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CHEMISTRY DEPARTMENT.

A thesis entitled

"Some Aspects of Mass Spectrometry"

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By

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CHAPTER I

The Mass Spectra of some Phthalocyanines.

Copper phthalocyanine and the halogenated derivatives examined all have melting points of 550°C or greater. To obtain the mass spectra some source modifications as well as the heated probe described in Chapter II were necessary. Heat was supplied by the platinum filament which could either be in contact with the sample or isolated from it by a glass wall as shown in Fig. VII. The former type of probe was employed during this work because intense local heat is possible and the temperature of the platinum filament quickly varies with changes in the current passing through it. The mass spectrum of copper phthalocyanine can be obtained using both types of probe. The substituted derivatives, however, require more heat and this cannot be supplied by heating through a glass wall without melting the probe. The major ions of the spectrum of copper phthalocyanine thus obtained are shown in Table I column II.

Fragments containing copper or chlorine give ions corresponding to all combinations of the isotopes. Table II has been included to facilitate recognition of these groups of ions by their abundance ratios. For convenience only the ion containing the most abundant isotopes, namely copper 63 and chlorine 35, is discussed. Neither phthalonitrile nor any of its chlorinated derivatives was present in any of the compounds studied.

(a) Copper Phthalocyanine.

This spectrum was obtained using the filament in contact with the compound under examination. Repeatedly scanning the mass range as the sample temperature was raised from the normal operating temperature to that of red-hot platinum gave the following result. Initially only ions of m/e = 128 and below were obtained. As the overall temperature was raised ions were observed up to m/e = 575. Further increase however resulted in ions of m/e 128 and below only being recorded. Fig. I shows the molecule copper phthalocyanine and a proposed thermal depolymerization into phthalonitrile molecules and copper.

These observations may be explained as follows. The hot filament depolymerizes the molecules near it and the phthalonitrile thus produced becomes ionized and fragmented. A general increase in temperature allows evaporation of the copper phthalocyanine and normal fragmentation of this molecule occurs yielding ions up to m/e = 575. Further heating results in complete depolymerization yielding only the spectrum of phthalonitrile (M.W. 128). The spectrum shown in Table I column III is one such in which ions up to m/e = 575 were recorded. The spectrum of phthalonitrile was obtained and is shown in Table I column I. Comparison between this spectrum and the spectrum of copper phthalocyanine below m/e = 128 shows good agreement and confirms that phthalo-

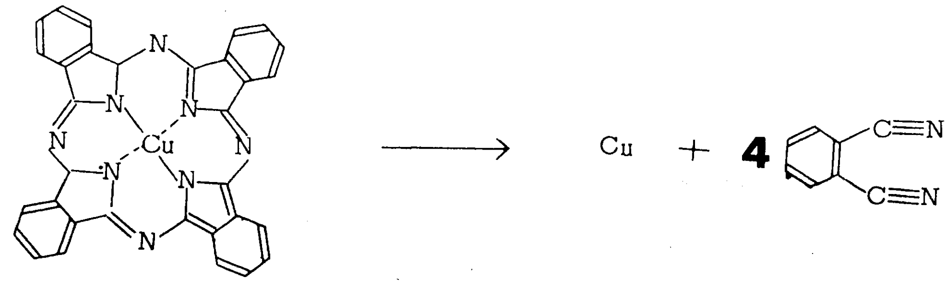

N
N
N
Cu
N
N
N
N
N
Cu
+
4
C≡N
C≡N

FIG I

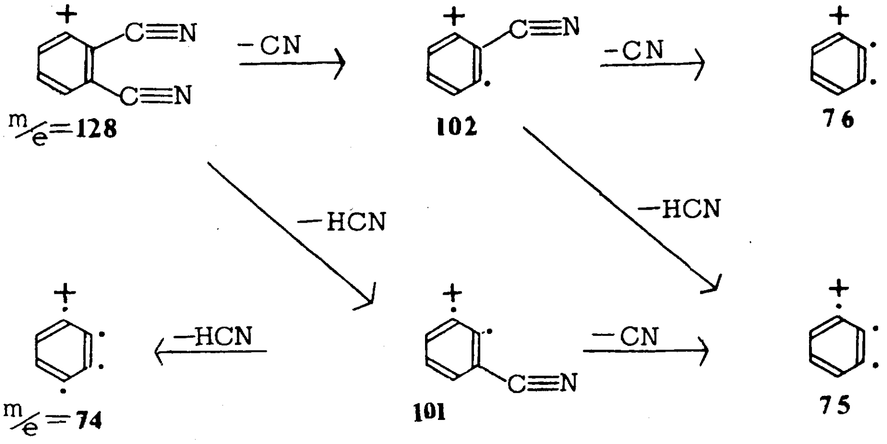

+
C≡N
C≡N
m/e=128
−CN
102
−CN
76
−HCN
−HCN
m/e = 74
−HCN
101
−CN
75

FIG II

nitrile is being formed in the above process. Fig. II shows the breakdown of phthalonitrile. The ion at m/e = 191 is 63 mass units above m/e = 128 and the abundance ratio of the ions m/e = 191 and m/e = 193 is 7 : 3, indicating that it is one quarter of the phthalocyanine nucleus plus a copper atom (The natural abundance ratio Cu^{63} : Cu^{65} is 7 : 3). Ions at m/e = 63 and 65 in the ratio of 7 : 3 also confirm the presence of copper in the parent molecule. The parent ions singly and doubly charged are present at m/e = 575 and 287.5 respectively and the isotopic ions present with them correspond to one copper atom. However, the isotope ratios are not in good agreement; a consequence of the limited resolving power and the high m/e values. The unusual stability of the copper phthalocyanine molecule is demonstrated by the exceedingly large abundance of the parent molecular ion in the spectrum shown in column II. The only difference between thermal and electron-impact-induced dissociations is that a copper atom is combined with one quarter of the phthalocyanine nucleus in the latter and a parent molecular ion is observed.

b) <u>Copper 3, 6 octachlorophthalocyanine.</u>

From the mass spectrum of this compound shown in Table I, column VII it can be seen that the hexa, hepta and nonachloro derivatives are present as impurities. The parent ion is at m/e = 847, $Cu^{63} C_{32} H_8 N_8 Cl_8^{35}$ and a doubly charged parent ion occurs at m/e = 423.5.

The base peak at m/e = 196 is in a group the abundance ratio of which confirms the presence of two chlorine atoms. This suggests that the ion is a dichlorinated phthalonitrile. The position of the substituents cannot be deduced. Loss of chlorine is observed to a small extent. M/e = 259 and its associated ions correspond to the addition of a copper atom to the above fragment. The other ions are chlorinated phthalonitrile fragments derived from the impurities, e.g. m/e = 162, monochlorophthalonitrile and m/e = 230 trichlorophthalonitrile. Copper ions are also observed at m/e = 63 and m/e 65. The ions at m/e = 35, 36, 37 and 38 corresponding to Cl^{35}, HCl^{35}, Cl^{37} and HCl^{37} were so large that to normalize the spectrum with respect to them would be pointless. The chlorine and hydrogen chloride are formed by thermal decomposition of the halogenated copper phthalocyanine in high vacuum.

c) Copper dodecachlorophthalocyanine.

The spectrum is shown in Table I column V. Neither the singly nor doubly charged parent molecular ion was present in this spectrum. This may be expected as the amount of substitution in the molecule requires a higher temperature for volatilization which facilitates depolymerization. However, the ion at m/e = 293, $Cu^{63}\ C_8\ HN_2\ Cl_3^{35}$ indicates that electron-impact-induced dissociation is occurring. The ion at m/e = 230, $C_8\ HN_2\ Cl_3^{35}$, namely trichlorophthalonitrile is the base peak of the spectrum. The other major ions correspond to di- and tetrachlorophthalonitrile.

This type of compound is produced by chlorination of copper phthalocyanine which accounts for the presence of the impurities. The name dodecachloro- is used in this case because the chlorination has been continued until the analysis was consistent with twelve chlorine atoms per molecule. Thermal depolymerization gives the chlorinated quarter fragments of the phthalocyanine nucleus. Thermal decomposition yields chlorine and hydrogen chloride in large amounts giving the ions at m/e = 35, 36, 37 and 38. The ions at m/e 63 and 65 are very small because thermal depolymerization is the most prominent process.

d) Copper 3, 6 hexachlorophthalocyanine.

The spectrum is shown in Table I column VI. Impurities can be seen in it ranging from the unsubstituted to the octachloro-copper phthalocyanine. Basically the latter compound is made by combining three dichlorophthalonitrile molecules, one phthalonitrile and a copper salt. However, impurities of mono- and trichlorophthalonitrile are present in the dichlorophthalonitrile and a range of compounds is produced, the even chlorine content derivatives being the most abundant. In the case of some of the high mass ions of low abundance the resolving power was not sufficient to separate the ions due to each isotope combination. A broad band resulted and the abundance quoted is the maximum value of the band. In more abundant groups of ions in the parent molecular ion region those peaks which are resolved are listed and the presence of the ions of very small isotope contributions is inferred from the calculated values as shown in the tables. The value of each isotope contribution is calculated from the expression

$$(A\ Cu^{63} + B\ Cu^{65})^m\ (C\ Cl^{35} + D\ Cl^{37})^n$$

where A & B and C & D are the isotope ratios and "m" and "n" are the number of atoms of Cu and Cl present respectively. For six chlorine atoms and one copper atom present in a molecule eight ions are produced and their ratios are found from the above expression using $Cu^{63} : Cu^{65}$ as 7 : 3 and $Cl^{35} : Cl^{37}$ as 3 : 1 to be 5,103 : 12,393 : 12,879 : 7,425 : 2,565 : 531 : 61 : 3. As can be seen the abundance of the last two ions is so small that they could not be measured. The ions of m/e = 575 to 847 correspond to the parent molecular ions of the range of chlorinated copper phthalocyanine molecules present. That those ions are parent ions is indicated by comparison with the spectrum of the octachloro-derivative Table 1, column VII which shows no ready loss of chlorine from the molecular ion. The presence of a nonachloro-derivative in the octachloro- spectrum also suggests that the hepta and hexachloro- ions present are parent molecular ions.

Doubly charged ions corresponding to the more abundant parent molecular ions are observed. The ions m/e = 128, 162 and 196 are all abundant ions and a very small one occurs corresponding to $Cu^{63}\ C_8\ H_2\ N_2\ Cl_2^{35}$.

The very abundant ions m/e = 35, 36, 37 and 38 also occur in this spectrum and show that thermal decomposition is occurring. Some loss of chlorine is observed from the substituted phthalonitrile fragments and from the parent ions. Beynon and his co-workers obtained the spectrum of copper tetrachlorophthalocyanine using an M. S. 8. double focusing instrument(1) and showed that the loss of chlorine and hydrogen chloride did occur from the parent molecular ion. The lack of resolving power of the M. S. 2. instrument does not allow conclusions to be drawn about the behaviour of the parent molecular ions.

e) Copper monochlorophthalocyanine.

The spectrum is shown in Table I column IV. Parent ions are present corresponding to copper phthalocyanine and the mono- and dichloro- derivatives. The molecule of copper phthalocyanine is known to be abnormally stable but the monochloro- derivative is known to thermally decompose under vacuum to yield chlorine and hydrogen chloride.(2) The comparative abundances of the parent molecular ions m/e = 575 and m/e = 609 together with the fact that no appreciable ion occurs at m/e = 162 and m/e = 225 confirms this. The abundances of m/e = 35, 36, 37 and 38 are also very large and ions at m/e = 63 and 65 are present.

The general conclusion about this technique is, therefore, that the ions in the spectra are formed by three processes.

(a) Electron impact induced dissociation.

(b) Thermal depolymerization.

(c) Thermal decomposition.

To recognize any pure copper phthalocyanine the only ions necessary are the parent molecular ion and the phthalonitriles derived from it by depolymerization. In cases where substitution is such that the molecule depolymerizes without giving a parent ion possible structures can be deduced by examination of the phthalonitrile derivatives observed.

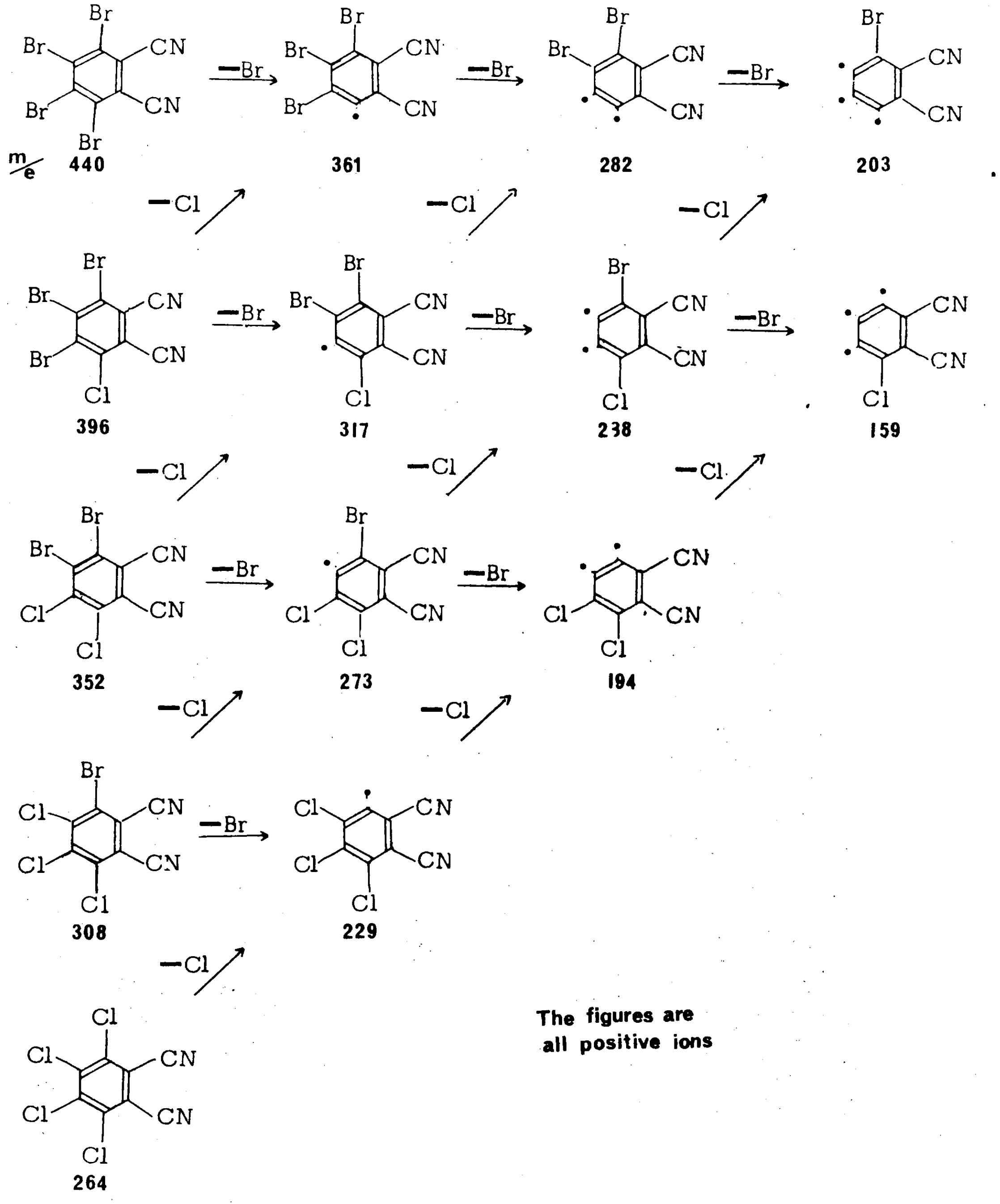
Three dyes which were suspected of being halogenated derivatives of copper phthalocyanine were examined using the information gained from the cracking pattern of the chlorinated derivatives. These dyes are referred to as A, B and C. To obtain the mass spectra exactly the same technique was used as was employed for the chlorinated derivatives. The spectra are shown in Table III, tabulated from (m/e = 194) the value of the least substituted phthalonitrile present, the only information used. In the lower mass region the ions m/e = 35, 36, 37 and 38 are present in excessive abundance showing the presence of chlorine. The equally abundant ions of m/e = 79, 80, 81 and 82 and m/e = 158, 160, and 162 prove the presence of bromine.

The three dyes gave spectra which differed only in the relative abundances of the major groups of ions. A marked similarity between these spectra and that of copper dodecachlorophthalocyanine indicated that the dyes were halogenated derivatives of copper phthalocyanine. Values were calculated for the isotope abundance ratios of the ions which would be produced for all possible combinations of chlorine and bromine to a maximum of four present in one phthalonitrile ion. One copper atom was then included and the complete set of calculations repeated. The results are shown in Table IV. The m/e value listed is that of the ion containing the isotopes Cl^{35}, Br^{79} and Cu^{63}.

In all three spectra an ion is observed at m/e = 425 which corresponds to a tribrominated phthalonitrile ion combined with one copper atom. The abundance ratios of the ions in this group are not in good agreement but no other atomic combination yields m/e = 425. No copper atom appears to be attached to a tetrasubstituted phthalonitrile ion, but the structure of this type of ion is not known definitely. Other ions of the same type but differently halogenated also appear combined with a copper atom showing that a mixture is present. The loss of bromine from a fragment is very facile as can be seen: the loss of chlorine or the nitrile group is not. The abundances quoted for brominated ions in the following discussion of each dye appear to be very low because the first ion in a group containing bromine atoms is of low abundance. However, comparison of the abundance of this ion in all three shows the general variation.

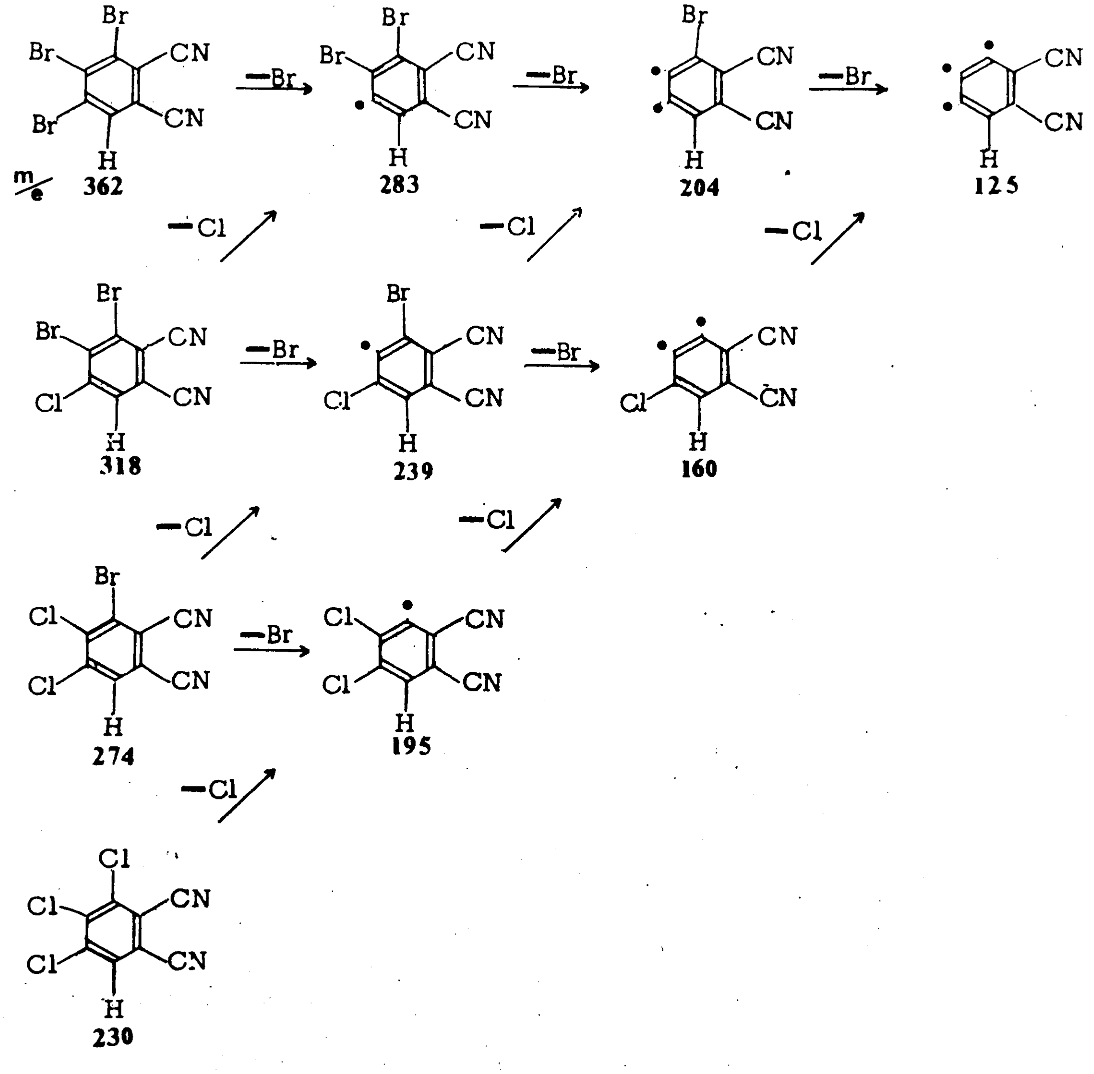
Unknown Dye A.

