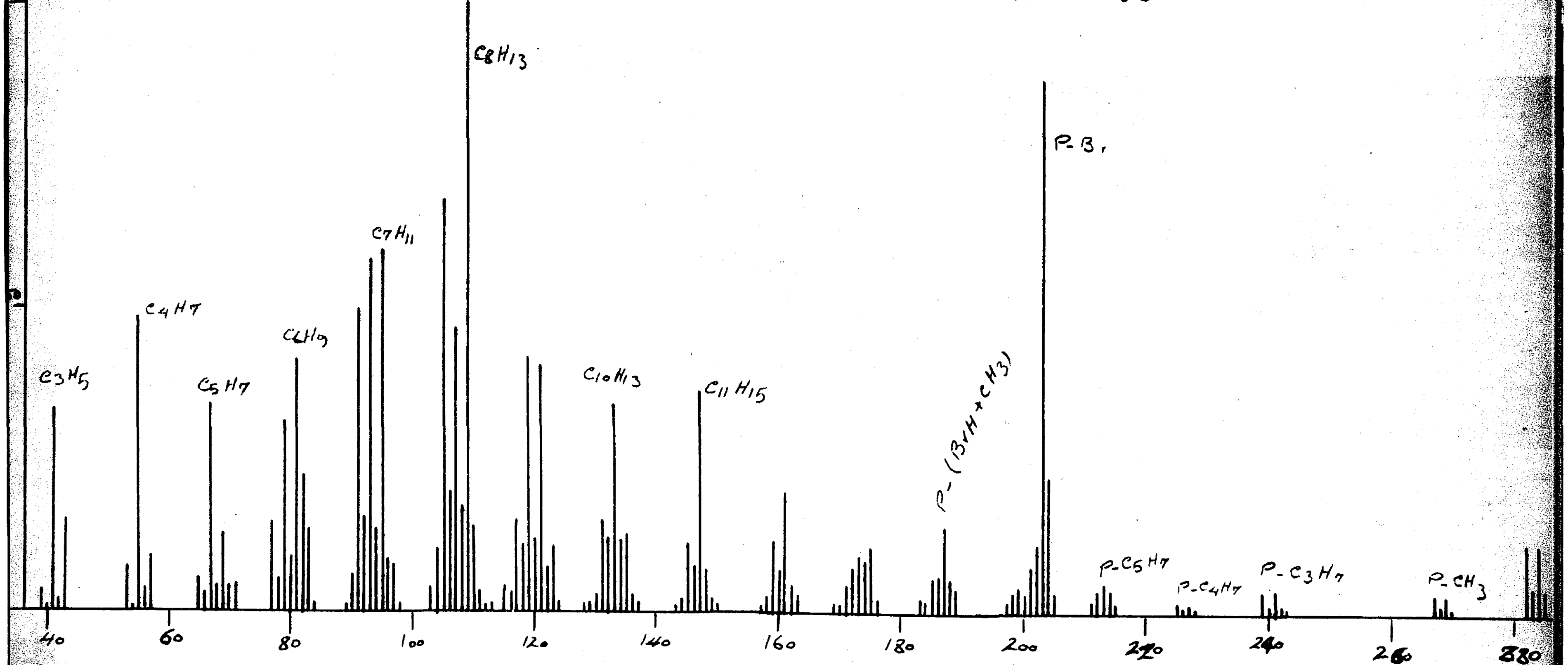
M.S.9



ω-bromolongifolene (G.01)