By using the information in Table IV the following tetrasubstituted phthalonitrile ions were recognized. The abundances of the monoisotopic ions are shown below together with their mass to charge



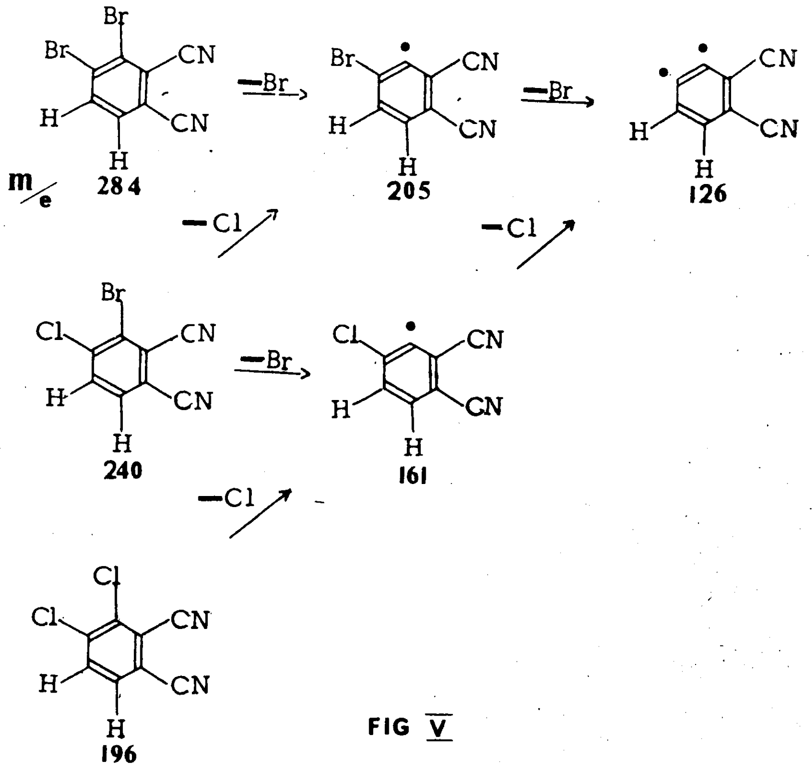
The figures are all positive ions

FIG III



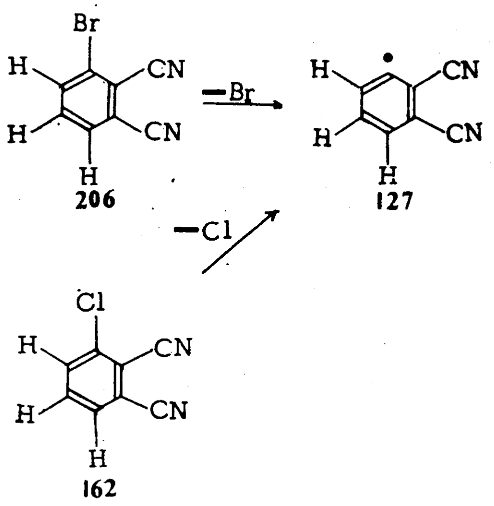
The figures are all positive ions

FIG IV



m/e
284
205
126
240
161
196
−Br
−Cl
Br
Cl
H
CN

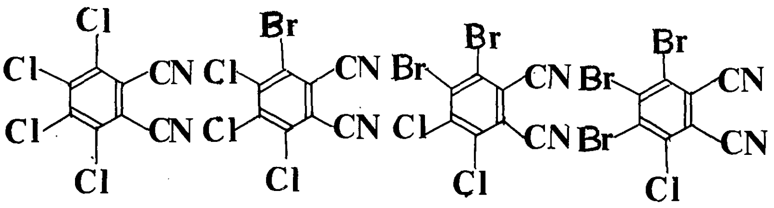
FIG V



206
127
162
−Br
−Cl
Br
Cl
H
CN

FIG VI

values. The base peak is an ion of the group m/e = 264.



m/e	264	308	352	396
% Abundance	74.0	29.3	9.5	1.4

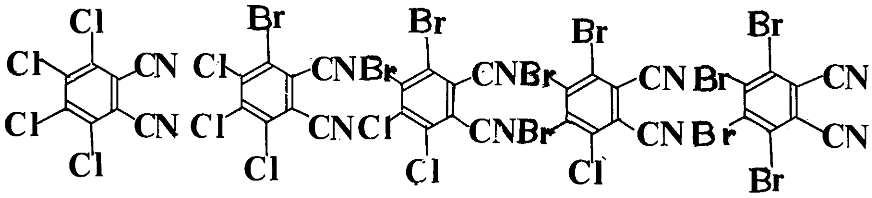
Fig. III summarizes the fragmentation that occurs in the above ions and the figures IV, V and VI indicate the breakdown of phthalonitrile ions which are trisubstituted or less. Even although the loss of chlorine is not significant it has been accounted for in the above figures.

As was the case with copper dodecachlorophthalocyanine no parent ion was observed. However, the dye must be a mixture because of the presence of trisubstituted and disubstituted phthalonitrile fragments in the spectrum together with the ions shown above. Because of the absence of a parent molecular ion the constitution of the most abundant component of the mixture can only be estimated by consideration of the tetrasubstituted phthalonitrile fragments which are formed by depolymerization. The absence of any tetra-brominated phthalonitrile ion in this spectrum suggests that the dye contains slightly more chlorine than bromine.

No structure can be drawn for the most abundant component of the mixture because so many possible isomers exist.

Unknown Dye B.

The following tetra substituted phthalonitrile fragments were recognized in the spectrum of this mixture.



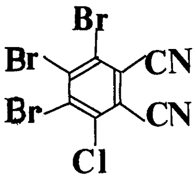
m/e	264	308	352	396	440
% Abundance	27.5	44.8	48.2	17.2	3.4

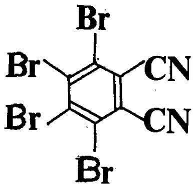
The base peak is an ion of the group m/e = 352.

The abundance of the fully chlorinated phthalonitrile fragment has fallen considerably in this spectrum while that of the brominated fragments has increased. A fully brominated phthalonitrile ion is also present. This suggests that the amount of bromine present in this mixture is greater than in sample A.

Unknown Dye C.

The significant tetrasubstituted phthalonitrile ions in this spectrum are as follows.





m/e	396	440
% Abundance	21.0	18.9

The abundance of the tetrabrominated fragment has greatly increased and the tri-substituted ion is the only other fully substituted fragment of significant abundance present. The bromination of this dye is almost complete and hence the dye must consist mainly of copper hexadecabromo-phthalocyanine.

After this examination had been concluded the manufacturers who had supplied the samples were asked for the analyses in terms of halogen content.

The results are as follows.

Unknown.	% Br.	Br. Atoms/mol.	% Cl.	Cl. Atoms/mol.
A.	40.1	7.2	21.0	8.5
B.	57.0	11.4	7.9	3.6
C.	67.35	15.0	1.3	0.6

In terms of halogen content the mass spectrometric examination had placed the dyes in their correct order. It was also stated that these dyes had been prepared by bromination of copper phthalocyanine followed by chlorination.

The presence of incompletely substituted molecules together with a range of isomeric fully substituted derivatives is thus compatible with the spectra.

TABLE No. I

PERCENTAGE ABUNDANCE

m/e	I	II	III	IV	V	VI	VII
35				17.04	216.2	206.0	218.3
36				71.85	1075.	999.7	1072.
37				5.55	71.28	67.67	79.40
38				23.07	359.1	329.7	347.4
50	16.40		18.41	15.33	12.47	15.38	
50.5	0.70						
51	7.83		10.29	9.63	5.94	12.30	
52	2.79		5.14	5.18	3.56	7.69	
53	1.67		1.25		1.19	3.07	
61	1.42		1.71				
62	1.44		2.17				
63	2.14	27.30	29.23	40.74	16.63	5.38	8.30
64	4.62		11.52	5.37	51.48	15.38	1.25
65	1.07	11.40	11.85	17.04	7.72	2.31	3.60
73	1.43		2.11		10.69	2.38	
74	3.57		4.29	3.87	8.31	4.76	
75	12.86		16.43	13.99	14.61	19.22	
76	9.28		12.50	11.11	8.71	10.76	
77	6.87		5.87	5.92	2.37	5.76	
78	0.71		1.95	1.48			
79	2.85		0.60				
86	0.14		0.99	0.37		0.67	
87	0.14		1.32	0.74		0.98	
88	1.43		2.41	1.48		2.07	
98	0.71		1.05	1.11		3.07	
99	2.14		3.76	1.63	9.00	12.30	
100	3.57		6.27	4.07	8.31	15.38	1.62
101	25.71		25.74	19.26	2.01	42.29	3.57
102	2.85		6.27	3.70		7.69	0.71
103	1.21		9.90	6.66		3.07	
104			1.32			2.30	
127					2.97	14.61	7.00
128	100.0	8.40	100.0	100.0	8.91	100.0	8.75
129	8.57		15.01	11.85		16.91	
161					14.25	5.38	31.00
162					4.75	32.29	57.96
163					11.88	8.46	28.60
164					2.37	10.70	19.45
165					0.20	1.54	10.72
191		23.10	5.94	51.85			
193		10.50	2.64	21.22			

TABLE I (continued)

m/e	I	II	III	IV	V	VI	VII
196					49.89	28.45	100.0
198					33.26	18.46	70.40
200					5.54	3.01	11.10
230					100.0		21.16
232					100.0		21.16
234					38.90		6.96
236					3.96		0.78
259					7.32	4.23	
261					12.67	4.99	
263					11.88	2.69	
264					76.82		
265					*	0.38	
266					105.3		
268					49.89		
270					13.46		
272					1.01		
287.5		29.40	3.63	40.74		6.92	
288.5		13.65	2.64	25.87		3.92	
293					11.68		1.98
295					24.95		5.95
297					23.76		7.15
299					12.27		4.37
301					4.75		1.98
303.5				Unresolved			
304.5	-			0.37			
305.5							
321.5						4.99	
322.5						5.38	
323.5						2.30	
324.5						0.38	
334					1.98		
336					2.77		
338					4.36		
340					2.18		
342					0.80		
355.5						3.46	
356.5						6.15	
357.5						4.99	
358.5						1.92	
359.5						0.38	
360.5						-	

*obscured by adjacent peaks

TABLE I (continued)

m/e	I	II	III	IV	V	VI	VII
389.5						2.30	0.70
390.5						4.99	1.30
391.5						5.77	1.50
392					3.76		
392.5						3.07	1.00
393.5						1.15	0.30
394					9.70		
394.5						0.36	-
395.5							
396					10.89		
398					8.91		
400					4.36		
402					1.98		
423.5							0.5
424.5							1.40
425.5							1.90
426.5							1.50
427.5							0.80
428.5							0.30
429.5							-
430.5							-
431.5							-
432.5							-
575		100.0	5.28	100.0		23.01	
577			2.97	56.35		13.84	
609				11.11		10.76	
611				8.75		8.46	
613				1.51		1.54	
643	-			2.22 Unresolved		39.27	
645						45.37	
647						23.07	
649						9.22	
677						6.92	
679						11.53	
681						5.76	
683						3.04	
685						1.54	
711						34.60	
713						47.68	
715						33.84	
717						16.15	
719						3.85	

TABLE I (continued)

m/e	I	II	III	IV	V	VI	VII
721						-	
745						3.07 Unresolved	
747							
749							
751							
753							
755							
757							
779						7.69	0.8 Unresolv
781						11.54	
783						12.30	
785						8.46	
787						3.85	
789						0.77	
791						-	
793						-	
813							Unresolv 0.6
↕							
829							
847						4.61 Unresolved	1.3
849							3.5
851							4.6
853							3.8
855							2.0
857							0.8
859							0.2
861							-
863							-
865							-
881							Unresolve 0.2
↕							
901							

I = phthalonitrile, II = copper phthalocyanine, III = copper phthalocyanine, IV = copper monochlorophthalocyanine, V = copper dodecachlorophthalocyanine, VI = copper 3:6 hexachlorophthalocyanine, VII = copper 3:6 octachlorophthalocyanine.

TABLE II

Empirical formula	m/e fragment	Isotope abundance ratio	Fragment plus copper	Isotope abundance ratio
$C_8H_4N_2$	128	-	191	7
			193	3
$C_8H_3N_2Cl^{35}$	162	3	225	21
$C_8H_3N_2Cl^{37}$	164	1	227	16
			229	3
$C_8H_2N_2Cl_2^{35}$	196	9	259	63
$C_8H_2N_2Cl^{35}Cl^{37}$	198	6	261	69
$C_8H_2N_2Cl_2^{37}$	200	1	263	25
			265	3
$C_8HN_2Cl_3^{35}$	230	27	293	189
$C_8HN_2Cl_2^{35}Cl^{37}$	232	27	295	270
$C_8HN_2Cl^{35}Cl_2^{37}$	234	9	297	148
$C_8HN_2Cl_3^{37}$	236	1	299	34
			301	3
$C_8N_2Cl_4^{35}$	264	81		
$C_8N_2CL_3^{35}Cl^{37}$	266	108		
$C_8N_2Cl_2^{35}Cl_2^{37}$	268	54		
$C_8N_2Cl^{35}Cl_3^{37}$	270	12		
$C_8N_2Cl_4^{37}$	272	1		

TABLE III

UNKNOWN COMPOUND A

M/e	% Abundance	M/e	% Abundance
194	25.4	310	58.2
196	16.9	312	42.4
198	2.8	314	15.0
205	6.5	316	5.6
206	14.4	347	1.9
207	6.5	349	6.8
208	14.1	351	9.0
229	18.4	353	9.6
231	18.4	352	9.6
233	6.5	354	18.0
235	0.8	356	16.9
264	74.0	358	7.3
266	100.0	396	1.4
268	50.8	398	4.2
270	13.5	400	4.2
272		402	2.8
273	18.0	425	2.2
275	12.4	427	8.5
277	9.0	429	16.4
279	2.8	431	16.1
308	29.3	433	9.3
		435	2.2

TABLE III

UNKNOWN COMPOUND B

M/e	% Abundance	M/e	% Abundance
194	46.5	347	17.2
196	31.0	349	44.8
198	5.2	351	58.6
229	24.1	353	55.2
231	24.1	352	48.2
233	6.9	354	100.0
235	0.8	356	91.4
238	20.6	358	44.8
240	27.5	361	24.1
242	6.9	363	12.0
264	27.5	365	6.9
266	36.2	396	17.2
268	18.9	398	56.9
270	4.1	400	68.9
272		402	39.6
273	8.6	404	5.2
275	15.5	425	10.3
277	8.6	427	50.0
282	5.2	429	84.5
284	10.3	431	81.0
286	10.3	433	44.8
288	5.2	435	10.3
308	44.8	440	3.4
310	87.9	442	13.8
312	62.0	444	20.7
314	22.4	446	13.8
		448	3.4

TABLE III

UNKNOWN COMPOUND C

M/e	% Abundance.	M/e	% Abundance
205	48.4	358	48.4
206	31.6	361	37.9
207	48.4	363	27.4
208	31.6	365	18.3
239	18.9	396	21.0
241	25.2	398	69.5
243	6.3	400	82.0
284	14.7	402	44.2
286	31.6	404	10.5
288	21.0	425	13.7
290	6.3	427	57.9
347	18.3	429	100.0
349	48.4	431	94.7
351	63.1	433	50.5
353	48.4	440	18.9
354	42.0	442	61.0
355	42.0	444	90.5
356	42.0	446	61.0
357	48.4	448	14.7

TABLE IV

Number and type of atoms present		M/e of entire Phthalo nitrile	Isotopic Abundance Ratio of Ions produced					Number of atoms present	M/e of entire Phthalo nitrile	Isotopic Abundance Ratio of Ions produced					
Br	Cl							Cu							
1		206	1	1				1	269	7	10	3			
2		284	1	2	1			1	347	7	17	13	3		
3		362	1	3	3	1		1	425	7	24	30	16	3	
4		440	1	4	6	4	1	1	503	7	31	54	46	19	3
	1	162	3	1				1	225	21	16	3			
	2	196	9	6	1			1	259	63	69	25	3		
	3	230	27	27	9	1		1	293	189	270	148	34	3	
	4	264	87	108	54	12	1	1	327	567	999	702	246	43	3
1	1	240	3	4	1			1	303	21	37	19	3		
1	2	274	9	15	7	1		1	337	63	132	94	28	3	
1	3	308	27	54	36	12	1	1	371	189	459	414	168	37	3
2	1	318	3	7	5	1		1	381	21	58	56	22	3	
2	2	352	9	24	22	8	1	1	415	63	195	226	122	31	3
3	1	396	3	10	12	6	1	1	459	21	79	114	78	25	3

CHAPTER II

The instrumentation which was carried out during the course of this work is described under the following headings.

1) The Heated Probe.
2) Data Processing Equipment.
3) A Radio-Frequency Mass Spectrometer.

1) The Heated Probe.

Mass spectrometers with electron bombardment ion-sources are mostly used to examine compounds in the vapour phase. Gases and volatile liquids can be admitted directly into the instrument through a gas sampling system at room temperature. Less volatile liquids and low melting solids (up to 300°C) can be introduced using a heated inlet system.(3) Less volatile compounds and those which decompose in the heated inlet system can be evaporated directly into the ion chamber using a glass probe which has been described by Reed.(4) Compounds which are involatile above about 350°C cannot be examined by the above sample handling systems.

In order to study several compounds with melting points in the region of 550°C the standard source had to be slightly modified and a sample probe constructed which had a small platinum wire furnace built into its end. The complete probe unit is shown in position in

Fig. VII(a) along with the modifications to the conventional Nier type source assembly. The constructional details of the probe are as follows.

I) The length is such that the end is near but not touching the repeller plate and is directed through the hole in it.

II) The probe and insulating sleeving are made of Pyrex glass.

III) The platinum filament which is the furnace of the probe is formed by winding the wire on a hypodermic needle as former.

IV) The filament is then insulated with Pyrex sleeving, positioned and sealed into place.

V) Copper leads are covered with plastic sleeving and the cone end is sealed with Araldite.

VI) The filament can be in the sample cavity (position A) or isolated from it (position B) as shown in Fig. VII. In position B it is necessary to evacuate the probe to prevent its disrupting when the filament is white hot.

VII) A glass-to-metal seal is fitted with a B.10 socket and this allows attachment of the probe to the standard ion source of the M.S.2 as shown.

VIII) The power is supplied through a "Variac" and a stepdown transformer which allows continuous variation of the voltage and a maximum power output of 40 watts.