$C_{15}H_{23}Br$

M.W. = 282



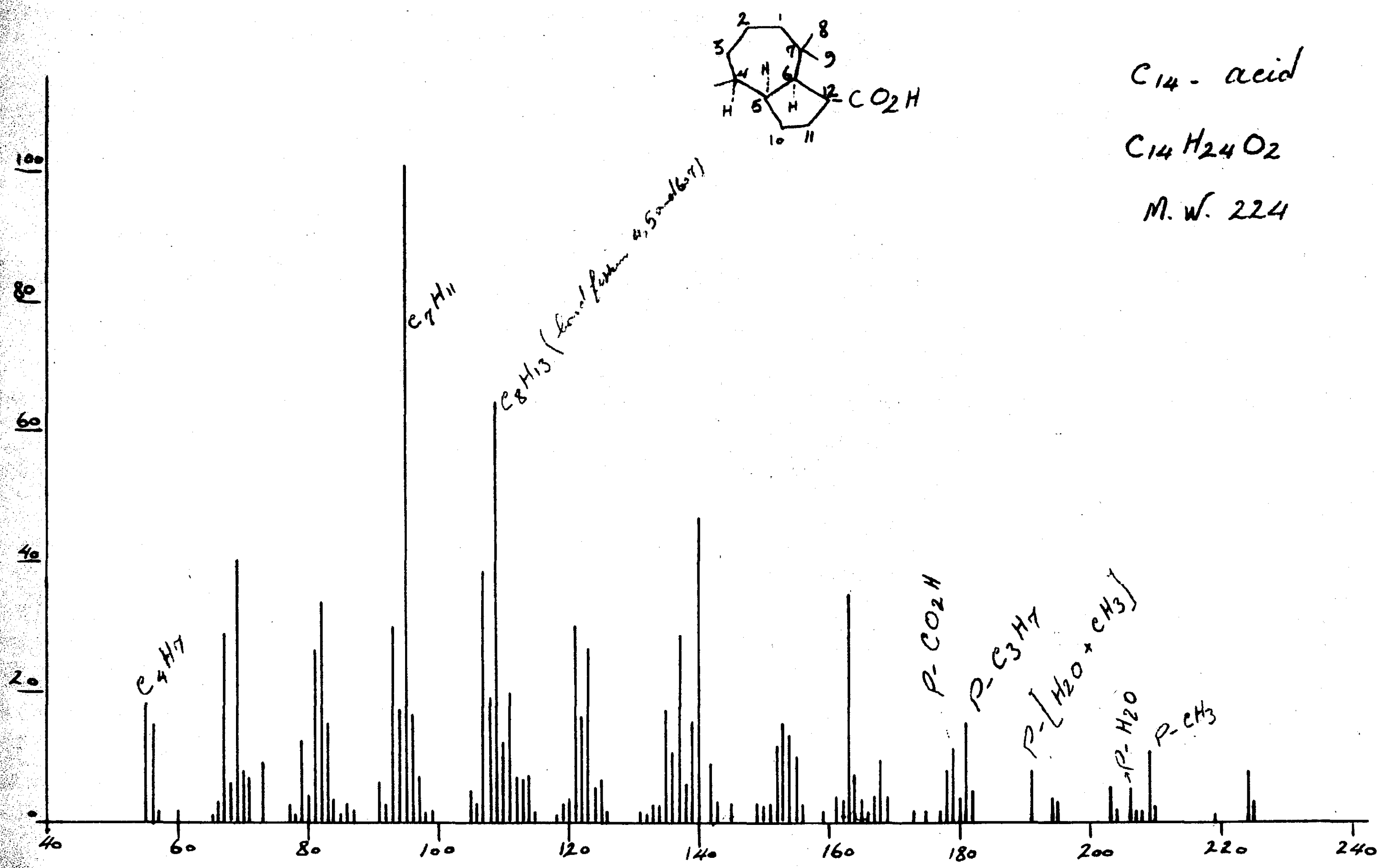
M.S.2

G.O.2.

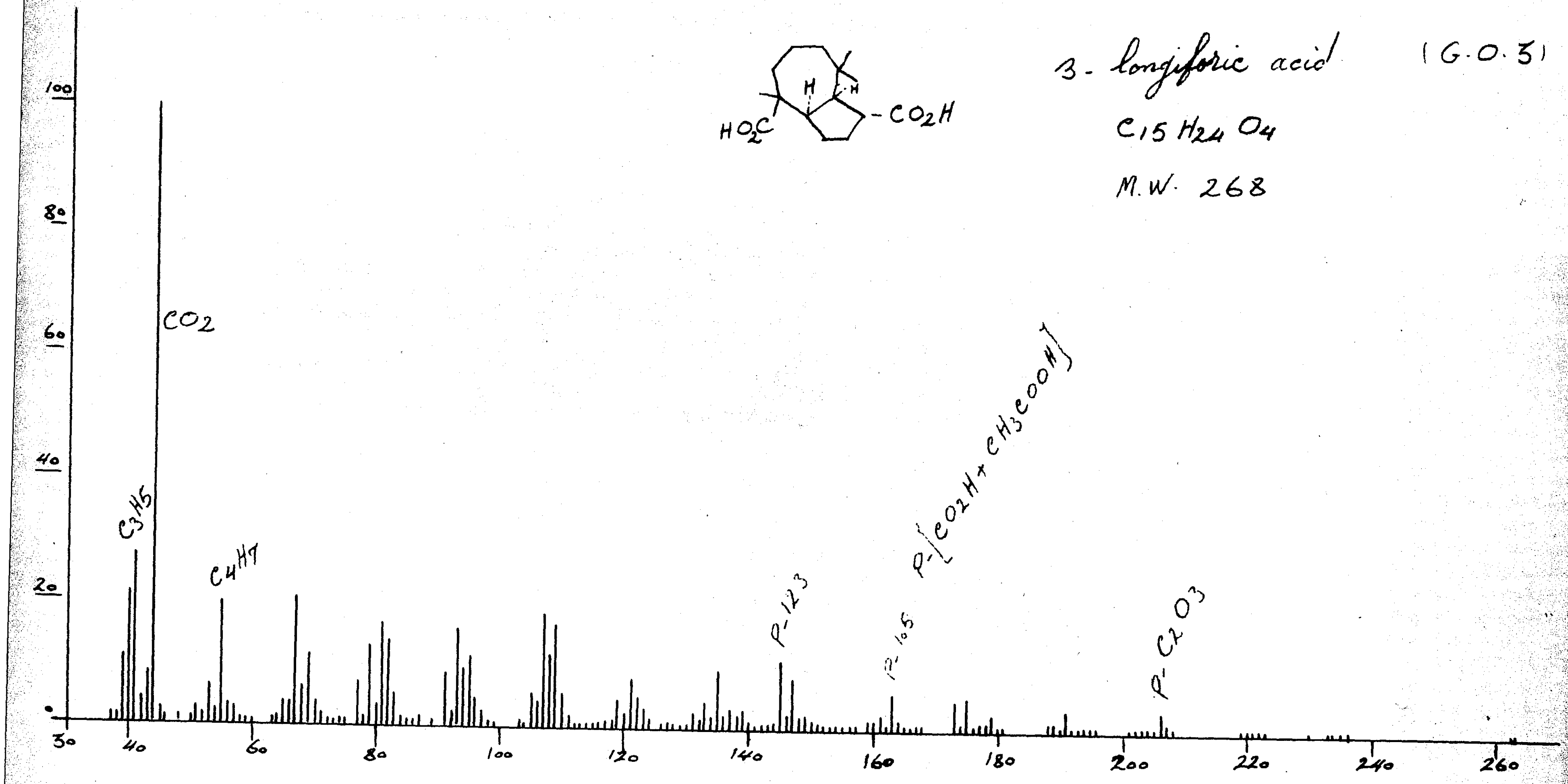
C_{14} - acid

$C_{14}H_{24}O_2$

M.W. 224



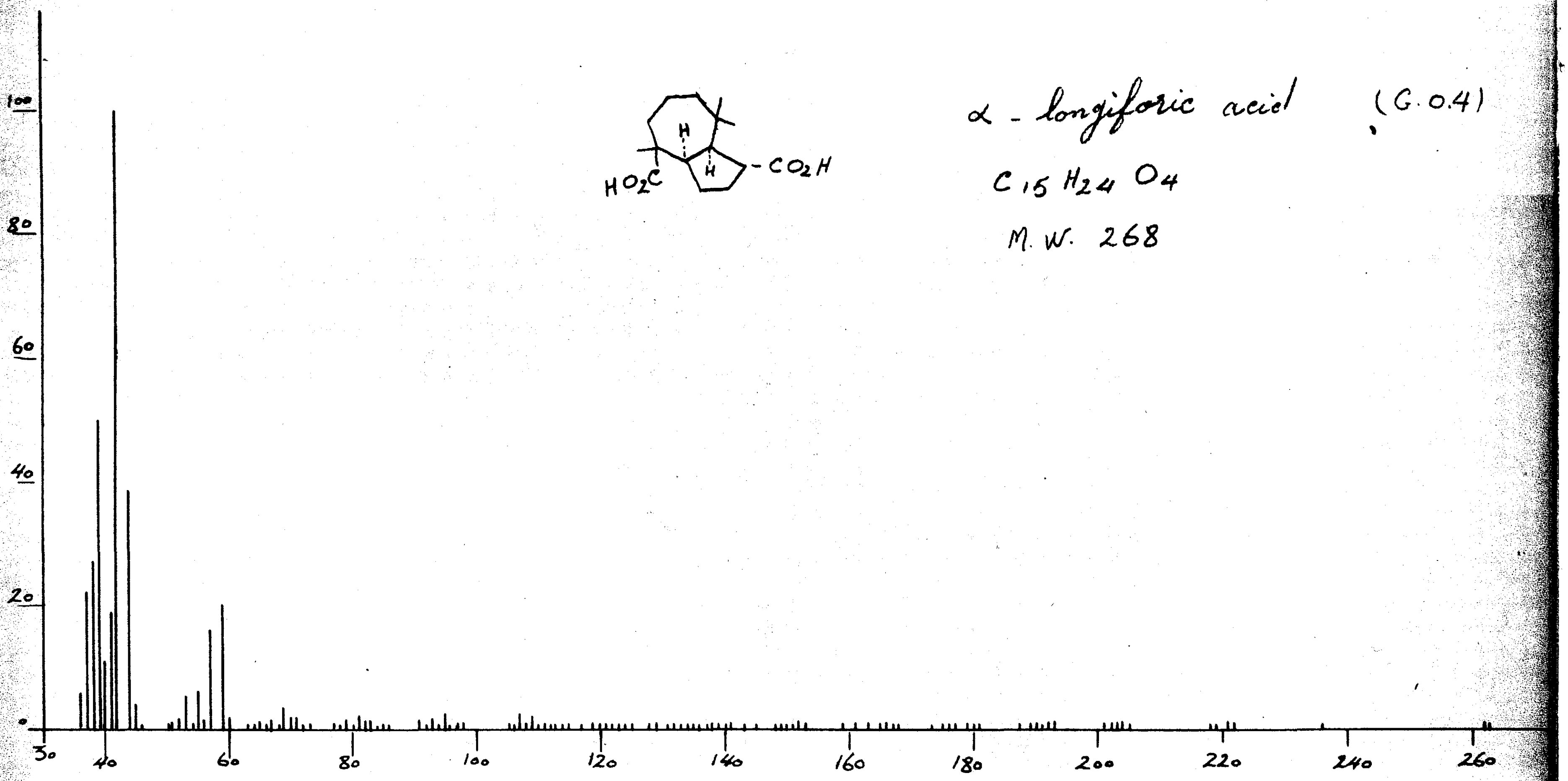
M.S.2.