The condensation of involatile material in the ion-chamber is red-

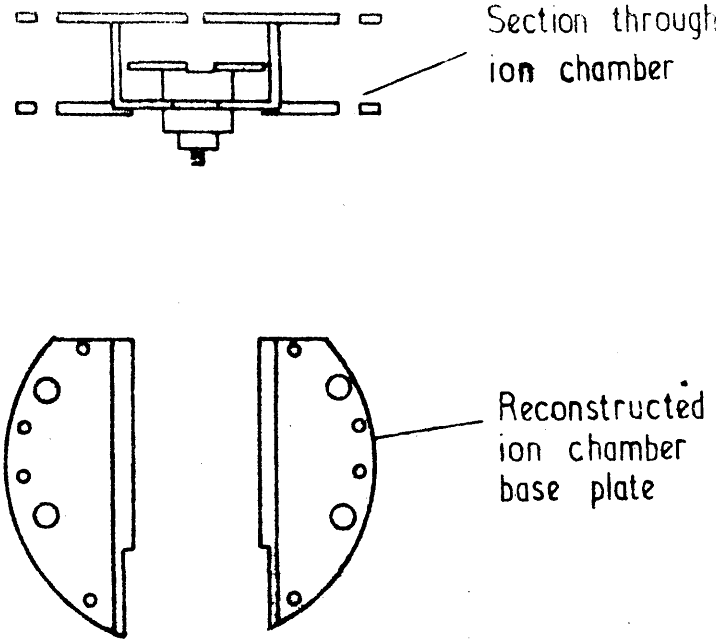


FIG VIIb

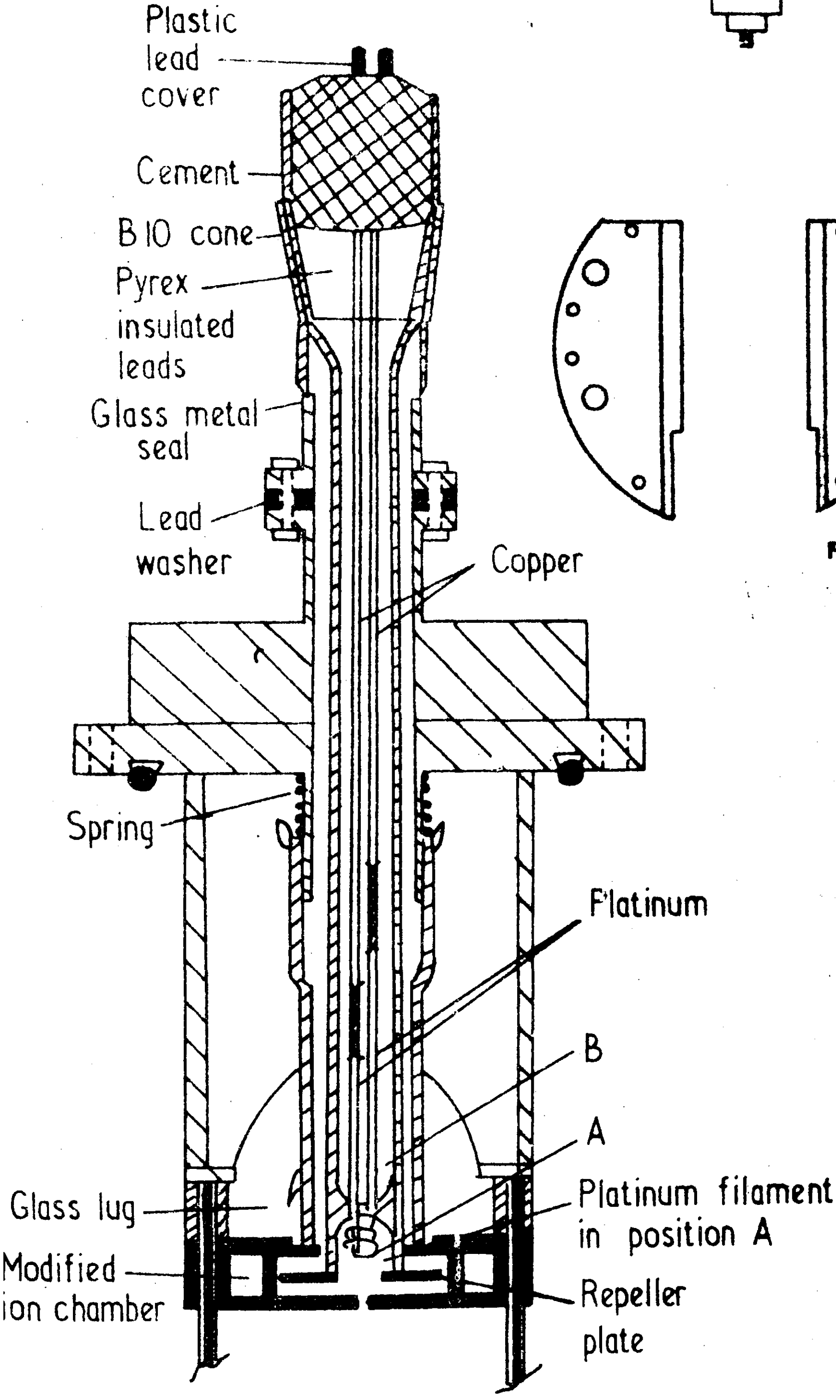


FIG VIIa

uced by drilling a 2 mm hole in the Nier repeller plate to allow evaporation of the material from the heated probe directly into the electron beam. Frequent cleaning is still necessary, however, and other source modifications were made to allow removal of the ion-chamber without stripping down the whole source. These are:-

1) The bottom of the ion chamber is brazed on and a new set of base plates constructed as shown in Fig. VII(b).

2) The sample inlet tube is set on a spring and has a glass lug attached.

When the nuts of the support columns are loosened the base plates of the ion chamber sag. The sample inlet tube is depressed on its spring so that it clears the ion chamber electrodes. The ion chamber can then be removed for cleaning. The modifications in no way affected the performance of the ion source. This probe was used continuously during the examination of the phthalocyanines.

2) Data Processing Equipment.

Modern mass spectrometers are capable of supplying a vast amount of data very quickly in the form of a trace upon a chart. Processing this data is laborious and time consuming. Some simple devices were devised to facilitate this work and they are discussed below.

A. A device which simultaneously measures and normalizes peaks on a trace recorded mass spectrum.

A mass spectrum is commonly recorded as a set of traces of different sensitivity on a photographic chart. The peak heights are measured with a rule, the largest is taken as the base peak and all others are normalized, i.e. quoted as a percentage of it. Fig. VIII shows the construction of a simple device which combines the above operations. The principle used is that of similar triangles. A sheet of Perspex (4ft. x 1ft. x 1/16th. in.) is machined straight along one edge and a line is scribed parallel to it one inch away on the underside. A metre rule graduated in millimetres and having a transverse slot cut at the zero end is attached to the Perspex by means of butterfly nuts and screws through a hole and slot which are countersunk on the underside. A metal bar with a true edge and two G clamps are also required.

The chart is fixed to the bench (by sellotape) and the Perspex sheet placed over it with the scribed line on the desired galvanometer trace. The metal bar is brought firmly up to the edge of the Perspex and clamped there. The metre rule is then set by locking nuts so that its zero mark is on the scribed line and the 100.0 mark just touches the top of the base peak as shown. The normalized height of any given peak is read off by sliding the device along the bar until the rule just touches the top of it.

To obtain the greatest accuracy the trace on which the base peak is almost equal to the full chart width is first selected, and all peaks above 10% are measured. One the height of which is about 9%

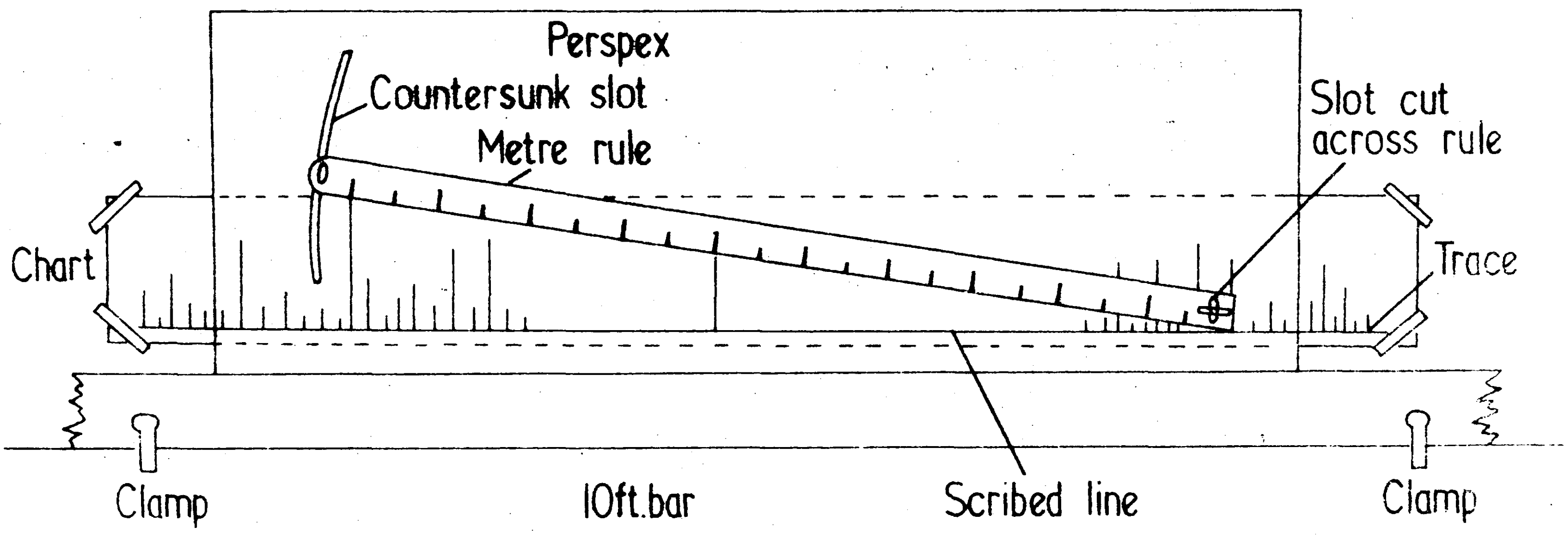

Perspex
Countersunk slot
Metre rule
Slot cut across rule
Chart
Trace
Clamp
10ft.bar
Scribed line
Clamp

FIG VIII

is then measured carefully, say 9.15% and the device is then set up on the next more sensitive trace making the reading 91.5 on the rule for this peak height. All below 10% can then be accurately measured, the reading on the rule being divided by ten to give its normalized value. This process can be repeated for values under 1%. Other conversion factors may be found convenient. Using this device a spectrum containing 200 peaks can be measured in an hour to a higher accuracy than by conventional means.

The device can be simplified if accuracy to only 1% is required. A twelve inch rule graduated in tenths is used and the perspex sheet is replaced by a bar (12 in. x 1 in.) on which a line is scribed. Only one butterfly nut and screw are required for attachment at the zero end of the rule. The method of operation is the same but the bar is not used.

B. A device to facilitate the use of metastable nomograms.

Standard logarithmic nomograms have been devised and published by Beynon(5). The customary way to find which ions are related by a transition is to use a piece of plastic with a line scribed onto it. During use, however, this plastic slips and it is inconvenient if one wishes to select one particular value of m_1 and vary m_2 to find the metastable ion (m_*) or vice versa.

The device is shown in Fig. IX. The overall size is 3' x 1'. It consists of 1/8" thick hardboard with the three scales on it as shown. The numbering (50 - 200) and (100 - 400) on opposite sides of the scales covers a wide range of the transitions normally encountered. For lower or higher values the numbering (25 - 100) and (200 - 800) can be used. Two cursors are attached as shown. Strong thread from the point of the fixed one passes through a teflon block on the other which is movable and supports a lead weight that keeps the thread tension constant as the length required between the two points varies. The instrument is set along the edge of the laboratory bench so that the lead weight and movable cursor have freedom of movement.

C. A device for use during mixture analysis.

During the examination of mixtures it was necessary to subtract the spectra of known compounds from the spectrum of an unknown mixture. Mathematically, trial and error of this sort is very time consuming.

The device is shown in Fig. X. The overall size is 5' x 1'. The peaks are represented by sliding black plastic rods 100 mm long interspaced by partitions of white which extend under the front panel to the foot of the board which is open. The abundance values are set using the movable perspex scale which is graduated to 100 in mms and the accompanying instrument which can be inserted at the bottom of the board or in the small hole at the top of the peak. The mass scale is engraved on the front panel and extends over three hundred mass units. The required numbers can be written in with a crayon. Subtraction is done by sliding the black rods down one millimetre for each one percent

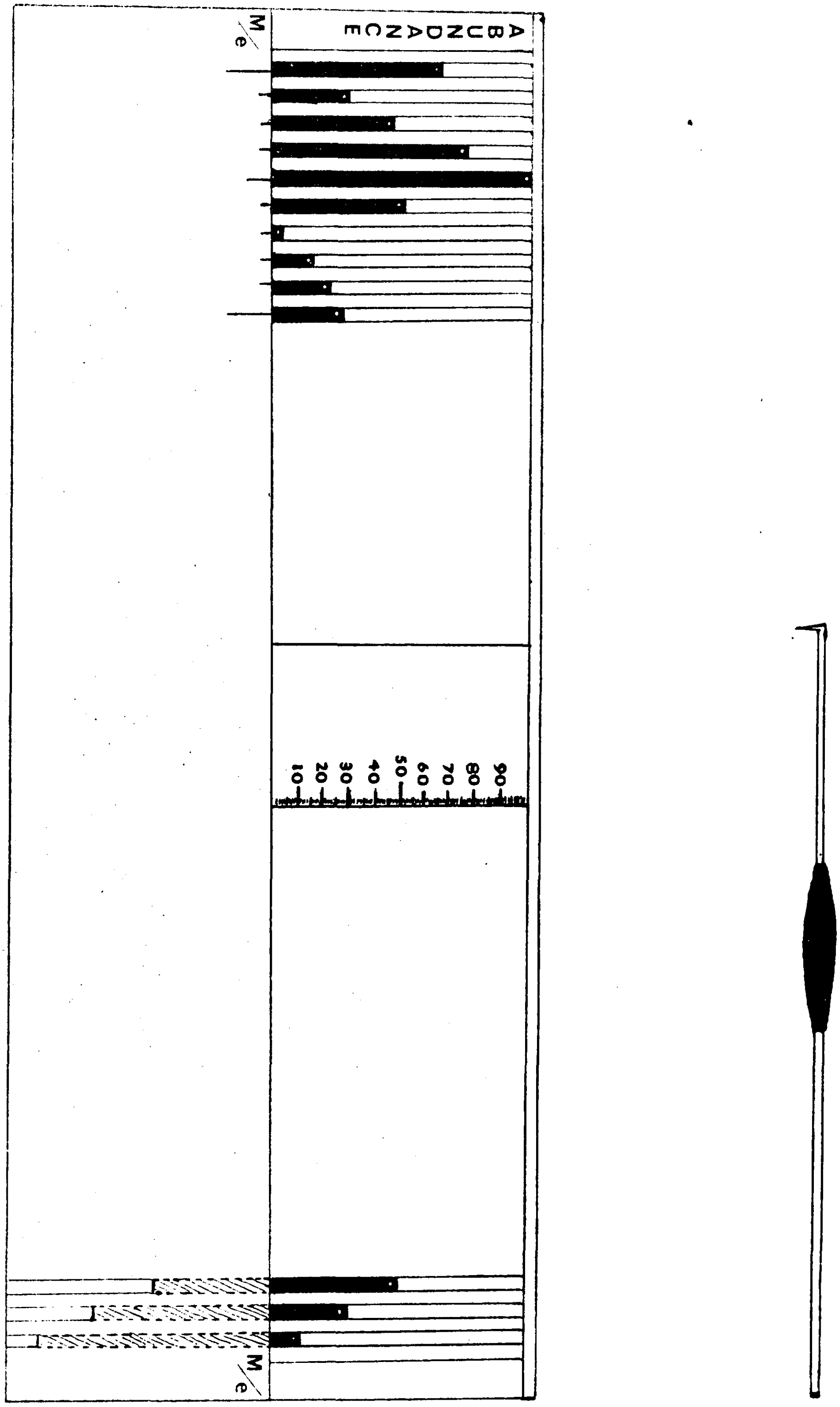


FIG X

to be removed.

When it is qualitatively confirmed that a component is present exact calculations can be done. The spectrum which remains is a line diagram in good relief and is very helpful in attempting to recognize structural features.

3) A Radio-Frequency Mass Spectrometer.

Among the time of flight instruments the radio-frequency mass spectrometer has been the subject of growing interest during the last few years.(6)(7)(8) Two of its advantages are its relatively small size and low cost of construction, but these are offset by its low resolving power and the delicate construction of the mass spectrometer source. However, it is ideally suited as an instrument for the study of many problems concerning small molecules, e.g. deuteration studies on propene etc. It is also useful for instrumental development such as new methods of ion production and sample handling.

The instrument here discussed incorporates the improvements of Elbeck, Locherer, Ruf and Schutze(9) upon Redhead's(10) modifications of the original Bennett tube.(11)

The problem consisted of translating the theory into a working laboratory model. The parts designed included the vacuum system, the grid structure, the complete mass spectrometer assembly and the collector unit.

The instrument was first constructed using dry batteries for D.C.

potentials and an accumulator for the filament current. An unresolved beam of ions was obtained which was of the order of magnitude expected and it was decided to construct electronically operated power supplies. An oscilloscope was added so that the adjustment of the important parameters would be simplified during construction. The oscilloscope would also serve as a means of recording the mass spectrum produced by the complete instrument.

The separation of positive ions is effected in the following manner. The ions are formed by electron bombardment in the ion source and are drawn out by the total collector potential. The ions passing the total collector then enter the analyser. This consists of an odd number of equally spaced grids to which a constant D.C. bias is applied. Three adjacent grids form a Bennett stage,(11) the centre one of which carries a radio-frequency voltage 180° out of phase with that on the other two. While penetrating the sorting structure ions are thus accelerated or decelerated according to the phase of the radio-frequency voltage as they enter the field of each grid. The maximum amount of kinetic energy is acquired only by ions of one particular m/e value for a particular value of the frequency of the radio-frequency voltage. At one frequency setting ions of one m/e value thus gain the maximum kinetic energy from every field of the analyser assembly through which they pass. All other ions gain a lesser amount.

The final grid of the sorting structure is one to which a high positive potential is applied the value of which is calculated to retard the passage of all ions except those having the maximum kinetic energy. The ions which pass through strike the collector plate and are recorded by conventional means. Secondary electron emission from the collector is suppressed by a negative field situated before it. Scanning the mass range is achieved by varying the frequency range of the radio-frequency generator.

The Vacuum System.

Fig. XI shows the schematic diagram of the complete vacuum system. The rotary pump used is an Electrical Ltd. type P.S.R.I. with a pumping speed of 28 litres per minute. The diffusion pump by the same makers is a type A.O.P. 25 with a pumping speed of 25 litres per second.

The seals above the diffusion pump are of neoprene and those below are of rubber smeared with Apezion M grease.

The system can reach a vacuum of 10^{-5} mms. mercury in one hour from starting cold. During running the diffusion pumps can be isolated by closing the baffle valve and Audco valve number one. The mass spectrometer head region can then be opened up to the atmosphere. The working vacuum can be restored in twenty minutes. The vacuum is recorded by using a Penning gauge attached as shown. A Tesla tube is incorporated to register the rough vacuum when starting up to determine the time at which to switch on the diffusion pumps.

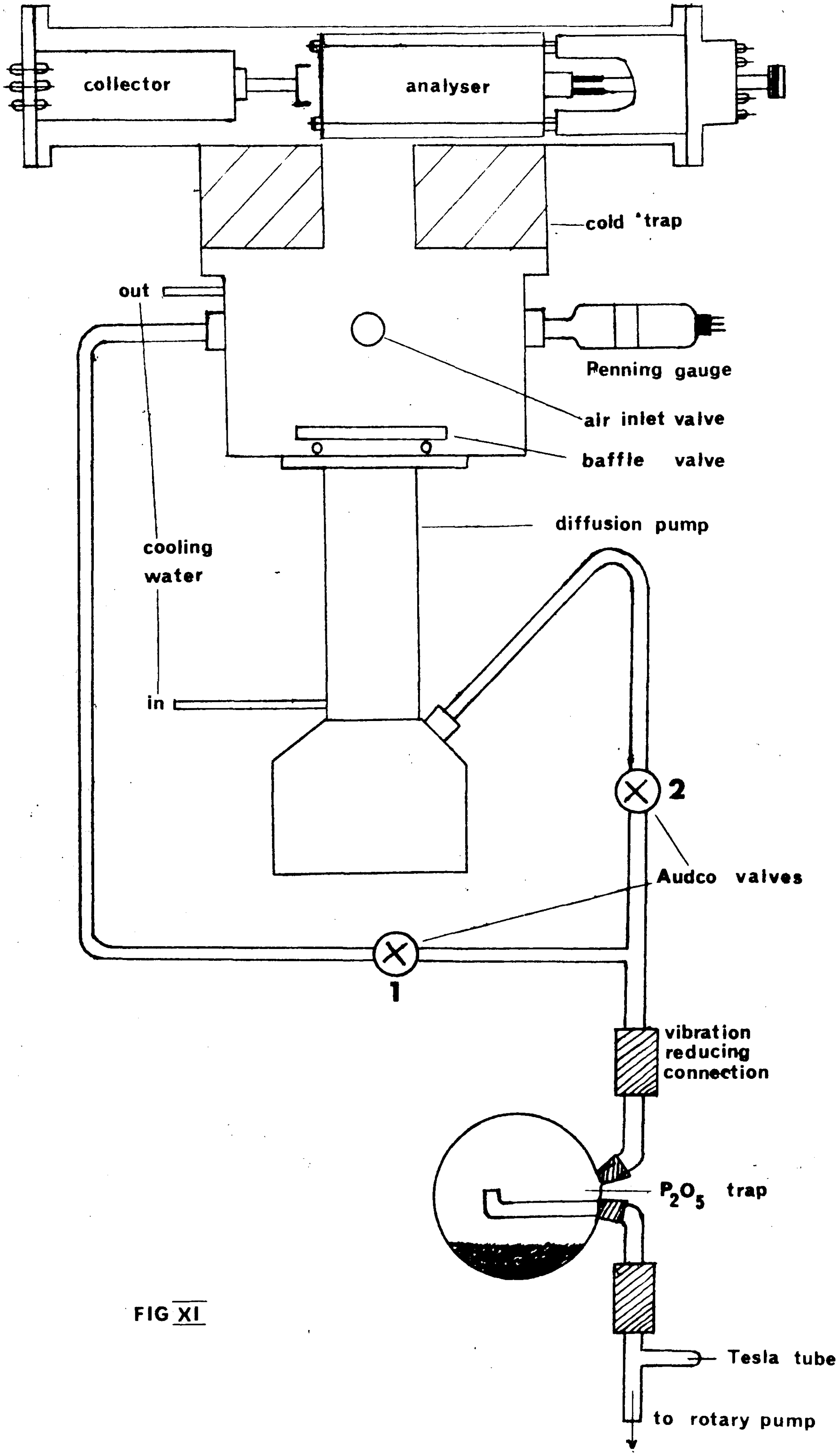

collector
analyser
cold trap
out
Penning gauge
air inlet valve
baffle valve
diffusion pump
cooling water
in
2
Audco valves
1
vibration reducing connection
P_2O_5 trap
Tesla tube
to rotary pump

FIG XI

The grids and sorting structure.

The choice of a standard M.S.2. type ion source unit as the base for mounting the analyser assembly dictated the fact that four columns would be for support. The special requirements of the grid plates are that all must be identical, and must have parallel tungsten wires of diameter 0.01 mm. across the central hole. The wires must be of even tension and make good electrical contact. The plate shape best suited for accuracy of construction is square.

The material used in the construction was brass of known uniform thickness from which the individual plates were cut, soldered together and machined as a unit. The parallel wires were laid in position by placing them in the jig shown in Fig. XIIa which was part of the winding apparatus in Fig. XIIb. When the winding was completed electrical contact was made by screwing on two bars of brass as shown in Fig. XIII. Physical contact was made by applying Araldite along the inner edges of the two bars and baking at 100°C.

The normal Nier type ion source, modified to allow removal of the ion chamber without dismantling the complete unit was used.(12) For insulation quartz spacers and silica tubing were also required, together with four nichrome support rods screwed to a length of three centimetres at both ends to allow for variation of inter section spacing during trials. The electrical contacts to the analyser grids were made by individual screws mounted on a brass rod which carries the voltage.

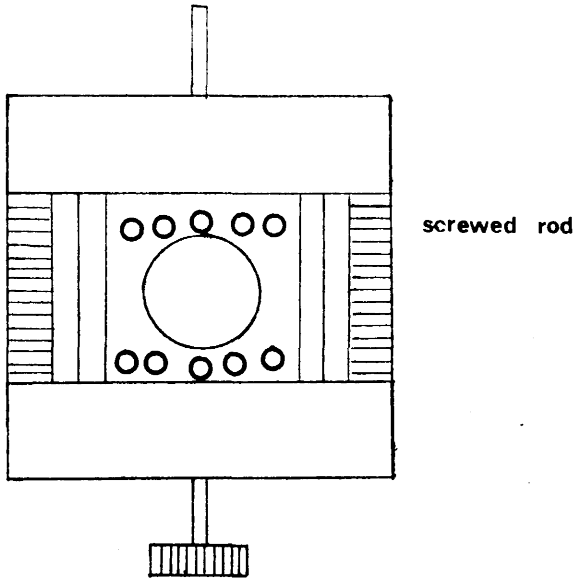


FIG $\overline{\text{XIIa}}$

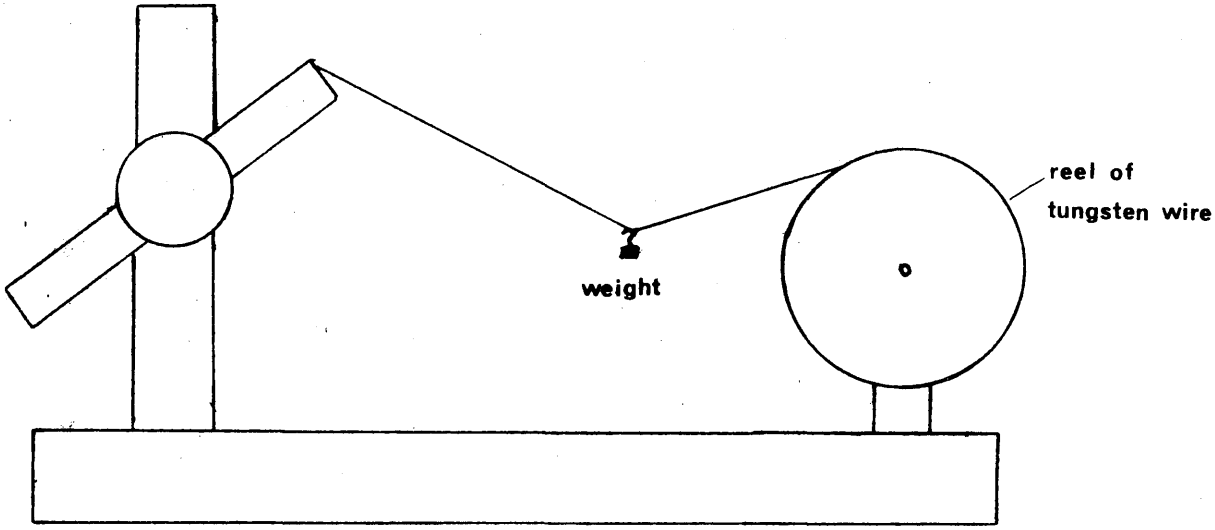


FIG $\overline{\text{XIIb}}$

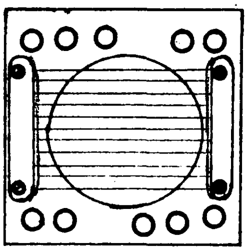


FIG $\overline{\text{XIII}}$

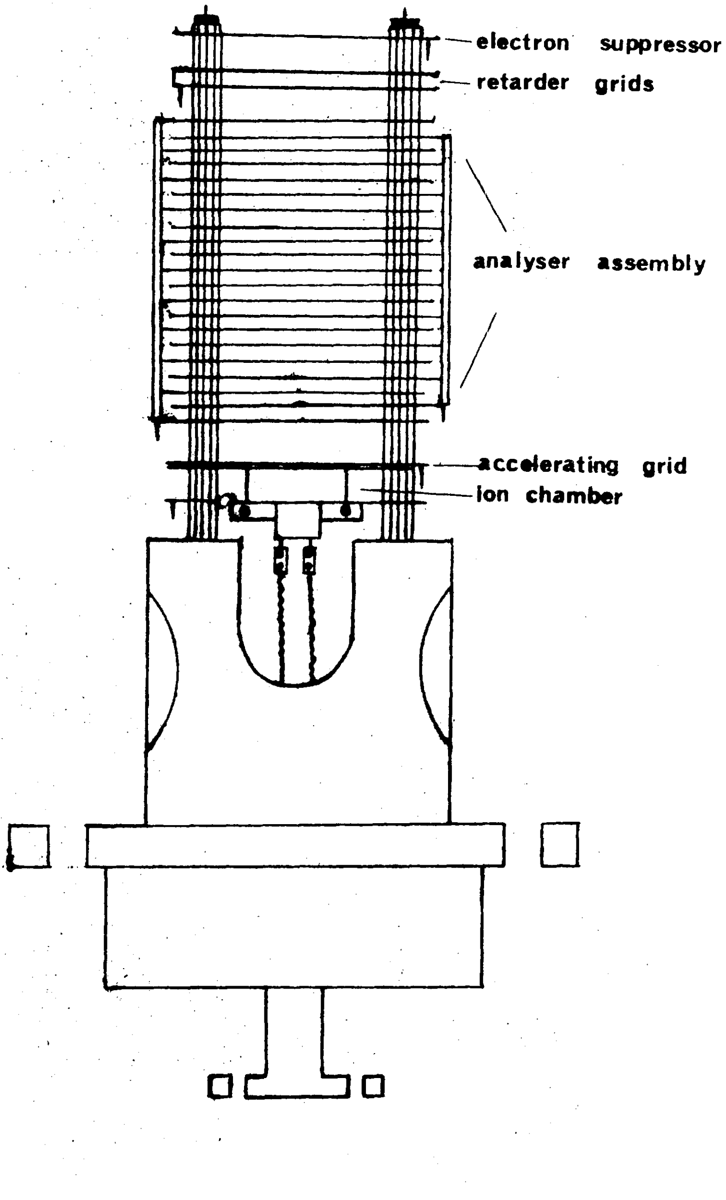

electron suppressor
retarder grids
analyser assembly
accelerating grid
ion chamber

FIG XIV

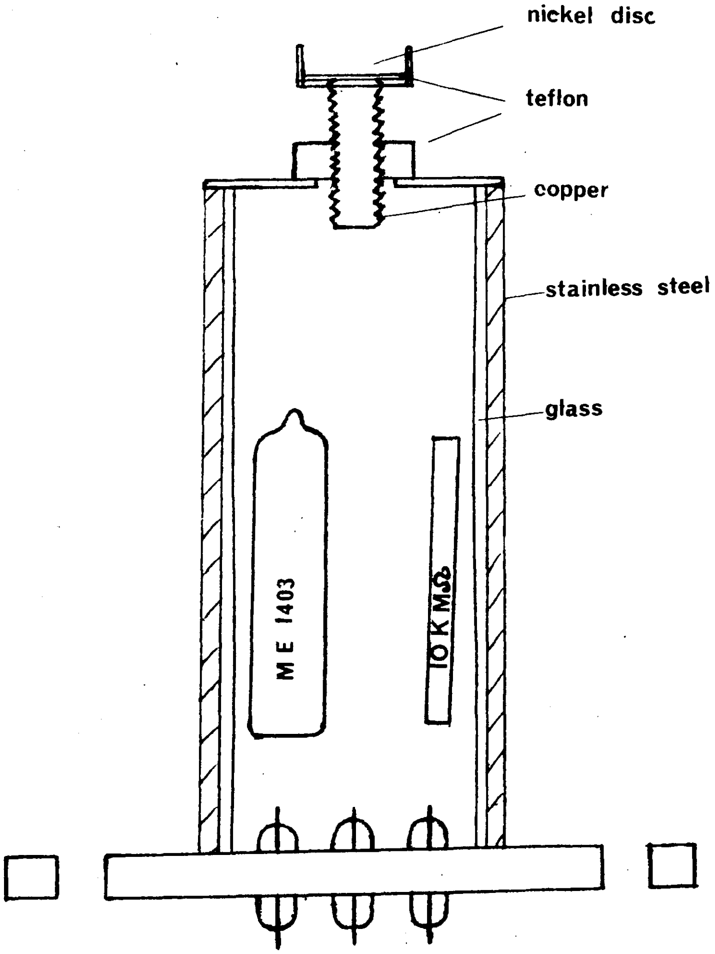

nickel disc
teflon
copper
stainless steel
glass
ME 1403
10 K MΩ

FIG XV

The final assembly of the unit is shown in Fig. XIV.

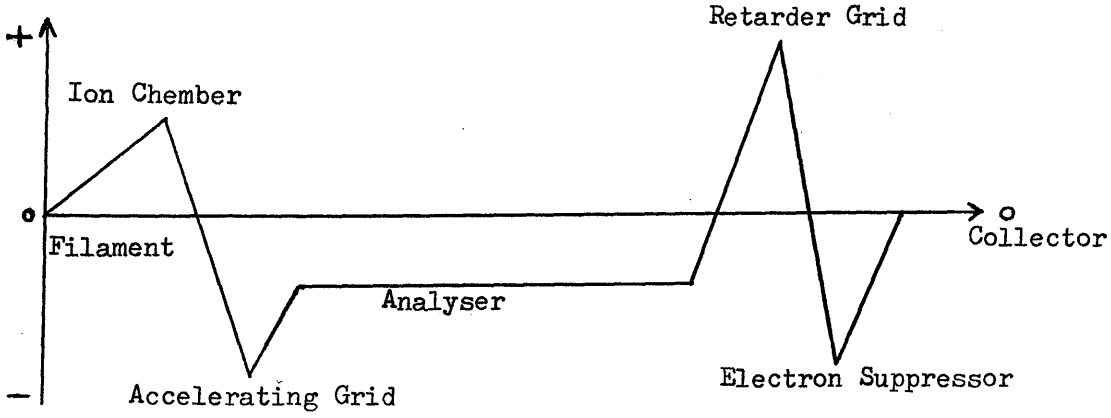
The collector assembly is shown in Fig. XV. An electrometer valve M.E. 1403 and a 10 K MΩ resistor are included in this unit. The casing is of stainless steel inside which a glass tube has been placed for insulation. The collector is a polished nickel plate and is seated on a teflon case as shown. A screwed copper rod makes electrical contact and also allows for future modification of the overall length of the analyser section during testing.

Both analyser and collector assemblies are shown in position in the vacuum system schematic diagram Fig. XI.

The electronic circuits for the mass spectrometer were constructed to order and were as follows.

(a) <u>The Power supplies.</u>

The approximate variation of the D.C. potential along the total ion path is shown schematically below in Fig. XVI.



The best working values for each section will be found by experiment. Variable supplies were made as follows.

1)	Electron suppressor	- 250 v.
2)	Retarder potential	+ 720 v.
3)	Analyser	- 250 v.
4)	Accelerator	- 250 v.
5)	Trap	+ 250 v.
6)	Case	+ 150 v.
7)	Ion-Repellor	± 9 v. relative to case.

(b) The filament power unit to give an output of five amps.

(c) The oscilloscope with its time base and requisite supplies.

(d) The electrometer amplifier using an M.E. 1403 as the electrometer valve.

The radio-frequency generator and emission control units have not yet been built. The presence of an unresolved beam of ions can be recorded on the oscilloscope and on a micro-ammeter in order to get maximum efficiency before attempting to resolve the ion beam.

The complete mass-spectrometer and vacuum system has been mounted in a frame and the electronic supplies discussed above in a separate unit. This has been a long term job because of the time required in getting parts ordered and also made. However, a basically sound vacuum system, a first class set of power supplies; and recording system are now available and the job of finding the correct parameters and modifying the designed mass-spectrometer into a working instrument can now be undertaken.

CHAPTER III.

The Mass Spectra of Some Sesquiterpenoids.

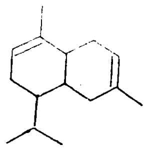
The improvement of spectroscopic techniques in recent years and the development of the combined G. L. C. and the mass spectrometer has enabled a more thorough investigation of natural products to be made. The essential oils of plants contain a range of mono-, sesqui-, di- and triterpenoids. The sesquiterpenoids have not been investigated previously using a mass spectrometer although isolated cases have been reported(13). This study was made to obtain some reference spectra of pure specimens of such structures to assist an investigation into the essential oils and to correlate the structures with the cracking patterns observed.

The spectra of twenty sesquiterpenoids obtained using standard conditions are shown in Table VI and the metastable ions are shown in Tables VII and VIII together with calculated values corresponding to the possible transitions.

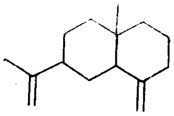
The Sesquiterpene Hydrocarbons.

a) Unsaturated Hydrocarbons.

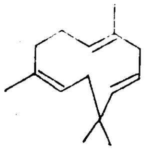
The compounds of this type examined were β-selenene, β-gurjunene, caryophyllene, clovene, humulene, ledane, patchulane, and clovane, the structures of which together with α-cedrene, longifolene and cadinene,



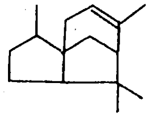
cadinene



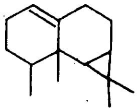
β-selinene



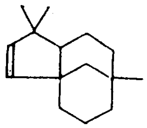
humulene



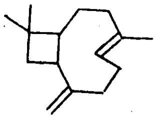
α-cedrene



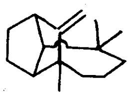
β-gurjunene



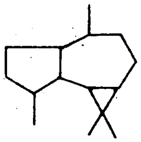
clovene



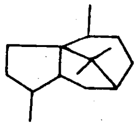
caryophyllene



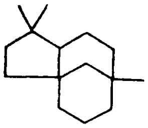
longifolene



ledane



patchulane



clovane

FIG XVII

are shown in Fig. XVII. The latter three spectra were obtained from the set of uncertified mass spectra(13). To simplify the discussion of the unsaturated compounds Table V has been included.

The existing work on non-aromatic hydrocarbons by mass spectrometry has been described fully by Beynon(14), Biemann(15), McLafferty(16), and others.

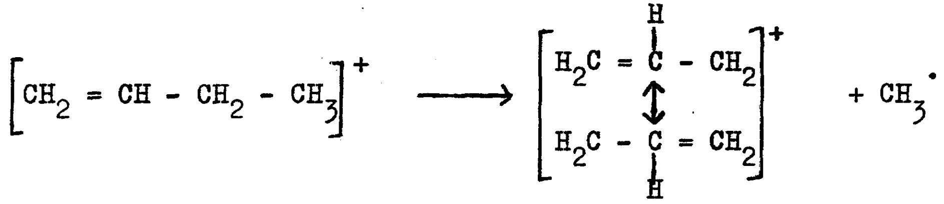
Studies in monoterpenoids have been reported by Reed(17), Von-Sydow(18) and Thomas(19).

The basic empirical rules for hydrocarbon fragmentation can be summarized as follows:-

a) $CH_3 - CH_3^{+} \longrightarrow CH_3^{+} + CH_3^{\bullet}$

b) $CH_3 - CH_2 - CH_2^{+} \longrightarrow CH_3^{+} + CH_2 = CH_2$

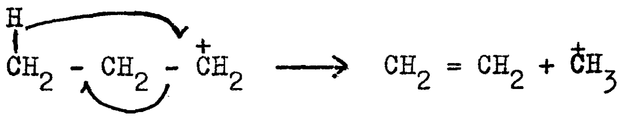
c)



$$\left[CH_2 = CH - CH_2 - CH_3\right]^{+} \longrightarrow \left[\begin{matrix} H_2C = CH - CH_2 \\ \updownarrow \\ H_2C - CH = CH_2 \end{matrix}\right]^{+} + CH_3^{\bullet}$$

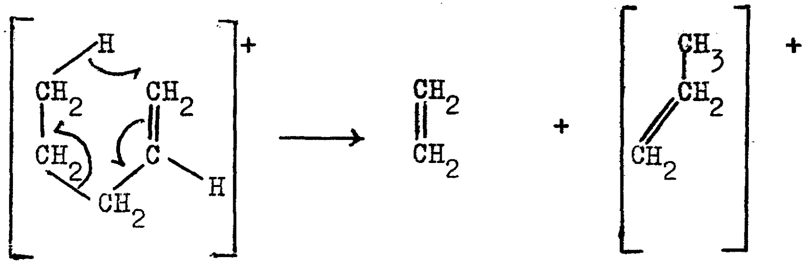
Rearrangements with hydrogen transfer are also possible.

d)



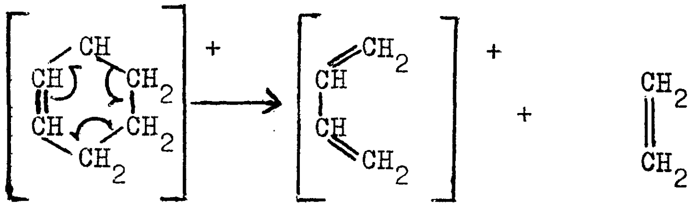
$$\overset{H}{C}H_2 - CH_2 - \overset{+}{C}H_2 \longrightarrow CH_2 = CH_2 + \overset{+}{C}H_3$$

e)



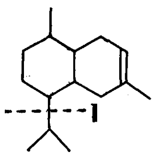
A rearrangement common to terpenes is that of the retro Diels-Alder.

f)

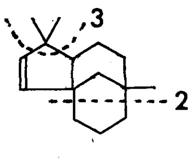


It is well established that the order of ion stability is tertiary > secondary > primary and the same is true of free radicals.