3- longifolic acid (G.O.3)

$C_{15}H_{24}O_4$

M.W. 268

M.S.9



α - longiforic acid (G.0.4)

$C_{15}H_{24}O_4$

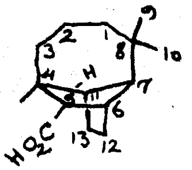
M.W. 268

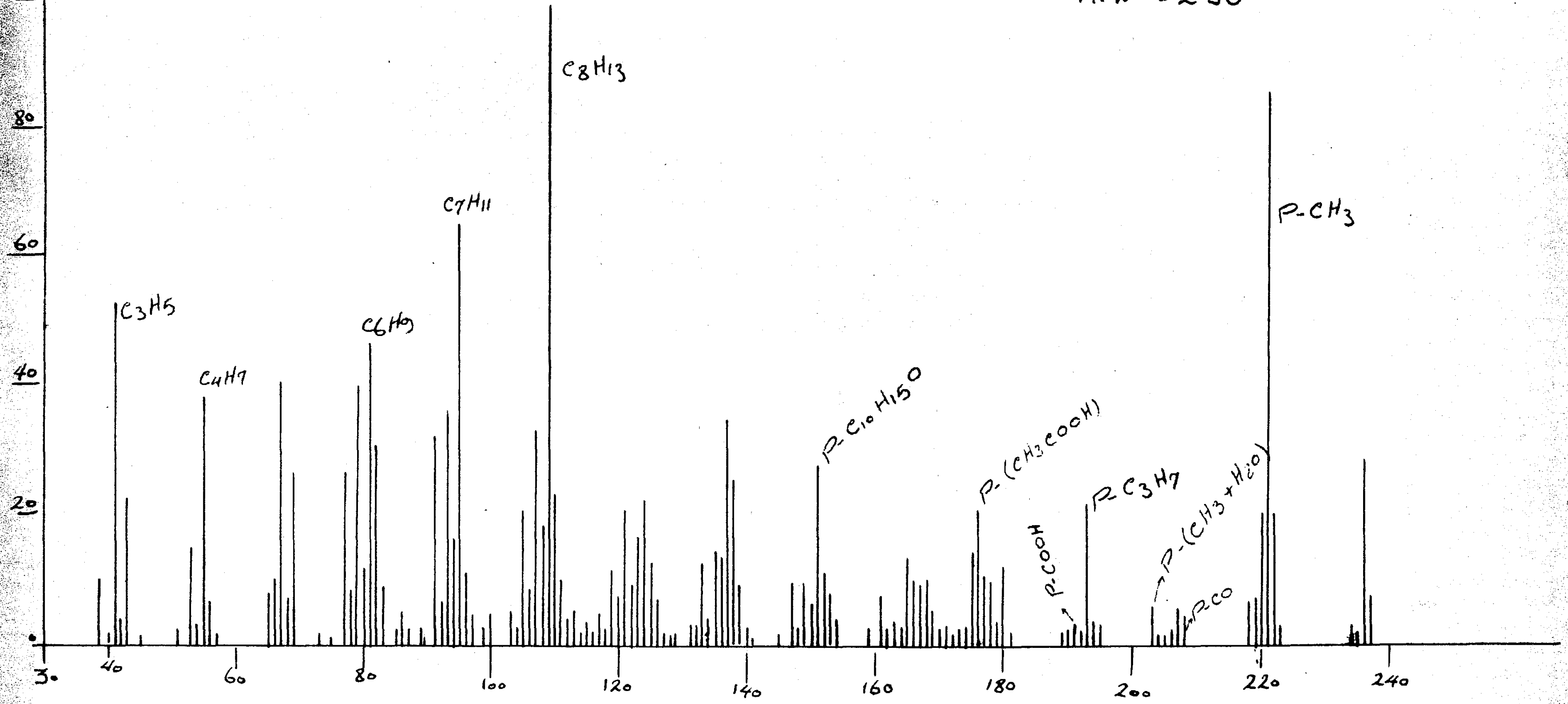
M.S.9

Iso longifolic acid (G.O.5)