The isomeric compounds listed in Table V show the same ions but variations occur in their relative abundances. The parent ions at m/e = 204 vary in abundance according to the nature of the ring structure and the number of double bonds present. Humulene and caryophyllene have an eleven and nine membered ring respectively and this coupled with the double bonds in these rings makes for easy fission with elision of large fragments. The abundant ions in these spectra occur lower in the mass range: the base peak being at m/e = 41 in both cases. The structures which contain five and six membered rings have a more abundant parent ion and the spectrum is more prominent throughout the whole range. No characteristic cracking pattern has been observed for any of the structures because so many pathways of decomposition could lead to the same ion. Consideration of clovene and cadinene illustrates the difficulty.



CADINENE.



CLOVENE.

TABLE V

M/e	1	2	3	4	5	6	7	8
204	6	68	9	2	1	10	21	42
189	51	76	21	2	2	3	3	52
175	2	7	4	1	1	1	1	15
162	14	16	23	1	1	1	4	17
161	100	100	93	3	4	6	23	-
148	2	8	8	2	3	4	4	19
147	11	22	29	6	4	13	9	30
136	-	2	1	2	1	6	8	18
135	1	6	6	3	2	7	5	51
133	17	29	32	6	15	4	7	56
122	1	6	6	4	1	11	4	23
121	5	13	10	19	5	30	17	46
119	8	32	14	9	9	9	100	-
109	4	7	5	5	2	17	8	51
107	14	21	38	18	11	20	7	76
105	38	53	67	22	21	11	29	71
95	16	19	10	6	5	12	6	61
94	3	3	5	10	5	15	8	78
93	19	21	40	67	25	100	52	100
92	7	7	11	13	9	16	16	32
91	43	48	73	47	40	14	21	88
81	13	23	23	19	13	17	10	43
79	23	18	46	45	41	17	12	73
77	26	22	43	41	28	12	17	52
69	10	11	21	10	22	11	33	63
67	15	14	31	50	27	16	8	46
65	13	9	21	18	13	5	7	26
55	23	25	37	33	21	17	22	
53	17	16	31	52	30	14	13	
43	7	22	21	18	1	13	10	
42	3	3	12	11	7	3	4	
41	51	56	100	100	100	34	51	
39	23	38	49	34	14	17.6		

1 = Clovene; 2 = Cadinene; 3 = β-Gurjunene; 4 = Humulene;
5 = Caryophyllene; 6 = β-Selenene; 7 = α Cedrene; 8 = Longifolene

HYDROCARBON. METASTABLE TRANSITIONS.

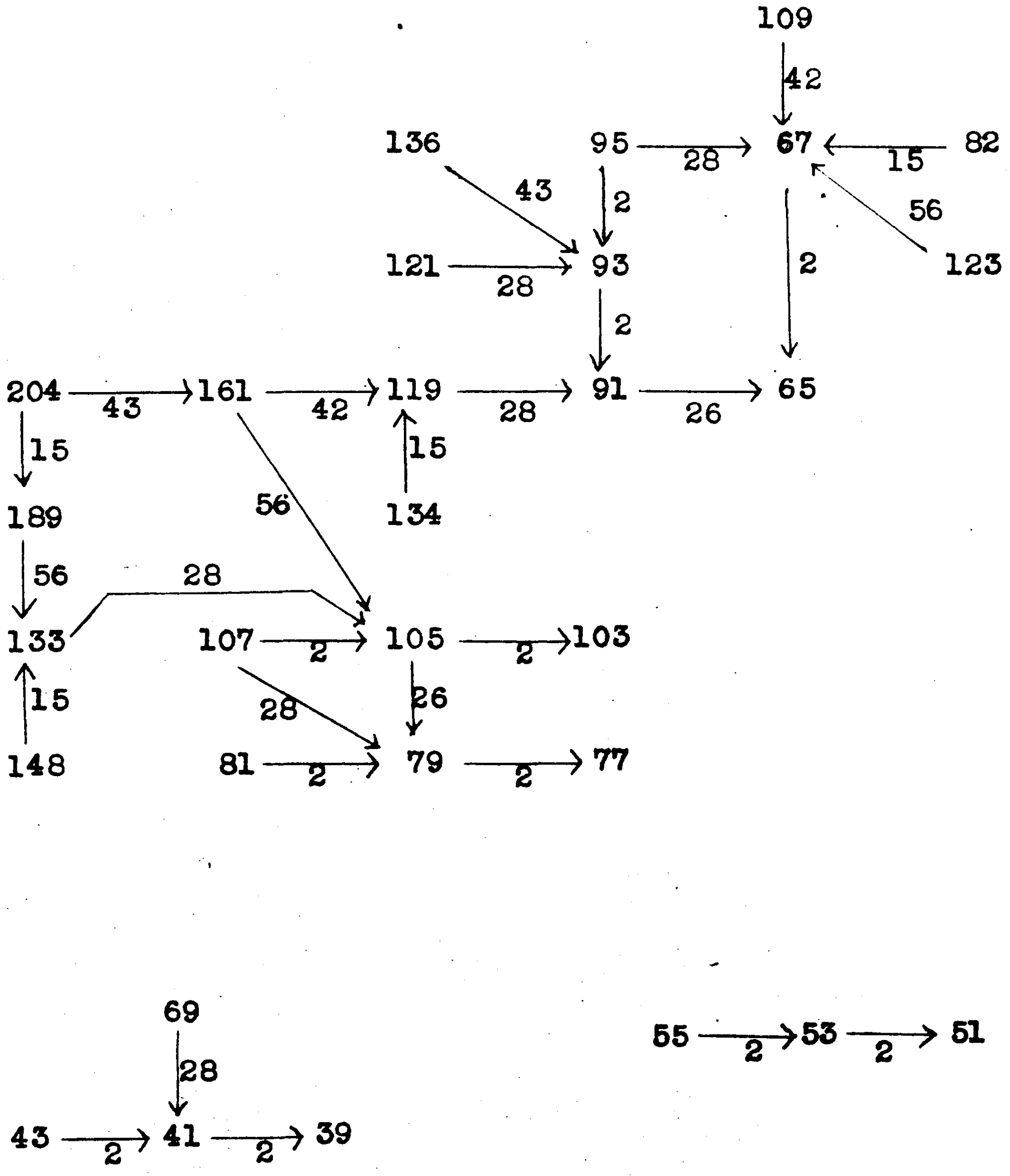


FIG XVIII

The base peak in both spectra occurs at m/e = 161. In cadinene a single fission only is required at (1). The bond to be broken is not a favourable one. In clovene at least two processes (2) and (3) could result in the loss of forty-three mass units. Each requires two bond fissions accompanied by one hydrogen transfer.

The metastable ions occurring in the spectra of the hydrocarbons and alcohols are listed in Tables VII and VIII. The possible transitions giving rise to these were calculated and the interconnexions are shown in Fig. XVIII for the hydrocarbons and Fig. XIX for the alcohols.

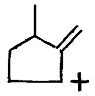
These figures indicate that the major processes yield the same set of ions in the spectra of both types of compound. This is interesting because the stability of the product ion and the way in which the energy is distributed may greatly influence the mode of fragmentation. The common neutral fragments are 2, 15, 28, 42, 43 and 56.

The pathways of decomposition lead to four different ions being formed. These are at m/e = 39, 65, 77 and 91. The corresponding formulae are $C_3H_3^+$, $C_5H_5^+$, $C_6H_5^+$ and $C_7H_7^+$. Allowing for the positive charge these contain 2, 3, 4 and 4 double bond equivalents respectively. The m/e values listed at intermediate points in the interconnexion diagrams can have a variety of isomeric formulae.

Although it is not possible to deduce the correct structure certain possibilities may be eliminated. An example is the base peak at m/e = 95 in cedrol which is formed in a single step as follows.

$$m/e = 151 \longrightarrow m/e = 95 + 56 \qquad m_{*} = 59.8.$$

The ion m/e = 95 does not go to m/e = 93 and m/e = 91 but goes to m/e = 67. The fission process suggested in the discussion of cedrol following yields the structure (a) for the base peak.



This structure agrees with the observed metastable ions in that it cannot easily rearrange to the tropyllium ion. The metastable interconnexion diagram is useful in that it will thus help to confirm the possible structures derived from breakdown processes.

b) Saturated Hydrocarbons.

Three fully saturated hydrocarbons namely ledane, clovane and patchulane were examined. The parent molecular ions are at m/e = 206 and the spectra differ from those of the unsaturated hydrocarbons only in that some of the ions are two mass units heavier. Loss of 15 and 43 mass units occurs in all cases. The base peak of ledane and patchulane is at m/e = 41; both spectra being very similar. It is of interest to note that the structures of these two compounds differ only in the attachment of the carbon atom substituted with the gem dimethyl group. The structure of clovane is basically a bicyclic six membered ring system attached to a five membered one. A gem dimethyl group is present in the five membered ring. The spectrum is more abundant and the base peak occurs at m/e = 135. This represents a loss of 71 mass units (C_5H_{11}) and probably corresponds to loss of the five membered ring together with one hydrogen atom.

Conclusions.

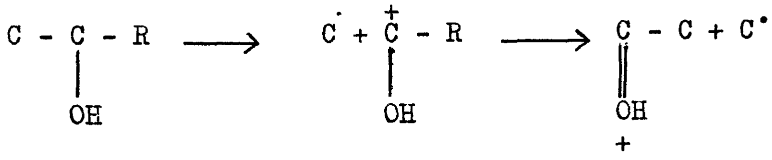
Although correlation of the structure of the sesquiterpene hydrocarbons with the cracking pattern observed is ambiguous each spectrum is different in the abundance of the major ions and can be used as a reference to confirm the identity of an unknown structure by comparison.

The Sesquiterpene Alcohols.

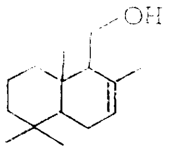
Twelve sesquiterpene alcohols, the complete structures of which are shown in Fig. XX were examined. The presence of the hydroxyl group directs the fragmentation to some extent in these molecules. The previous work on alcohols is extensive and has been summarized by Beynon(20), Reed(21), Biemann(22), and Djerassi(23). A series of monoterpene alcohols has been studied by Von-Sydow(18). Elimination of water from the cyclohexanol parent molecular ion has been shown to be a 1 : 3 or 1 : 4 process by Shannon(24).

The processes in which the influence of the hydroxyl group manifests itself are as follows.

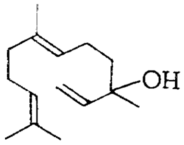
a)



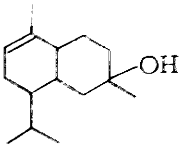
$$C-\underset{\underset{OH}{|}}{C}-R \longrightarrow \dot{C}+\underset{\underset{OH}{|}}{\overset{+}{C}}-R \longrightarrow \underset{\underset{\underset{+}{OH}}{\|}}{C}-C+C^{\bullet}$$



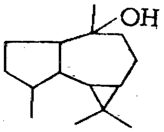
driminol



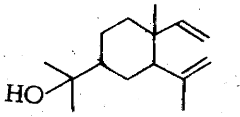
nerolidol



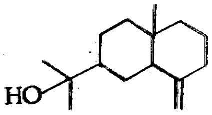
δ-cadinol



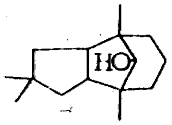
ledol



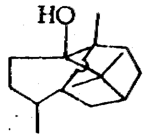
elemol



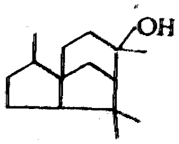
eudesmol



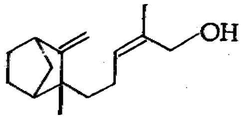
α-caryophyllene
alcohol



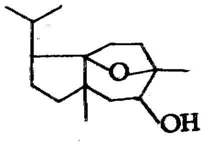
patchouli
alcohol



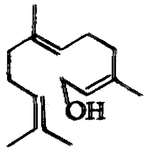
cedrol



santalol



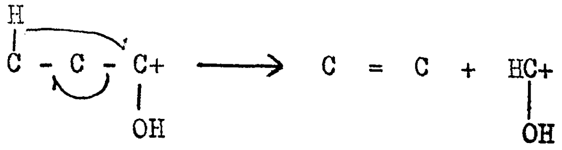
daucol



farnesol

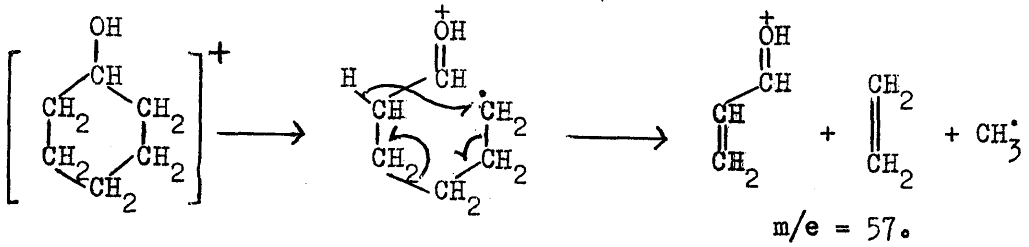
FIG XX

b)



$$H{-}C{-}C{-}C^{+}(OH) \longrightarrow C=C + HC^{+}(OH)$$

c)



Suitable substitution leads to homologues of m/e = 57 being formed. The loss of water occurs in all cases studied. Metastable ions exist for the process:-

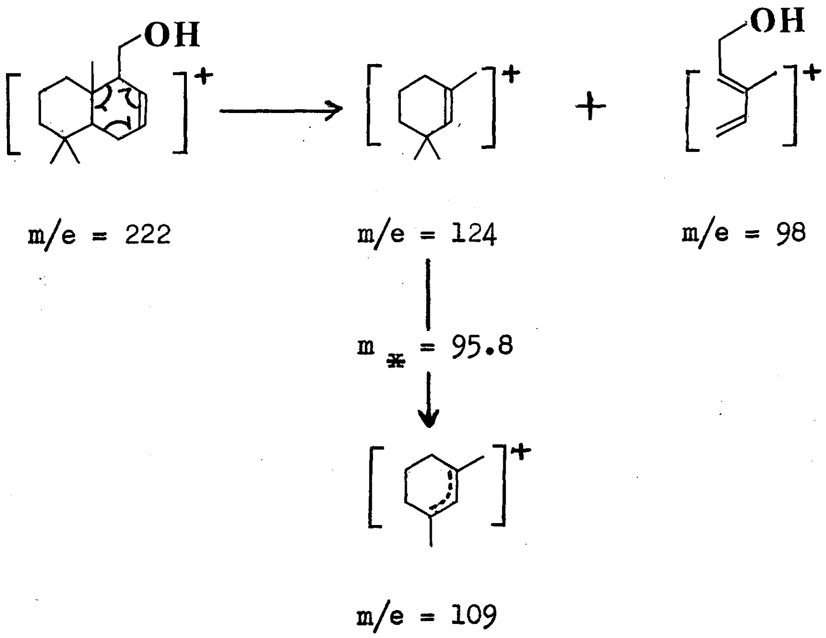
$$P+ \longrightarrow (P - {}^{+}H_2O) + H_2O$$

which proves this to be an electron impact induced dissociation. In cases where the parent molecular ion is very small such a metastable ion is not observed. That the process is also governed by the temperature of the heated inlet system is well illustrated in the case of patchouli alcohol in which the abundance of the parent ion changed from 80% to 20% over a few degrees centigrade.

The hydrocarbon ion at $(P - {}^{+}H_2O)$ produced by the above processes is abundant in all examples and comparison with the metastable tables shows that a significant part of the spectrum is due to the fragmentation of this hydrocarbon. The hydrocarbon produced by both processes may not be the same because thermal dehydration is 1 : 2 whereas the loss of water from the parent alcohol ion may be 1 : 3 or 1 : 4. The alcohols are discussed individually below with reference to ions which result from the influence of the hydroxyl group. The metastable ions observed in the spectra of the alcohols are reported in Table VIII and these have been used to confirm possible fragmentation processes in the following discussion.

XVIII Driminol.

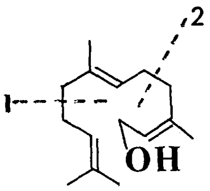
The interesting features of driminol are that it is a primary alcohol and has a double bond which may participate in a retro Diels-Alder process. The abundances of the parent molecular ion and the ion $(P - H_2O)^+$ are 10.9% and 1.5% respectively. The base peak m/e = 109 could arise in the following way:-



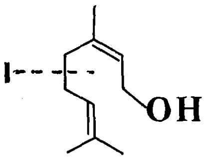
The loss of 31 mass units (CH_2OH) from the parent ion is facilitated by the double bond.

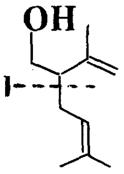
$m/e = 222 \longrightarrow m/e = 191 + 31 \qquad m_{*} = 164.3.$

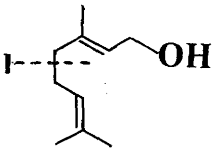
XX Farnesol.



The parent molecular ion and $(P - H_2O)^+$ are of low abundance since the doubly allylic bond (1) cleaves readily to yield the stable ion m/e = 69; the base peak. The spectra of the three acyclic monoterpenes(18) (a) nerol, (b) lavandulol and (c) geraniol all have the same doubly allylic bond and have an outstanding base peak at m/e = 69 in a spectrum of otherwise low abundance.

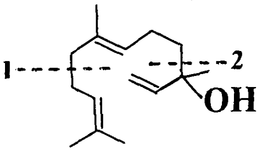

(a)


(b)


(c)

Fission at (2) gives rise to the ion m/e = 137. The fragment of mass 85 also formed by this process is not abundant because the oxygen atom is not in a position to stabilize the charge. The loss of 31 mass units occurs and the corresponding ion m/e = 191 is present in the spectrum. The metastable ions can be seen to have been formed by hydrocarbon transitions.

XIX Nerolidol.



The base peak is at m/e = 69 and is formed by fission of the doubly allylic bond (1) as in farnesol. The alcohol is tertiary in this case and fission at (2) yields the ion of m/e = 71 of 32.95% abundance, the enhanced stability resulting from the influence of the hydroxyl group and the double bond. The corresponding hydrocarbon residue m/e = 151 is of 0.75% abundance. The ion $(P - H_2O)^+$ is significant and gives rise to the usual hydrocarbon fragmentation pattern which is observed in all cases.

X Santalol.

This alcohol is interesting in that it is camphene with a side chain substituted for one of the gem dimethyl group. As well as being tertiary the side chain is allylic to the exomethylene group and is easily lost.

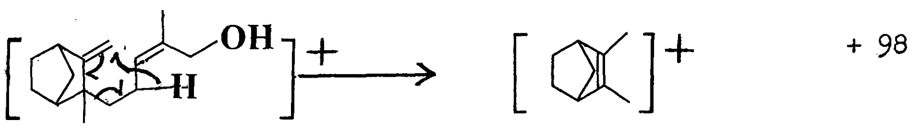
$$m/e = 220 \longrightarrow m/e = 121 + 99$$

The metastable ion m/e = 71.48 is the most abundant in the spectrum and corresponds to the transition:-

$$m/e = 121 \longrightarrow m/e = 93 + 28$$

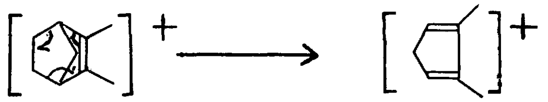
in which the base peak m/e = 93 is formed. The base peak in the spectrum of camphene is also m/e = 93.(17)

The exomethylene group can take part in a rearrangement as follows:-



m/e = 222 m/e = 122

The ion m/e = 122 can eliminate twenty eight units by a retro Diels-Alder to yield a stable ion.

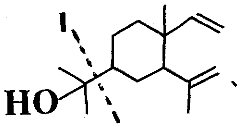


+ 28 $m_* = 72.43$

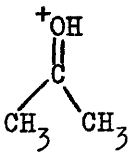
m/e = 122 m/e = 94

The metastable ion m_* 72.48 corresponds to the transition m/e = 202 ⟶ m/e = 121 + 81 and cannot be differentiated from the above process which yields m/e = 94. The ion m/e = 202 (10%) arises from the parent molecular ion by loss of water. Loss of thirty one mass units also occurs from the parent ion.

XIV Elemol.



This alcohol has the tertiary hydroxyl group substituted in the isopropyl side chain. The base peak is at m/e = 59 from cleavage at (1) which is as expected because of the stabilizing effect of two methyl groups and the hydroxyl group on the ion formed. The probable structure of m/e = 59 is



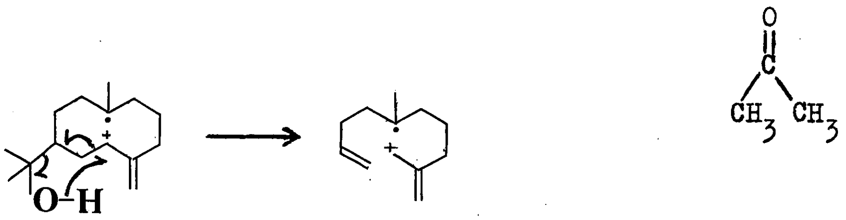
$$\overset{+}{O}H{=}C(CH_3)_2$$

with the oxygen accepting the positive

charge as shown. This has already been noted by Sharkey(25). The spectrum of α-terpineol(18) which has the same type of alcohol group also has a base peak of m/e = 59 as has eudesmol (discussed below). The ion m/e = 163 corresponds to retention of the positive charge on the olefinic fragment. The hydrocarbon in $(P - H_2O)^+$ is 10% of the base peak although the parent ion is of extremely low abundance (0.05%). Its formation is probably almost entirely due to thermal dehydration in the heated inlet system. The metastable ions formed are concerned with hydrocarbon transitions only.

<u>XVI Eudesmol.</u>

This alcohol like elemol has a base peak at m/e = 59. The abundance of the parent ion is 3.2% and the hydroxyl takes part in other fragmentation processes. The ion at m/e = 164 is very prominent having an abundance of 18.9%. The mechanism thought to give rise to it involves elimination of acetone by a six-membered transition state as follows:-



m/e = 222 m/e = 164 + 58

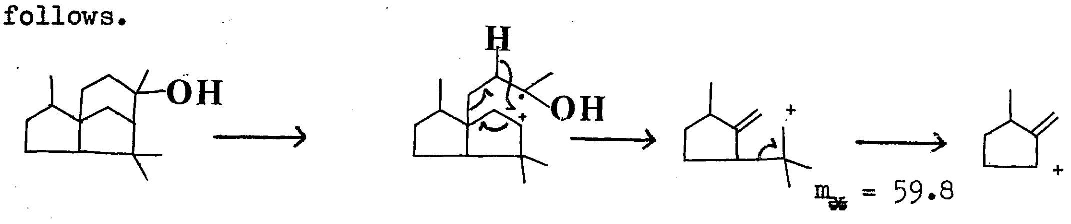
No metastable ion was observed for this process. This ion m/e = 164 occurs to a small extent (≈ 5%) in the spectra of other alcohols and it could be produced by loss of 15 plus 43 mass units from the parent molecular ion. Exact mass measurement proved the constitution of the ion m/e = 164 in this case to be $C_{12}H_{20}$. This agrees with the loss of acetone. The loss of 15 and 56 mass units from m/e = 164 occurs, the metastable ions for which can be seen in Table VIII.

XI Cedrol.

This is a tricyclic tertiary alcohol which on thermal dehydration would yield α-cedrene the spectrum of which was available(13). By comparison of the spectra of the hydrocarbon and the alcohol the following ions can be seen to be formed as a consequence of the presence of the hydroxyl:-

m/e = 165, 151, 150, 149, 135, 95, and 71.

The base peak is at m/e = 95 and a possible route for its formation is as follows.



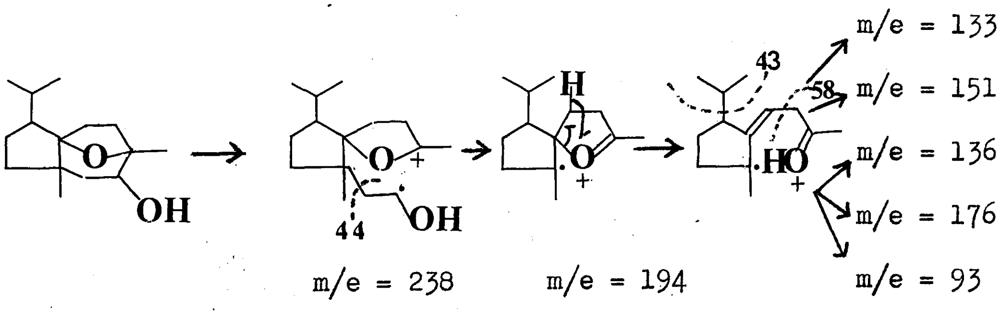
m/e = 222 m/e = 151 m/e = 95

If the charge goes initially to the hydroxyl substituted carbon m/e = 71 is formed by the above process. The formation of m/e = 150 from m/e = 222 could result from the above fission without hydrogen transfer. The metastable ion for this transition occurs at m/e = 101.3.

The process m/e = 150 ⟶ m/e = 135 + 15 occurs with the corresponding metastable ion at m/e = 121.5.

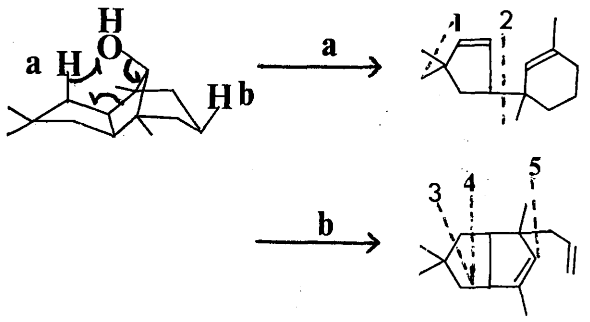
IX Daucol.

Daucol is a secondary alcohol which contains an oxygen bridge. The parent ion is at m/e = 238 (2.8%). Table VIII shows that the fragmentation is strongly influenced by the oxygen atoms. Because two oxygen atoms are present precise mass measurements were carried out on three of the major ions. They were the base peak m/e = 151 ($C_{10}H_{15}O$), m/e = 194 ($C_{13}H_{22}O$) and m/e = 195 ($C_{13}H_{23}O$). The metastable ions show one interesting feature. The ion m/e = 194 is formed by loss of C_2H_4O from the parent ion. It loses 58 and 18 mass units. The base peak m/e = 151 also loses these two fragments. This suggests that the bridge oxygen atom takes part in a rearrangement to become a hydroxyl group after the elision of the first hydroxyl. Although no metastable ion was observed for the process it is thought that m/e = 194 loses the isopropyl group to yield m/e = 151. The suggested breakdown is as follows:-



XV α - Caryophyllene Alcohol.

This is a symmetrical secondary alcohol. The parent ion and $(P - H_2O)^+$ are abundant. An interesting feature is the loss of thirty-one mass units from the parent molecular ion. The elided fragment must include the oxygen atom. This can be explained by an initial fission at the hydroxyl substituted carbon atom followed by a rearrangement which involves a hydrogen from the seven membered ring or from one of the methyl groups on it. The base peak is at m/e = 41 as was the case with some of the hydrocarbons discussed earlier which had large rings. The loss of water can occur by two processes (a) and (b). The stereochemistry of this molecule which has been found by X - Ray(26) studies is shown below to illustrate the loss of water. The formation of other ions from $(P - H_2O)^+$ is indicated by the dotted lines.

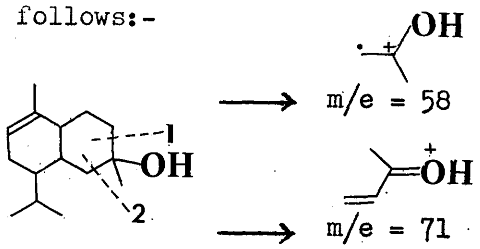


1) m/e = 189
2) m/e = 109 + m/e = 95
3) m/e = 148
4) m/e = 135
5) m/e = 163

The oxygen atom does not appear to influence the fragmentation greatly apart from the initial loss of thirty-one mass units.

XVII δ-Cadinol.

The parent molecular ion (m/e = 222) is of very low abundance (0.24%) but the ion $P -^{+}H_2O$ is 35.84% of the base peak. Comparison of the spectrum with that of cadinene(13) shows that the ions m/e = 164, 136, 71, 58 and 43 are formed as a result of the presence of the hydroxyl group. Apart from these ions the spectra are very similar both having the ion m/e = 161 as the base peak. The formation of m/e = 71 and m/e = 58 can be accounted for by fission on either side of the hydroxyl group as follows:-



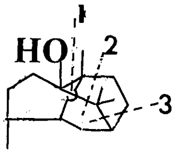
The metastable ions are concerned with the breakdown of the hydrocarbon fragments.

XIII Ledol.

This alcohol has a base peak of m/e = 43 which is the lower ion of a doublet and has the formula CH_3CO. This ion is commonly the base peak in the spectra of methyl ketones(27) and suggests that the alcohol has rearranged. The three membered ring could be the driving force for this. Correlation of the structure of this alcohol with the spectrum obtained was very ambiguous and it is suspected that the structure may be wrong.

XII Patchouli-Alcohol.

This alcohol has been examined by Biemann(28) as part of a study on epimers. The spectrum shown in Table VI has a parent ion at m/e = 222 of 80.97% abundance. The alcohol is tricyclic and the most favourable initial fissions (1), (2) and (3) are shown below.



Because many degradation paths are possible correlation with the mass spectrum is complicated and ambiguous. Metastable ions are present which could correspond to the following processes:-

$$m/e = 222 \longrightarrow m/e = 98 + 124$$

$$m/e = 222 \longrightarrow m/e = 138 + 84$$

$$m/e = 98 \longrightarrow m/e = 83 + 15$$

which yield very abundant ions.

Conclusions.

The spectra of the sesquiterpene alcohols studied show that the presence of the hydroxyl group generally gives rise to characteristic fragmentations which can be used to correlate the structure with the cracking pattern observed. Some features like the tertiary hydroxyl group in elemol and eudesmol or the doubly allylic bond in farnesol and nerolidol are diagnostic. With the more complex alcohols like ledol and patchouli-alcohol characteristic features are difficult to correlate because of the increase in the number of sites where initial fission could occur, without a fragment being elided. All the alcohols could, however, be easily recognized from their mass spectra.

Experimental.

The spectra were obtained using the heated inlet system method of sample introduction on a A.E.I. Ltd. M.S.9. double focusing mass spectrometer. The heated inlet system temperature was maintained at 190°C throughout the examination of the sesquiterpenoids.

[illegible] VI

PATCHUL[illegible] [illegible]o. [illegible]

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% A
		51	5.21			151	0.46				
		52	3.28	102	0.48	152	0.11				
		53	35.05	103	3.55						
		54	6.26	104.	1.97			204	0.93		
		55	58.92	105	22.80			205	0.42		
		56	5.01	106	4.76			206	2.54		
		57	3.50	107	35.94			207	0.45		
				108	9.00			208	0.08		
				109	7.88	159	0.13				
				110	2.99	160	0.13				
				111	0.53	161	1.48				
						162	0.64				
		63	1.48			163	5.72				
		64	0.59			164	1.31				
		65	15.42	115	3.71	165	0.34				
		66	5.75	116	1.68						
		67	46.72	117	4.48						
		68	7.25	118	0.88						
		69	22.45	119	8.62						
		70	1.36	120	2.31						
		71	0.39	121	21.90						
				122	8.20						
				123	5.24						
				124	0.79						
						175	0.20				
26	1.18					176	0.12				
27	25.46	77	38.80	127	0.52	177	0.64				
		78	8.65	128	1.28	178	0.16				
29	41.34	79	51.69	129	1.46	179	0.10				
30	0.83	80	8.17	130	0.60						
		81	38.68	131	2.08						
		82	15.98	132	0.52						
		83	3.81	133	3.65						
		84	0.34	134	1.08						
				135	8.09						
				136	1.73						
				137	0.68						
38	0.36										
39	31.89	89	0.78			189	0.60				
40	5.96	90	0.34			190	0.11				
41	100.0	91	51.03			191	5.98				
42	22.10	92	8.38			192	0.88				
43	17.61	93	44.09			193	0.10				
44	0.58	94	8.46								
		95	23.34	145	0.82						
		96	3.04	146	0.36						
		97	1.10	147	1.80						
				148	0.64						
				149	3.61						
50	0.87			150	1.44						

TABLE VI

LEDANE No. II

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abu
		51	3.40			151	0.79				
		52	1.93	102	0.24	152	0.04				
		53	21.16	103	1.77						
		54	4.40	104	0.85						
		55	44.22	105	10.78						
		56	5.21	106	2.91			206	4.23		
		57	3.23	107	37.60			207	0.65		
				108	9.25			208	0.08		
				109	13.37	159	0.15				
				110	3.42	160	0.04				
				111	0.66	161	0.42				
				112	0.12	162	1.29				
		63	0.81			163	18.38				
		64	0.38			164	3.62				
		65	9.60	115	1.18	165	1.02				
		66	3.63	116	0.54	166	0.20				
		67	44.62	117	1.87						
		68	6.47	118	0.43						
		69	28.32	119	4.03						
		70	1.98	120	1.38						
		71	0.67	121	20.66						
				122	13.78						
				123	6.35						
				124	2.18						
				125	0.27	175	0.05				
26	0.89					176	0.04				
27	16.32	77	20.32	127	0.14	177	0.55				
28	4.08	78	5.02	128	0.39	178	0.32				
29	27.20	79	36.07	129	0.55	179	0.06				
30	0.57	80	6.18	130	0.14						
		81	41.16	131	0.53						
		82	33.84	132	0.18						
		83	6.75	133	1.56						
		84	0.54	134	0.83						
				135	15.09						
				136	3.38						
				137	0.96						
38	0.59			138	0.28						
39	23.90			139	6.09	189	0.10				
40	4.93										
41	100.0	91	27.42	141	0.17	191	1.56				
42	9.35	92	4.86	142	0.07	192	0.29				
43	19.32	93	35.05	143	0.09	193	0.03				
44	0.59	94	10.29	144	0.06						
		95	31.60	145	0.25						
		96	5.52	146	0.10						
		97	1.46	147	0.83						
				148	0.59						
				149	4.81						
50	0.64			150	4.32						

TABLE VI

CLOVANE No.

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Ab
		51	1.45	101	0.11	151	2.79				
		52	0.67	102	0.24	152	0.28				
		53	8.04	103	0.67						
		54	1.42	104	0.42						
		55	18.72	105	4.31						
		56	2.40	106	4.70			206	12.82		
		57	3.22	107	4.94			207	2.16		
				108	2.43			208	0.43		
		59	2.67	109	2.26						
		60	0.36	110	2.09						
		61	0.09	111	0.47	161	3.87				
		62	0.16	112	0.13	162	0.86				
		63	0.70	113	0.09	163	22.20				
		64	0.66	114	0.04	164	3.75				
		65	3.50	115	0.66	165	0.88				
		66	1.70	116	0.36	166	0.20				
		67	14.71	117	0.70						
		68	5.48	118	0.28						
		69	14.20	119	1.74						
		70	1.62	120	1.06						
		71	5.60	121	14.73						
		72	0.40	122	5.64						
		73	0.09	123	3.24						
24	0.42	74	0.39	124	0.52	174	0.12				
25	1.90	75	0.34	125	0.20	175	0.28				
26	7.73	76	0.25	126	0.21	176	0.13				
27	1.18	77	7.49	127	0.40	177	0.43				
28	6.22	78	2.28	128	2.53	178	0.24				
29	3.22	79	15.29	129	0.55	179	0.15				
30	0.43	80	7.22	130	0.17						
31	1.21	81	21.04	131	0.36						
32	0.03	82	6.58	132	0.16						
		83	1.86	133	1.17						
		84	1.70	134	3.63						
		85	0.66	135	100.0						
36	0.46	86	0.15	136	14.89						
37	3.23	87	0.08	137	8.67						
38	3.89	88	0.19	138	1.18						
39	14.19	89	0.27	139	0.11	189	2.29				
40	3.60	90	0.15	140	0.07	190	0.54				
41	28.85	91	9.66	141	0.12	191	18.72				
42	9.90	92	3.35	142	0.08	192	1.90				
43	41.27	93	18.48	143	0.09	193	0.36				
44	3.73	94	23.84	144	0.07						
45	0.56	95	25.81	145	0.28						
46	0.07	96	3.87	146	0.16						
47	0.05	97	1.43	147	1.41						
48	0.05	98	2.33	148	0.43						
49	0.13	99	1.13	149	1.36						
50	0.40	100	0.43	150	14.81						

CARYOPHYLLENE

No. IV

M/E	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	%Abund.	M/e	% Ab
		51	5.75	101	0.06						
		52	5.42	102	0.43						
		53	29.71	103	2.98						
		54	4.48	104	1.55			204	0.78		
		55	20.92	105	21.36			205	0.13		
		56	6.66	106	8.45			206	0.01		
		57	1.74	107	10.59						
		58	0.34	108	2.01						
		59	0.14	109	2.46	159	0.17				
				110	0.43	160	0.15				
				111	0.35	161	3.51				
		62	0.17	112	0.05	162	1.18				
		63	1.38			163	0.30				
		64	0.63			164	0.07				
		65	13.39	115	2.44						
		66	5.23	116	1.12						
		67	26.91	117	3.27						
		68	5.42	118	0.90						
		69	22.27	119	8.76						
		70	1.56	120	7.08						
		71	0.52	121	5.15						
				122	1.06						
				123	0.73						
				124	0.09						
25	0.13	75	0.27			175	0.92				
26	0.87	76	0.25			176	0.70				
27	21.62	77	27.92	127	0.26	177	0.09				
		78	8.22	128	0.87	178	0.06				
29	20.48	79	40.87	129	0.89						
30	0.41	80	7.76	130	0.30						
31	0.17	81	13.31	131	1.57						
32	0.10	82	2.63	132	0.38						
		83	0.80	133	14.69						
				134	3.26						
				135	1.59						
				136	0.78						
37	0.37			137	0.23						
38	0.91										
39	33.86	89	0.63			189	1.63				
40	10.07	90	0.29			190	0.22				
41	100.0	91	40.20	141	0.18	191	0.03				
42	6.66	92	8.73	142	0.10						
43	0.20	93	25.12	143	0.18						
44	0.63	94	4.65	144	0.09						
		95	4.83	145	0.57						
		96	0.66	146	0.23						
		97	0.19	147	3.54						
				148	3.37						
49	0.08			149	0.75						
50	1.19			150	0.14						

TABLE VI

β-SELENENE No. V

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Ab
		51	3.16	101	0.10	151	0.25				
		52	1.90	102	0.18	152	0.25	202	0.18		
		53	13.95	103	0.92	153	0.07	203	0.09		
		54	0.56	104	0.51	154	0.05	204	8.99		
		55	17.33	105	11.26	155	0.06	205	1.65		
		56	2.27	106	3.93	156	0.05	206	5.96		
		57	2.24	107	20.15	157	0.08				
		58	3.09	108	6.39	158	0.05				
		59	0.52	109	17.03	159	0.49				
		60	0.30	110	2.58	160	0.23				
		61	0.11	111	1.45	161	5.92				
		62	0.20	112	0.20	162	1.43				
		63	1.00	113	0.08	163	0.72				
		64	0.47	114	0.03	164	0.16				
		65	4,82	115	0.85	165	0.09				
		66	2.10	116	0.39						
		67	15.84	117	1.04						
		68	6.78	118	0.41						
		69	11.08	119	9.18						
		70	1.33	120	2.94						
		71	0.91	121	30.26						
		72	0.30	122	11.08						
		73	0.14	123	4.69	173	0.08				
		74	0.18	124	0.60	174	0.08				
25	0.36	75	0.26	125	0.36	175	0.89				
26	0.17	76	0.24	126	0.09	176	0.65				
27	13.13	77	12.09	127	0.23	177	0.24				
28	2.57	78	3.17	128	1.14	178	0.08				
29	19.12	79	16.98	129	0.57						
30	0.28	80	34.29	130	0.19						
31	0.25	81	16.57	131	0.66						
32	0.03	82	12.60	132	0.26						
		83	2.99	133	4.09						
		84	1.78	134	3.41						
		85	0.65	135	6.54						
36	0.14	86	0.11	136	5.72						
37	0.42	87	0.11	137	1.40	187	0.17				
38	0.81	88	0.03	138	3.10	188	0.05				
39	14.43	89	0.36	139	0.44	189	3.13				
40	4.02	90	0.11	140	0.08	190	0.51				
41	34.06	91	14.31	141	0.16	191	0.35				
42	2.99	92	16.39	142	0.11	192	0.09				
43	13.01	93	100.0	143	0.14						
44	0.51	94	15.05	144	0.09						
45	0.36	95	12.28	145	0.45						
46	0.05	96	3.36	146	0.65						
47	0.05	97	1.08	147	12.77						
48	0.05	98	0.16	148	4.29						
49	0.02	99	0.09	149	1.50						
50	0.87	100	0.02	150	0.47						