$C_{15}H_{24}O_2$

M.W. = 236



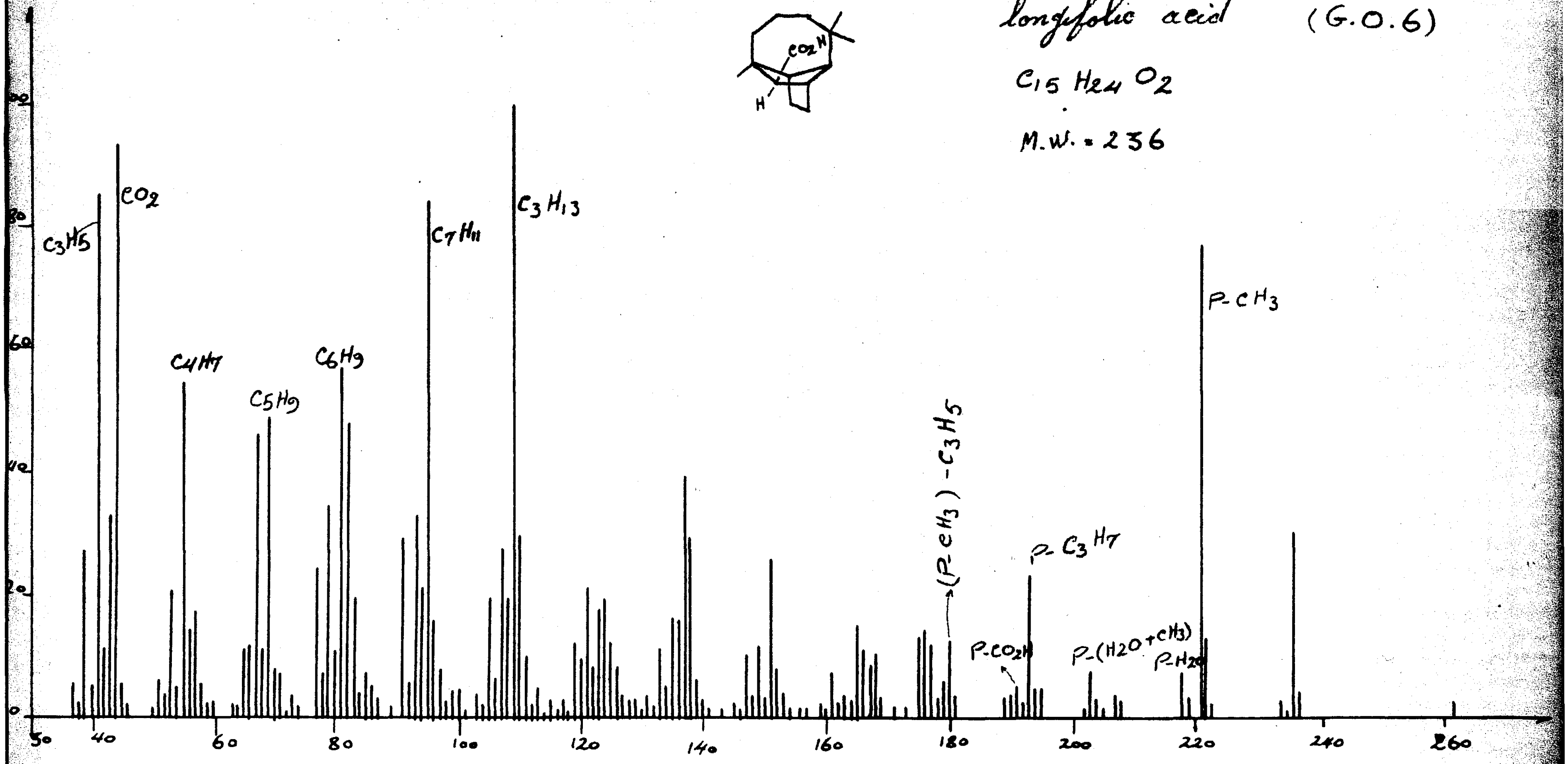


M.S.2

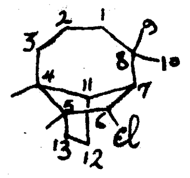
longifolic acid (G.O.6)