TABLE VI

β-GURJUNENE No. VII

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abun
		51	8.31								
		52	4.76	102	1.68			202	0.82		
		53	30.65	103	9.34			203	0.63		
		54	4.85	104	5.14			204	9.34		
		55	37.29	105	66.72			205	1.96		
		56	2.73	106	12.14			206	0.56		
		57	2.68	107	37.94	157	0.84				
				108	6.35	158	0.56				
				109	4.67	159	2.89				
				110	1.03	160	2.10				
						161	93.45				
		62	0.65			162	23.36				
		63	2.75			163	3.83				
		64	1.77								
		65	21.40	115	13.17						
		66	4.95	116	5.79						
		67	31.11	117	17.84						
		68	2.80	118	4.30						
		69	20.56	119	14.48						
		70	1.68	120	9.64						
		71	0.84	121	10.37						
		72	0.29	122	6.26						
				123	1.83	173	1.17				
		74	0.31			174	1.03				
25	0.40	75	0.77			175	4.02				
26	1.80	76	0.74			176	1.31				
27	26.45	77	42.89	127	2,80	177	0.09				
28	2.81	78	11.21	128	6.63						
29	29.72	79	46.16	129	8.50						
30	1.10	80	6.35	130	4.28						
31	0.03	81	22.42	131	11.12						
32	1.14	82	4.67	132	3.17						
		83	2,80	133	31.77						
				134	8.50						
				135	6.50						
				136	1.31						
						187	0.63				
38	1.13					188	0.54				
39	38.30	89	1.68			189	20.65				
40	7.48	90	0.84			190	3.27				
41	100.0	91	72.51	141	1.87	191	0.54				
42	11.77	92	11.21	142	1.40						
43	21.40	93	40.09	143	2.43						
44	0.93	94	5.51	144	1.47						
		95	10.37	145	10.27						
		96	1.49	146	2.89						
		97	0.84	147	29.20						
				148	7.84						
				149	1.49						
50	1.68										

TABLE VI

CLOVENE

No. VIII

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abun
		51	6.95	101	0.31	151	0.05	201	0.02		
		52	0.05	102	1.12	152	0.16	202	0.08		
		53	16.58	103	5.41	153	0.14	203	0.14		
		54	2.02	104	2.64	154	0.07	204	5.67		
		55	22.88	105	37.51	155	0.09	205	1.12		
		56	1.57	106	6.10	156	0.07	206	0.10		
		57	1.07	107	13.83	157	0.18				
		58	0.40	108	3.52	158	0.11				
		59	0.18	109	4.47	159	1.52				
		60	0.05	110	0.48	160	1.28				
		61	0.11	111	0.09	161	100.00				
		62	0.44	112	0.02	162	14.14				
		63	2.53	113	0.10	163	1.17				
		64	1.17	114	0.11	164	0.09				
		65	13.06	115	7.24	165	0.06				
		66	2.90	116	3.14	166	0.03				
		67	14.81	117	9.69	167	0.03				
		68	1.73	118	2.42	168	0.02				
		69	10.47	119	7.64	169	0.02				
		70	0.70	120	9.53	170	0.02				
		71	0.49	121	5.21	171	0.03				
		72	0.25	122	1.00	172	0.03				
		73	0.31	123	0.50	173	0.30				
		74	0.27	124	0.05	174	0.25				
		75	0.08	125	0.04	175	2.08				
		76	0.08	126	0.17	176	0.62				
27	17.11	77	25.98	127	1.28	177	0.08				
28	2.69	78	7.22	128	3.65	178	0.03				
29	17.11	79	23.23	129	3.54	179	0.02				
30	0.51	80	3.01	130	1.94	180	0.01				
31	0.06	81	12.95	131	8.28	181	0.01				
32	0.04	82	1.49	132	2.64	182	0.01				
		83	1.25	133	17.47	183	0.03				
		84	0.16	134	3.17	184	0.02				
35	0.02	85	0.08	135	1.41	185	0.03				
36	0.10	86	0.07	136	0.23	186	0.02				
37	0.30	87	0.17	137	0.04	187	0.19				
38	0.75	88	0.18	138	0.02	188	0.22				
39	22.88	89	1.33	139	0.18	189	50.28				
40	4.15	90	0.52	140	0.04	190	8.18				
41	50.46	91	43.01	141	0.93	191	0.75				
42	2.98	92	7.27	142	0.54	192	0.05				
43	6.96	93	19.24	143	0.93	193	0.01				
44	0.032	94	2.72	144	0.70	194	0.02				
45	0.05	95	15.16	145	5.70	195	0.01				
46	0.03	96	1.57	146	3.67	196	0.02				
47	0.08	97	0.82	147	10.47	197	0.01				
48	0.05	98	0.10	148	1.86	198	0.02				
49	0.14	99	0.04	149	0.38	199	0.02				
50	0.10	100	0.03	150	0.09	200	.01				

TABLE VI

DAUCOL

No. IX

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abur
		51	0.98	101	0.11	151	100.0				
		52	0.60	102	0.05	152	11.70				
		53	5.35	103	0.33	153	4.53				
		54	0.91	104	0.20	154	0.79				
		55	13.15	105	3.07	155	0.15	205	1.15		
		56	1.64	106	0.63			206	0.18		
		57	2.46	107	7.95			207	0.03		
		58	1.55	108	4.78			208	0.05		
		59	0.82	109	4.42	159	0.68	209	0.07		
		60	0.04	110	1.38	160	1.94	210	0.09		
		61	0.06	111	1.94	161	0.69				
		62	0.08	112	0.55	162	0.26				
		63	0.32	113	0.61	163	0.34				
		64	0.11	114	0.21	164	0.12				
		65	2.11	115	0.26	165	0.33				
		66	0.85	116	0.15	166	0.32				
		67	5.48	117	0.87	167	0.73				
		68	1.16	118	0.23	168	0.28				
		69	11.03	119	2.16	169	0.09				
		70	1.51	120	0.72			220	1.85		
		71	8.41	121	4.85			221	0.41		
		72	0.51	122	1.53			222	0.06		
		73	0.13	123	5.04			223	1.11		
24	0.05	74	0.11	124	1.42			224	0.16		
25	0.18	75	0.12	125	1.41	175	1.57				
26	1.06	76	0.13	126	0.93	176	3.67				
27	7.51	77	6.08	127	0.20	177	2.02				
28	1.66	78	1.15	128	0.07	178	0.28				
29	8.14	79	7.32	129	0.13	179	0.17				
30	0.22	80	1.45	130	0.08	180	0.60				
31	0.93	81	9.70	131	0.44	181	0.36				
		82	1.46	132	0.22	182	0.10				
		83	3.37	133	17.85	183	0.05				
		84	1.76	134	2.60						
35	0.02	85	3.64	135	5.31						
36	0.07	86	0.56	136	24.20						
37	0.23	87	0.16	137	4.65	187	0.49				
38	0.35	88	0.06	138	3.17	188	0.08	238	2,80		
39	6.40	89	0.16	139	6.95			239	0.42		
40	1.51	90	0.31	140	7.40			240	0.04		
41	25.40	91	6.90	141	0.77	191	0.10				
42	2.09	92	2.36	142	0.11	192	0.21				
43	44.52) 10.62)	93	20.10	143	0.07	193	7.41				
44	0.70	94	7.40	144	0.08	194	30.54				
45	1.83	95	6.04	145	0.32	195	9.07				
46	0.06	96	1.85	146	0.09	196	1.00				
		97	9.30	147	0.66	197	0.08				
		98	1.10	148	0.22						
		99	0.80	149	10.29						
50	0.34	100	0.62	150	4.43						

TABLE VI

SANTALOL

No. X

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Ab
		51	3.35	101	0.10	151	2.06	201	0.08		
		52	2.23	102	0.37	152	0.78	202	10.00		
		53	13.12	103	2.57	153	2.06	203	2.05		
		54	1.84	104	1.30	154	0.53	204	0.43		
		55	25.07	105	21.97	155	0.11	205	1.71		
		56	2.21	106	8.27	156	0.09	206	0.03		
		57	3.12	107	33.77	157	0.27	207	0.07		
		58	1.12	108	10.98	158	0.21				
		59	0.49	109	8.90	159	3.19				
		60	0.07	110	2.45	160	1.34				
		61	0.13	111	1.38	161	4.03				
		62	0.27	112	0.36	162	2.68				
		63	1.26	113	0.16	163	2.85				
		64	0.49	114	0.05	164	0.67				
		65	8.31	115	1.64	165	0.34				
		66	4.71	116	0.68	166	0.12	216	0.08		
		67	16.69	117	3.57	167	0.05	217	0.03		
		68	5.73	118	1.41			218	1.12		
		69	15.65	119	19.43			219	0.20		
		70	1.64	120	9.36			220	1.45		
		71	2.96	121	59.20	171	0.11	221	0.21		
		72	0.92	122	32.08	172	0.09	222	0.03		
		73	0.10	123	5.98	173	1.16				
		74	0.24	124	1.44	174	0.87				
25	0.34	75	0.29	125	1.58	175	0.56				
26	1.55	76	0.28	126	0.27	176	0.21				
27	13.69	77	24.99	127	0.55	177	0.87				
28	1.60	78	5.61	128	0.51	178	0.31				
29	21.22	79	34.56	129	0.71	179	0.43				
30	0.44	80	6.07	130	0.38	180	0.06				
31	3.38	81	11.66	131	3.87						
32	0.10	82	2.75	132	4.03						
		83	2.85	133	6.70						
		84	6.14	134	4.41						
		85	1.15	135	6.68	185	0.15				
36	0.12	86	0.04	136	1.83	186	0.07				
37	0.34	87	0.08	137	1.91	187	6.16				
38	0.68	88	0.03	138	0.79	188	0.99				
39	17.58	89	0.66	139	0.43	189	3.99				
40	3.71	90	0.25	140	0.08	190	0.83				
41	44.48	91	33.02	141	0.24	191	1.08				
42	2.57	92	10.83	142	0.15	192	0.62				
43	25.49	93	100.0	143	0.39	193	0.10				
44	1.22	94	86.61	144	0.25	194	0.05				
45	1.20	95	29.35	145	3.40						
46	0.06	96	3.60	146	2.34						
47	0.05	97	1.99	147	4.00						
48	0.08	98	1.07	148	2.44						
49	0.13	99	0.25	149	1.55						
50	1.08	100	0.04	150	0.77	200	0.08				

CEDROL

No. XI

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abu
		51	3.40	101	0.10	151	70.80				
		52	1.87	102	0.28	152	9.50	202	0.12		
		53	15.33	103	1.69	153	0.99	203	0.12		
		54	2.50	104	0.99	154	0.10	204	15.62		
		55	32.98	105	21.44			205	2.57		
		56	5.54	106	6.21			206	0.38		
		57	10.37	107	29.45	157	0.07	207	14.15		
		58	2.97	108	19.08	158	0.06	208	2.26		
		59	5.29	109	28.64	159	0.41	209	0.17		
		60	0.29	110	3.48	160	1.14				
		61	0.14	111	2.52	161	30.21				
		62	0.34	112	1.79	162	6.61				
		63	1.01	113	1.46	163	3.37				
		64	0.53	114	0.28	164	7.21				
		65	7.21	115	1.82	165	10.70				
		66	2.61	116	0.79	166	1.45				
		67	23.02	117	2.57	167	1.39				
		68	4.94	118	1.28	168	0.17				
		69	49.52	119	32.11						
		70	4.40	120	12.72						
		71	14.82	121	25.54						
		72	10.48	122	13.99			222	4.75		
		73	1.50	123	10.95	173	0.18	223	0.76		
24	0.08	74	0.31	124	1.53	174	0.04	224	0.06		
25	0.32	75	0.62	125	0.63	175	1.59				
26	1.57	76	0.95	126	0.11	176	0.68				
27	12.00	77	18.66	127	0.40	177	5.65				
28	1.49	78	4.26	128	0.98	178	2.19				
29	14.76	79	25.57	129	0.82	179	2.71				
30	0.39	80	5.27	130	0.37	180	0.60				
31	1.61	81	42.90	131	1.67	181	0.07				
32	0.32	82	16.14	132	0.64						
		83	8.55	133	13.77						
		84	2.05	134	5.96						
35	0.08	85	1.14	135	24.09						
36	0.14			136	6.09						
37	0.30	87	0.09	137	7.22	187	0.09				
38	0.54	88	0.05	138	1.66	188	0.09				
39	14.00	89	0.66	139	0.89	189	6.12				
40	3.14	90	0.29	140	0.19	190	0.93				
41	58.50	91	25.42	141	0.22	191	0.15				
42	3.92	92	12.36	142	0.18	192	0.06				
43	47.12) 13.50	93	33.38	143	0.22	193	1.10				
44	1.05	94	11.53	144	0.17	194	0.21				
45	3.15	95	100.0	145	0.94						
46	0.14	96	11.38	146	0.87						
47	0.04	97	3.55	147	11.15						
48	0.06	98	0.76	148	5.75						
49	0.22	99	6.75	149	19.36						
50	0.96			150	77.00						

TABLE VI

PATCHOULI ALCOHOL No. XII

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abu
		51	4.71			151	9.24				
		52	2.50	102	0.65	152	2.74	202	0.27		
		53	22.89	103	2.75	153	2.59	203	0.25		
		54	4.70	104	1.40	154	0.50	204	21.88		
		55	60.32	105	39.09			205	3.35		
		56	7.76	106	8.06			206	0.97		
		57	14.17	107	43.56			207	25.06		
		58	1.64	108	21.91			208	3.71		
		59	4.50	109	38.79	159	1.23	209	0.32		
		60	0.35	110	9.81	160	1.09				
		61	0.11	111	27.51	161	48.89				
		62	0.28	112	5.72	162	9.11				
		63	1.35	113	0.88	163	2.88				
		64	0.70	114	0.12	164	5.05				
		65	10.40	115	3.23	165	6.21				
		66	3.77	116	1.47	166	1.78				
		67	44.21	117	3.87	167	1.87				
		68	8.46	118	1.55	168	0.17				
		69	45.38	119	25.12						
		70	8.00	120	9.91			220	0.29		
		71	14.28	121	36.11			221	0.48		
		72	1.54	122	19.34			222	80.97		
		73	0.44	123	27.36	173	0.38	223	13.47		
		74	0.29	124	11.11	174	0.27	224	1.20		
25	0.45	75	0.58	125	46.93	175	3.79				
26	2.95	76	0.46	126	6.05	176	1.55				
27	22.80	77	23.72	127	1.22	177	1.34				
28	5.20	78	8.12	128	4.25	178	1.26				
29	30.21	79	32.61	129	1.55	179	15.31				
30	0.76	80	15.71	130	0.85	180	3.35				
31	1.91	81	77.72	131	2.93	181	0.31				
32	0.32	82	35.02	132	1.21						
		83	70.89	133	16.55						
		84	20.28	134	7.22						
35	0.15	85	7.01	135	29.06						
36	0.45	86	0.40	136	8.80						
37	0.70	87	0.13	137	17.55						
38	1.30			138	67.56						
39	23.75	89	0.83	139	9.31	189	21.37				
40	5.04	90	0.46	140	1.10	190	3.28				
41	100.0	91	32.52	141	0.49	191	1.39				
42	17.51	92	7.06	142	0.33	192	0.20				
43	58.55	93	45.64	143	0.38	193	1.49				
44	1.28	94	17.14	144	0.26	194	0.45				
45	3.12	95	48.51	145	2.96						
46	0.16	96	11.06	146	1.11						
47	0.05	97	17.73	147	16.36						
		98	79.21	148	7.31						
		99	10.60	149	8.18						
50	1.51	100	1.38	150	2.16						

TABLE VI

LEDOL No.XIII

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abu
		51	3.87	101	0.12	151	5.22				
		52	2.45	102	0.56	152	1.22	202	0.16		
		53	19.07	103	1.63	153	0.65	203	0.23		
		54	3.70	104	0.83			204	20.46		
		55	46.09	105	31.32			205	3.44		
		56	4.83	106	8.82			206	0.35		
		57	7.28	107	46.72			207	3.64		
		58	4.34	108	23.34			208	0.53		
		59	3.57	109	65.91	159	0.68				
		60	0.19	110	8.94	160	0.73				
		61	0.16	111	38.46	161	35.70				
		62	0.31	112	5.37	162	8.00				
		63	1.15	113	0.81	163	2.18				
		64	0.64			164	2.47				
		65	8.52	115	1.55	165	5.76				
		66	3.36	116	0.69	166	1.93				
		67	41.02	117	2.35	167	0.71				
		68	6.62	118	0.85						
		69	73.83	119	18.36						
		70	7.03	120	6.51						
		71	22.78	121	35.42						
		72	2.47	122	66.15			222	8.24		
		73	0.45	123	17.93	173	0.23	223	1.27		
		74	0.23	124	4.26	174	0.20	224	0.12		
25	0.48	75	0.37	125	6.49	175	2.82				
26	2.30	76	0.51	126	3.22	176	1.70				
27	17.89	77	18.37	127	2.98	177	0.28				
28	3.15	78	3.80	128	1.51	178	0.24				
29	21.90	79	3.30	129	0.81	179	4.28				
30	0.45	80	8.52	130	0.38	180	1.45				
31	1.93	81	57.19	131	1.73	181	0.20				
32	0.11	82	40.61	132	0.71						
		83	19.52	133	15.74						
		84	3.88	134	4.94						
		85	20.04	135	12.74						
		86	0.70	136	7.39						
37	0.43	87	0.26	137	6.39	187	0.16				
38	0.70	88	0.08	138	7.86	188	0.18				
39	19.80	89	0.53	139	6.72	189	16.41				
40	4.26	90	0.20	140	3.92	190	2.58				
41	76.15	91	27.84	141	0.63	191	0.42				
42	11.02	92	5.96	142	0.21	192	0.09				
43	100.0	93	41.08	143	0.33	193	0.42				
44	9.55	94	12.61	144	0.23	194	0.26				
45	4.06	95	45.10	145	1.41						
46	0.17	96	12.37	146	0.86						
47	0.07	97	8.37	147	19.57						
48	0.05	98	15.00	148	14.59						
49	0.05	99	2.62	149	12.89						
50	1.11	100	0.25	150	2.35						

TABLE VI

ELEMOL

No. XIV

M/e	% Abund.	M/e	%Abund.	M/e	%Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Ab
		51	3.41	101	0.07	151	0.43				
		52	2.02	102	0.31	152	0.18	202	0.08		
		53	21.41	103	1.07	153	0.33	203	0.13		
		54	2.90	104	0.51	154	0.16	204	9.88		
		55	31.25	105	19.90	155	0.06	205	1.65		
		56	2.86	106	6.03	156	0.05	206	0.20		
		57	5.34	107	40.62	157	0.08	207	0.62		
		58	1.63	108	17.44	158	0.08	208	0.09		
		59	100.0	109	16.60	159	0.35				
		60	3.38	110	2.89	160	0.59				
		61	0.23	111	1.32	161	39.87				
		62	0.22	112	0.15	162	10.06				
		63	1.02	113	0.10	163	10.42				
		64	0.44			164	4.68				
		65	6.61	115	0.85	165	0.75				
		66	3.57	116	0.37	166	0.10				
		67	33.98	117	1.35						
		68	27.92	118	0.82						
		69	26.27	119	18.02						
		70	3.84	120	6.36						
		71	14.09	121	33.65						
		72	1.48	122	7.34			222	0.05		
		73	0.25	123	11.69	173	0.21	223	0.01		
		74	0.19	124	1.83	174	0.11				
25	0.32	75	0.37	125	0.93	175	3.23				
26	1.81	76	0.23	126	0.44	176	1.45				
27	12.91	77	14.92	127	0.45	177	0.30				
28	2.69	78	5.02	128	1.31	178	0.06				
29	15.37	79	30.36	129	0.56	179	0.12				
30	0.37	80	17.09	130	0.23	180	0.04				
31	11.13	81	47.03	131	0.97	181	0.06				
32	0.13	82	13.00	132	0.46						
		83	7.26	133	12.07						
		84	4.54	134	7.29						
35	0.03	85	1.84	135	23.14						
36	0.17			136	9.95						
37	0.32	87	0.10	137	2.88	187	0.12				
38	0.74	88	0.01	138	0.42	188	0.07				
39	17.70	89	0.41	139	1.03	189	16.88				
40	6.29	90	0.16	140	0.19	190	2.69				
41	4.08	91	19.18	141	0.20	191	0.29				
42	4.77	92	10.74	142	0.12	192	0.05				
43	34.92	93	71.18	143	0.17	193	0.04				
44	0.93	94	21.49	144	0.11						
45	2.41	95	26.26	145	0.91						
46	0.08	96	8.64	146	0.41						
		97	2.32	147	11.90						
		98	0.43	148	6.33						
		99	0.22	149	11.48						
50	0.84			150	1.42						