$C_{15}H_{24}O_2$

M.W. = 236



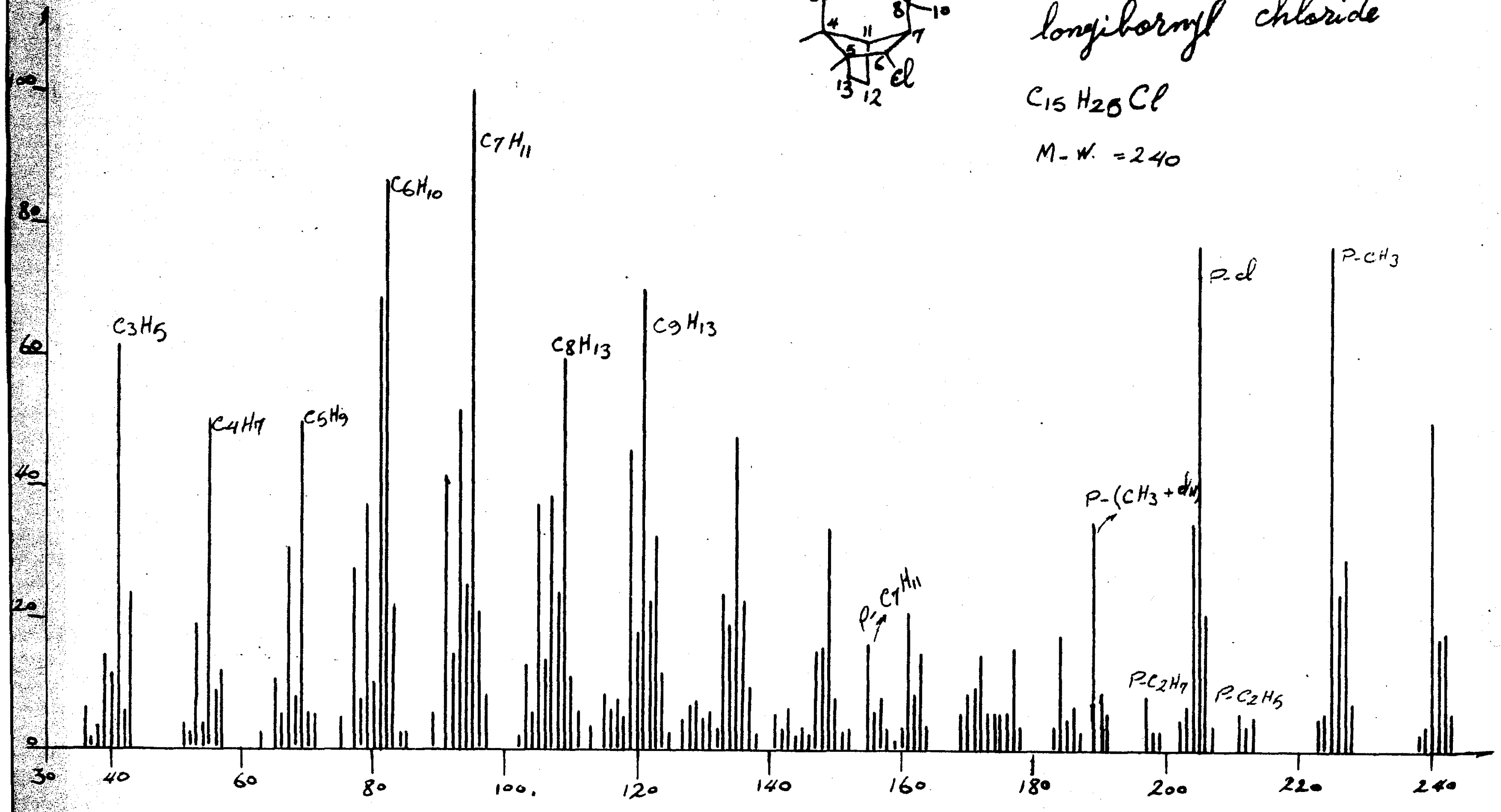
M.S.9



longibornyl chloride (G.O.7)

$C_{15}H_{25}Cl$

M.W. = 240

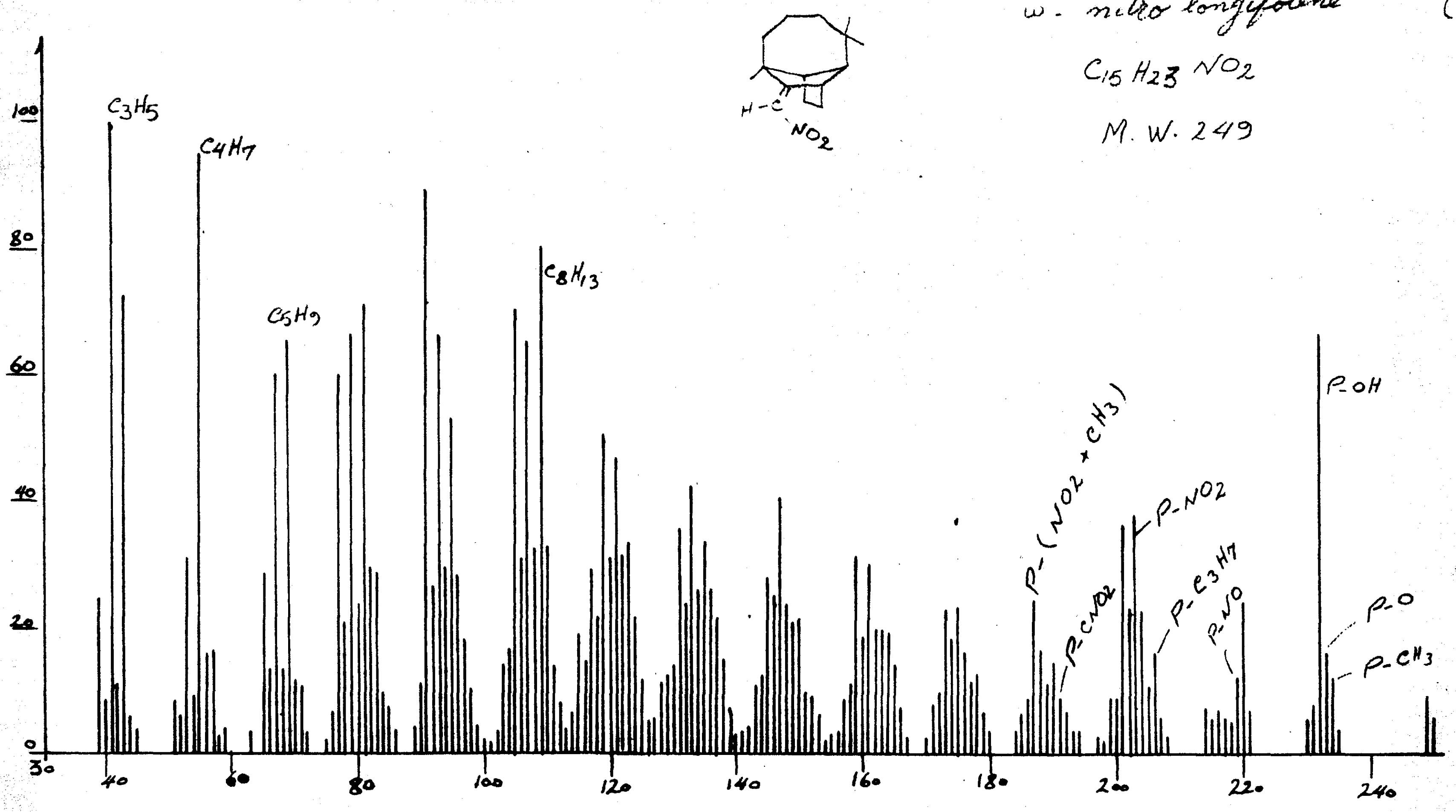


M.S.2

ω - nitro longifolene (G.0.9)

$C_{15}H_{23}NO_2$

M. W. 249

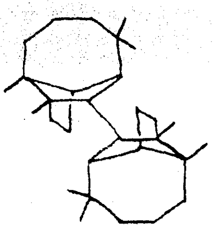


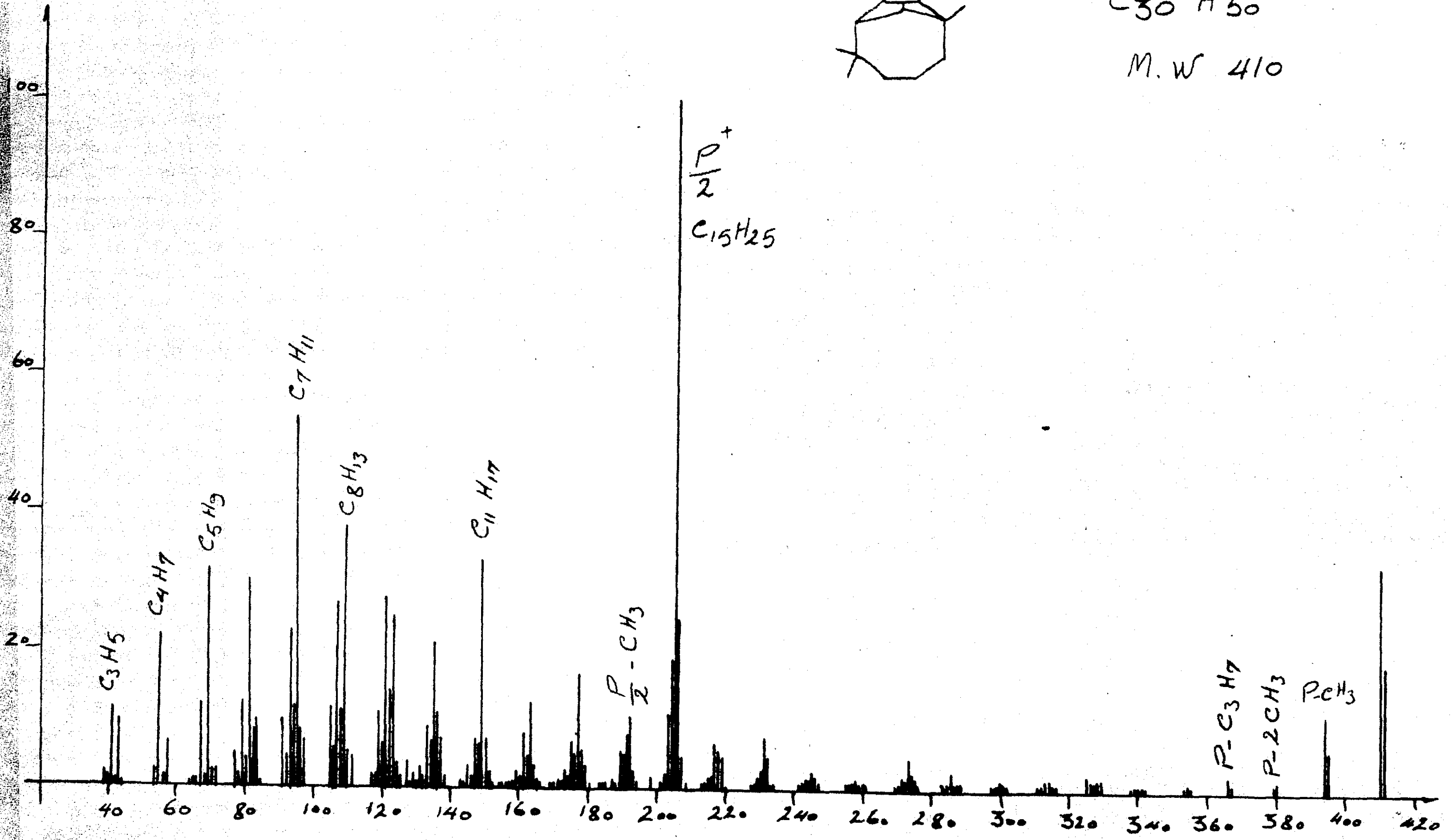
M.S.2

Dilongibornyle. (G.010)

$C_{30}H_{50}$

M.W 410





M.S.2.

REFERENCES

(1) Beynon, J.H., Mass Spectrometry and its application to Organic Chemistry, Elsevier, London, 1960, (page 5).

(2) Harrington, D.B., Advances in Mass Spectrometry, Pergamon Press, 1959, (p.249).

(3) Glenn, W.E., AECD, 3337 (UCRL-1628), (January, 1952).

(4) Bennett, W.H., Instrument, (1949), 22, 472.

(5) Bennett, W.H., Natl.Bur.Standards,Circ, (1953), 522, 111.

(6) Thomson, J.J., Phil.Mag., (1911), 21, 225.

(7) Thomson, J.J., Rays of positive Electricity and their application to chemical analysis, Longmans, Green & Co., London, 1913.

(8) Aston, F.W. and R.H. Fowler, Phil.Mag., (1922), 43, 514.

(9) Aston, F.W., Mass spectra and isotopes, Longmans, Green & Co. Inc., New York, 1942.

(10) Dempster, A.J., Phys.Rev., (1918), 11, 316.

(11) Classen, J., Jahrb.Hamburg.Wiss.Anst., Beiheft, (1907).

(12) Classen, J., Physik.Z., (1908), 9, 762.

(13) Bartky, W. and A.J. Dempster, Phys.Revs., (1929), 33, 1019.

(14) Craig, R.D. and G.A. Errock, Advances in Mass Spectrometry, Pergamon Press, 1959, (p.66).

(15) Reed, R.I., Fuel, (1960), 39, 341.

(16) Reed, R.I., J.Chem.Soc., (1958), 3432.

(17) Sharkey, A.G., J.L. Shultz and R.A. Friedel, Anal.Chem., (1956) 28, 934.

(18) Beynon, J.H., G.R. Lester and A.E. Williams, J.Phys.Chem., (1959), 63, 1861.

(19) Beynon, J.H., Mass Spectrometry and its application to Organic Chemistry, Elsevier, London, (1960, (p.345).

(20) Beynon, J.H., op. cit., (p.362).

(21) Beynon, J.H., op. cit., (p.354).

(22) Collin, J., Bull.Soc.Roy.Sci.Liege, (1952), 21, 446.

(23) Judson, C.M. and R.J. Francel, ASTM E-14 Meeting on Mass Spectrometry, San Francisco, May, 1955.

(24) Collin, J., Bull.Soc.Roy.Sci.Liege, (1954), 23, 194.

(25) Beynon, J.H., op. cit., (p.406).

(26) McLafferty, F.W. and R.S. Gohlke, Anal.Chem., (1959), 31, 2076.

(27) Reed, R.I., Fuel, Vol.xxxx, ((1960), pp.341-349.

(28) Beynon, J.H., op. cit., (p.387).

(29) Friedman, L., A.P. Irssa and G. Wilkinson, J.Amer.Chem.Soc., (1955), 77, 3689.

(30) Wilkinson, G., F.A. Cotton and J.M. Birmingham, J.Inorg. Nuclear Chem., (1956), 2, 95.

(31) McLafferty, F.W., Anal.Chem., (1956), 28, 306.

(32) Reed, R.I., Ion production by Electron Impact, Academic Press, London, New York, 1962.

(33) Happ, G.P. and Stewart, J.Amer.Chem.Soc., (1952), 74, 4404.

(34) Gohlke, R.S. amd F.W. McLafferty, ASTM E-14 Meeting, San Francisco, 1955.

(35) Sharkey, A.G., J.L. Shultz and R.A. Friedel, Anal.Chem., (1959) 31, 87.

(36) Ryhage, R. and E. Stenhagen, Arkiv.Kimi., (1959), 13, 523.

(37) McLafferty, F.W. and R. S. Gohlke, Anal.Chem., (1959), 2076.

(38) Ryhage, R. and E. Stenhagen, Act.Chem.Scand., (1957), 11, 196.

(39) Field, F.H., and J.L. Franklin, Electron impact phenomena, Academic Press, New York, 1957, pp.185-95.

(40) Friedman, L., Lewis and F.A. Long, J.Amer.Chem.Soc., (1953), 75, 2832.

(41) Honig, R.E., Phys.Rev., (1949), 75, 1319A.

(42) Langer, A., J.Phys. & Colloid Chem., (1950), 54, 618.

(43) McLafferty, F.W., Anal.Chem., (1959), 82, 31.

(44) Gilpin, J.A., Anal.Chem., (1959), 31, 935.

(45) McLafferty, F.W., Anal.Chem., (1956), 28, 306.

(46) Leng and Stall, Anal.Chem., (1961), 33, 707.

(47) Kinny and Cook, Anal.Chem., (1952), 24, 1391.

(48) Friedel, R.A., J.L. Shultz and A.G. Sharkey, Anal.Chem., (1956), 28, 926.

(49) A.P.I. Research Project No.44.

(50) Meyerson, S. and P.N. Rylander, J.Amer.Chem.Soc., (1957), 79, 842.

(51) idem ibid 1058.

(52) Meyerson, S. and P.N. Rylander, J.Chem.Phys., (1957), 27, 901.

(53) Rylander, P.N. and S. Meyerson, J.Amer.Chem.Soc., (1956), 78, 5799.

(54) Ourisson, G., unpublished work communicated privately.

(55) Mohler, F.L., J.Wash.Acad.Sci., (1948), 38, 193.

(56) Kistemaker, J., Ind.Chim.belge, (1954), 19, 597.

(57) O'Neal, M.J. and T.P. Weir, Anal.Chem., (1951), 23, 830.

(58) Stephen, S., Friedland and G.H. Lane, Jr., Anal.Chem., (1959), 31, 169.

(59) Beynon, J.H., op. cit., (p.406).

(60) Reed, R.I., Ion production by electron impact, Academic press, London, New York, 1962, (p.171).

(61) Beynon, J.H., op. cit., (p.371).

(62) Reed, R.I., op cit., (p.163).

(63) Biemann, K. and J. Seibl, J.Amer.Chem.Soc., (1959), 81, 3149.

(64) Quinn, L.D. and M.E. Hobbs, Anal.Chem., (1958), 30, 1400.

(65) McLafferty, F.W., Anal.Chem., (1957), 29, 1782.

(66) Mohler, F.L., L. Williams and E.J. Wells, Jr., and H.M. Dean, J.Chem.Phys., (1949), 17, 1358.

(67) Natalis, P., Bull.Soc.chim.Belges., (1960), 69, pp.519-533.

(68) Beynon, J.H., private communication.

(69) Schumb, W.C., M.S. Sherrill and S.B. Sweetser, J.Amer.Chem.Soc., (1937), 59, 2360.

(70) Page, J.A. and G. Wilkinson, Ibid., (1952), 74, 6149.