TABLE VI

α - CARYOPHYLLENE ALCOHOL No. XV

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Ab
		51	7.87	101	0.06	151	6.97				
		52	4.92	102	0.27	152	2.32	202	0.16		
		53	21.08	103	1.55	153	0.92	203	0.23		
		54	3.90	104	0.90	154	0.78	204	23.64		
		55	61.95	105	12.90	155	0.14	205	4.88		
		56	21.51	106	8.27	156	0.06	206	0.48		
		57	36.45	107	37.63	157	0.11	207	10.99		
		58	2.31	108	33.42	158	0.09	208	1.89		
		59	1.03	109	89.58	159	0.52	209	0.18		
		60	0.21	110	10.08	160	0.39				
		61	0.30	111	19.09	161	7.12				
		62	0.47	112	2.01	162	5.27				
		63	1.45	113	1.23	163	12.35				
		64	1.00	114	0.12	164	3.70				
		65	8.31	115	1.50	165	2.45				
		66	3.32	116	0.74	166	0.60				
		67	29.75	117	1.90	167	0.20				
		68	6.41	118	0.51	168	0.09				
		69	41.07	119	10.65						
		70	5.51	120	4.05			220	4.35		
		71	14.83	121	23.75			221	1.15		
		72	3.25	122	28.08			222	29.51		
		73	0.46	123	51.34	173	0.28	223	4.96		
24	0.11	74	0.68	124	9.92	174	0.19	224	0.41		
25	0.45	75	0.63	125	8.89	175	8.04				
26	3.71	76	0.83	126	9.83	176	3.76				
27	29.01	77	20.37	127	1.14	177	5.53				
28	5.85	78	10.41	128	0.12	178	1.00				
29	39.66	79	27.17	129	0.78	179	7.20				
30	1.14	80	18.25	130	0.36	180	4.09				
31	3.12	81	19.76	131	1.24	181	0.62				
32	0.28	82	16.05	132	0.50	182	0.08				
		83	25.81	133	8.89						
		84	5.60	134	3.05						
35	0.26	85	6.23	135	83.68						
36	0.38	86	3.15	136	18.42						
37	1.12	87	0.38	137	13.61	187	0.24				
38	3.18	88	0.40	138	7.04	188	0.31				
39	28.01	89	0.52	139	4.98	189	77.23				
40	5.87	90	0.29	140	0.61	190	12.62				
41	100.0	91	22.22	141	0.55	191	23.44				
42	30.83	92	5.28	142	0.26	192	5.44				
43	69.32	93	27.70	143	0.25	193	1.40				
44	2.53	94	17.09	144	0.17	194	0.33				
45	5.53	95	64.29	145	1.14						
46	0.38	96	15.79	146	0.43						
47	1.24	97	22.92	147	6.19						
48	0.65	98	15.32	148	29.10						
49	7.50	99	2.50	149	12.30						
50	3.97	100	0.14	150	4.68						

TABLE VI

EUDESMOL

No. XVI

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	Ab
		51	2.17	101	0.06	151	0.79	201	0.03		
		52	1.43	102	0.12	152	0.26	202	0.63		
		53	7.38	103	0.84	153	0.12	203	0.29		
		54	1.43	104	0.58	154	0.05	204	15.45		
		55	13.85	105	12.18	155	0.07	205	2.72		
		56	1.31	106	2.81	156	0.06	206	0.76		
		57	1.78	107	13.50	157	0.10	207	1.75		
		58	2.23	108	14.60	158	0.06	208	0.27		
		59	100.0	109	19.59	159	0.52	209	0.03		
		60	3.51	110	3.68	160	0.47	210	0.02		
		61	0.37	111	1.07	161	14.12				
		62	0.21	112	0.19	162	5.00				
		63	0.76	113	0.08	163	3.41				
		64	0.58	114	0.16	164	18.92				
		65	3.16	115	0.91	165	3.08				
		66	1.65	116	0.22	166	0.40				
		67	12.93	117	1.30	167	0.07				
		68	4.87	118	0.85	168	0.03	218	0.10		
		69	7.50	119	5.43	169	0.05	219	0.02		
		70	0.81	120	1.83	170	0.03	220	0.17		
		71	2.65	121	11.42	171	0.06	221	0.06		
		72	0.39	122	12.90	172	0.01	222	3.21		
		73	0.30	123	12.83	173	0.28	223	0.56		
24	0.07	74	0.29	124	1.39	174	0.15	224	0.05		
25	0.26	75	0.55	125	1.07	175	2.70				
26	1.33	76	0.33	126	0.17	176	0.84				
27	6.58	77	7.57	127	0.02	177	0.33				
28	1.76	78	3.64	128	0.02	178	0.34				
29	7.83	79	12.32	129	0.12	179	0.24				
30	0.40	80	4.35	130	0.31	180	0.07				
31	4.89	81	17.91	131	1.48	181	0.03				
32	0.10	82	11.27	132	0.49	182	0.03				
		83	5.06	133	6.97	183	0.01				
34	0.04	84	1.29	134	1.98	184	0.03				
35	0.13	85	0.48	135	8.55	185	0.06				
36	0.56	86	0.78	136	2.14	186	0.06				
37	0.26	87	0.22	137	0.86	187	0.46				
38	0.44			138	0.18	188	0.18				
39	7.64	89	0.34	139	0.24	189	14.66				
40	1.92	90	0.20	140	0.05	190	2.43				
41	22.58	91	11.40	141	0.26	191	0.72				
42	1.70	92	2.69	142	0.15	192	0.17				
43	19.13	93	15.33	143	0.31	193	0.10				
44	16.05	94	6.10	144	0.13	194	0.06				
45	1.67	95	14.80	145	1.28	195	0.03				
46	0.10	96	6.50	146	0.43						
47	0.25	97	2.52	147	5.77						
48	0.19	98	0.35	148	2.39						
49	1.87	99	0.15	149	34.28						
50	0.77	100	0.05	150	5.33	200	0.03				

δ- CADINOL

No. XVII

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% A
		51	3.64	101	0.13	151	0.67				
		52	1.90	102	0.29	152	0.42	202	0.25		
		53	12.32	103	1.92	153	0.12	203	0.18		
		54	1.54	104	1.37	154	0.05	204	35.84		
		55	22.95	105	45.05	155	0.07	205	6.19		
		56	3.73	106	7.94	156	0.13	206	0.67		
		57	0.27	107	8.56	157	0.35	207	1.43		
		58	19.19	108	4.41	158	0.15	208	0.28		
		59	1.95	109	8.42	159	1.61				
		60	0.09	110	1.26	160	2.43				
		61	0.06	111	0.74	161	100.0				
		62	0.24	112	0.10	162	14.58				
		63	1.17	113	0.31	163	1.57				
		64	0.47	114	0.06	164	2.23				
		65	6.49	115	2.47	165	0.40				
		66	2.31	116	1.13	166	0.10				
		67	12.61	117	3.26						
		68	2.43	118	2.34			218	0.06		
		69	19.39	119	48.00			219	0.01		
		70	3.01	120	13,92			220	0.14		
		71	17.11	121	24.92			221	0.02		
		72	1.06	122	4.17			222	0.24		
		73	0.17	123	2.77	173	0.10	223	0.03		
24	0.08	74	0.15	124	0.34	174	0.07				
25	0.24	75	0.26	125	0.21	175	1.03				
26	1.55	76	0.22	126	0.15	176	0.58				
27	16.21	77	19.51	127	0.69	177	0.41				
28	1.35	78	4.75	128	0.79	178	0.09				
29	13.92	79	29.34	129	1.21	179	0.36				
30	0.29	80	2.53	130	0.63	180	0.06				
31	1.17	81	24.23	131	2.19						
		82	2.94	132	0.97						
		83	1.87	133	8.22						
		84	0.67	134	8.77						
35	0.03	85	0.91	135	4.44						
36	0.10	86	0.08	136	7.81						
37	0.40	87	0.10	137	2.37	187	0.09				
38	0.73	88	0.07	138	0.47						
39	15.87	89	0.45	139	0.81	189	7.29				
40	3.38	90	0.24	140	0.10	190	1.14				
41	45.21	91	22.91	141	0.41	191	0.18				
42	4.21	92	14.05	142	0.36						
43	66.86	93	31.57	143	0.50	193	0.08				
44	1.52	94	18.14	144	0.26						
45	3.60	95	34.56	145	2.43						
46	0.09	96	3.68	146	1.27						
		97	0.91	147	4.96						
		98	0.12	148	3.34						
49	0.08	99	0.12	149	3.16						
50	0.78	100	0.02	150	1.28						

NEROLIDOL No. XIX

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Ab
		51	1.97	101	0.12	151	0.75				
		52	1.21	102	0.27	152	1.13	202	0.25		
		53	11.84	103	1.07	153	1.08	203	0.10		
		54	2.10	104	0.63	154	0.53	204	2.80		
		55	28.83	105	5.66	155	0.10	205	1.30		
		56	2.48	106	1.69	156	0.05	206	0.22		
		57	4.05	107	23.17	157	0.15	207	0.97		
		58	1.27	108	3.88	158	0.07	208	0.20		
		59	1.10	109	11.84	159	0.47				
		60	0.15	110	1.58	160	0.60				
		61	0.27	111	2.10	161	11.33				
		62	0.50	112	0.78	162	2.16				
		63	1.44	113	0.80	163	1.00				
		64	0.72	114	0.10	164	0.57				
		65	0.74	115	0.87	165	0.23				
		66	1.51	116	0.37	166	0.18				
		67	20.08	117	1.24	167	0.07				
		68	11.33	118	0.65			218	0.10		
		69	100.00	119	7.72			219	0.03		
		70	8.24	120	3.51			220	0.17		
		71	32.95	121	9.78			221	0.03		
		72	2.91	122	4.00			222	0.20		
		73	0.93	123	11.84	173	0.10	223	0.05		
24	0.17	74	0.33	124	1.86	174	0.08				
25	0.58	75	0.32	125	0.68	175	0.59				
26	1.42	76	0.28	126	0.42	176	1.40				
27	11.33	77	6.10	127	0.90	177	0.90				
28	0.68	78	1.42	128	0.42	178	0.40				
29	9.27	79	16.99	129	0.45	179	1.14				
30	0.63	80	10.81	130	0.15	180	0.40				
31	0.94	81	26.77	131	0.73	181	0.07				
32	0.17	82	9.27	132	0.48						
		83	5.99	133	4.48						
		84	0.50	134	3.13						
		85	1.23	135	9.78						
36	0.38	86	0.45	136	16.99						
37	0.88	87	0.08	137	3.34	187	0.15				
38	1.74	88	0.08	138	1.62	188	0.05				
39	11.33	89	0.53	139	0.75	189	2.27				
40	3.94	90	0.20	140	1.55	190	0.92				
41	68.48	91	7.72	141	0.40	191	0.22				
42	4.96	92	3.40	142	0.13	192	0.05				
43	32.29	93	49.94	143	0.13	193	0.08				
44	1.69	94	7.72	144	0.08	194	0.07				
45	41.19	95	11.07	145	0.50	195	0.12				
46	0.15	96	2.21	146	0.32						
47	0.03	97	3.24	147	1.62						
48	0.08	98	1.40	148	2.21						
49	0.37	99	0.67	149	1.23						
50	0.75	100	0.07	150	1.34						

TABLE VI

FARNESOL No. XX

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	% Ab
		51	2.47	101	0.10	151	0.41	201	0.02		
		52	1.49	102	0.25	152	0.19	202	0.23		
		53	8.96	103	0.39	153	0.12	203	0.08		
		54	1.13	104	0.22	154	0.03	204	2.14		
		55	13.94	105	3.35	155	0.04	205	0.41		
		56	1.80	106	1.04	156	0.04	206	0.18		
		57	4.50	107	7.40	157	0.12	207	0.29		
		58	8.34	108	1.73	158	0.04	208	0.15		
		59	0.79	109	7.19	159	0.33	209	0.03		
		60	0.10	110	1.09	160	0.16	210	0.06		
		61	0.15	111	1.29	161	2.66	211	0.02		
		62	0.23	112	0.25	162	0.56	212	0.02		
		63	0.80	113	0.08	163	0.35	213	0.01		
		64	0.57	114	0.02	164	0.20	214	0.02		
		65	2.11	115	0.35	165	0.13	215	0.02		
		66	1.13	116	0.16	166	0.18	216	0.02		
		67	11.02	117	0.43	167	0.05	217	0.01		
		68	11.53	118	0.24	168	0.02	218	0.03		
		69	100.0	119	4.64	169	0.02	219	0.01		
		70	6.71	120	1.98	170	0.03	220	0.16		
		71	2.95	121	5.53	171	0.03	221	0.03		
		72	0.33	122	2.92	172	0.02	222	0.72		
		73	0.09	123	5.60	173	0.08	223	0.12		
		74	0.34	124	1.21	174	0.04	224	0.02		
		75	0.25	125	0.30	175	0.24				
26	0.57	76	0.30	126	0.26	176	0.17				
27	1.87	77	4.71	127	1.15	177	0.27				
28	8.76	78	4.46	128	3.79	178	0.10				
29	10.20	79	6.45	129	0.55	179	0.76				
30	0.26	80	4.71	130	0.10	180	0.20				
31	1.23	81	12.41	131	0.38	181	0.05				
32	0.58	82	4.95	132	0.30	182	0.02				
33	0.03	83	2.62	133	2.46	183	0.03				
34	0.02	84	5.41	134	1.33	184	0.02				
35	0.27	85	0.97	135	3.87	185	0.05				
36	0.74	86	2.43	136	5.68	186	0.02				
37	0.76	87	0.09	137	3.46	187	0.13				
38	1.09	88	0.38	138	1.26	188	0.04				
39	10.42	89	0.19	139	0.58	189	0.90				
40	3.32	90	0.10	140	0.37	190	0.15				
41	46.57	91	5.19	141	0.12	191	0.95				
42	3.44	92	2.86	142	0.06	192	0.19				
43	25.35	93	19.75	143	0.29	193	0.08				
44	3.03	94	3.73	144	0.13	194	0.03				
45	0.42	95	7.61	145	0.82	195	0.02				
46	0.05	96	1.35	146	0.74	196	0.02				
47	0.68	97	1.72	147	0.64	197	0.01				
48	0.42	98	0.41	148	0.24	198	0.02				
49	5.61	99	0.10	149	0.41	199	0.01				
50	1.20	100	0.02	150	0.24	200	0.04				

TABLE VI

DRIMINOL

No. XVIII

M/e	% Abund.	M/e	% Abund.	M/e	% Abund.	M/e	%Abund.	M/e	% Abund.	M/e	% Abu
		51	1.03			151	0.37				
		52	0.50	102	0.12	152	0.39	202	0.09		
		53	4.17	103	0.79	153	0.27	203	0.15		
		54	0.59	104	0.48	154	0.06	204	1.45		
		55	12.76	105	7.80			205	0.44		
		56	1.92	106	0.15	156	0.09	206	0.07		
		57	1.57	107	8.83	157	0.12	207	1.45		
		58	0.95	108	2.51	158	0.09	208	0.24		
		59	0.18	109	100.0	159	0.47	209	0.06		
				110	6.65	160	0.18				
		61	0.03	111	1.27	161	1.62				
		62	0.06	112	0.15	162	0.36				
		63	0.26	113	0.03	163	0.62				
		64	0.18	114	0.97	164	0.15				
		65	2.25	115	0.97	165	0.18				
		66	0.68	116	0.42	166	0.24				
		67	5.94	117	1.24	167	0.09				
		68	1.98	118	0.45			218	0.12		
		69	17.81	119	6.11						
		70	2.57	120	1.95			220	0.92		
		71	0.77	121	6.47			221	0.21		
		72	0.06	122	2.63			222	10.90		
		73	0.06	123	9.04	173	0.18	223	1.68		
		74	0.03	124	39.88	174	0.12	224	0.18		
25	0.14	75	0.09	125	5.23	175	0.47				
26	0.79	76	0.09	126	0.42	176	0.53				
27	3.54	77	5.14	127	0.03	177	1.92				
28	0.87	78	0.97			178	0.47				
29	5.05	79	6.03	129	0.39	179	0.42				
30	0.65	80	3.01	130	0.27	180	0.09				
31	1.54	81	12.50	131	0.74						
		82	3.63	132	0.39						
		83	4.60	133	2.71						
		84	1.36	134	0.83						
		85	0.53	135	3.63						
36	0.18	86	0.03	136	2.07						
37	0.14	87	0.03	137	1.95	187	0.30				
38	0.21	88	0.06	138	1.09	188	0.12				
39	4.34	89	0.18	139	0.45	189	2.30				
40	0.91	90	0.09	140	0.33	190	0.65				
41	18.07	91	9.39	141	0.30	191	7.62				
42	1.24	92	1.92	142	0.15	192	1.68				
43	5.41	93	7.80	143	0.27	193	0.27				
44	1.33	94	1.89	144	0.18						
45	0.21	95	10.99	145	0.56						
46	0.03	96	2.39	146	0.21						
		97	5.05	147	1.24						
		98	5.49	148	0.59						
49	0.03	99	0.53	149	1.92						
50	0.29	100	0.03	150	0.56						

TABLE VII

M^* observed	I	II	III	IV	V	VI	VII	VIII	Transition	M^* Calculated
24.4	0.04	0.03	0.01	0.02	0.01	0.16	0.05	0.01	69 → 41 + 28	24.36
25.2	0.01	0.01		0.01	0.01	0.08		0.01	29 → 27 + 2	25.14
27.7	0.01				0.01	0.03		0.01	55 → 39 + 16	27.65
36.5	0.01	0.01	0.02		0.01		0.06	0.01	123 → 67 + 56	36.50
37.1	0.04	0.03	0.01	0.02	0.02	0.27	0.09	0.03	41 → 39 + 2	37.09
39.2	0.05	0.03	0.02	0.02	0.02	0.14	0.04	0.02	43 → 41 + 2	39.09
41.1		0.01	0.02	0.02	0.03	0.10	0.06	0.02	109 → 67 + 42	41.18
46.5	0.02	0.01	0.01	0.01	0.01	0.06	0.10	0.03	91 → 65 + 26	46.43
47.3					0.02				95 → 67 + 28	47.25
47.9			0.01					0.02		
49.1	0.01			0.01				0.01	53 → 51 + 2	49.07
51.1	0.02	0.01						0.01	55 → 53 + 2	51.07
54.8	0.05	0.03	0.02	0.01	0.03	0.10	0.11		82 → 67 + 15	54.74
57.2			0.02							
58.4	0.03	0.03	0.03	0.01	0.01	0.08	0.05	0.02	107 → 79 + 28	58.33
59.4	0.02			0.01	0.01	0.10	0.28	0.02	105 → 79 + 26	59.43
63.1	0.04	0.04	0.04	0.02	0.03	0.20	0.16	0.05	67 → 65 + 2	63.06
63.7	0.03	0.02	0.05	0.01	0.05	0.16	0.08	0.02	136 → 93 + 43	63.60
66.2	0.02		0.09	0.03	0.05	0.80				
66.5						0.38				
68.5								0.05	161 → 105 + 56	68.48
69.5						0.10		0.02	119 → 91 + 28	69.59
71.1			0.02						164 → 108 + 56	71.12
71.5	0.03				0.06	0.16			121 → 93 + 28	71.48
75.1	0.02	0.06	0.06	0.15	0.02	0.88	0.25	0.11	79 → 77 + 2	75.05
76.5			0.18							
77.1	0.16	0.09	0.14	0.08	0.08	0.50	0.28	0.07	81 → 79 + 2	77.05
78.1	0.04		0.16	0.08		0.40		0.04		
82.9								0.03	133 → 105 + 28	82.89
87.1			0.08							
88							0.15	0.12	161 → 119 + 42	87.96
88.5			0.17						206 → 135 + 71	88.47
89.1	0.15	0.08	0.11	0.06	0.14	0.90	0.16	0.08	93 → 91 + 2	89.04
90.2						0.10		0.04		

TABLE VII (Cont'd)

M^* observed	I	II	III	IV	V	VI	VII	VIII	Transition	M^* Calculated
91.1		0.04	0.02	0.02	0.08	0.10	0.25	0.04	$95 \rightarrow 93 + 2$	91.04
92						0.10		0.04		
93.1					0.02	0.10	0.14			
93.6					0.03		0.16	0.04	$189 \rightarrow 133 + 56$	93.59
97.6			0.05							
101.1	0.3			0.01		0.20		0.04	$105 \rightarrow 103 + 2$	101.04
103.2	0.4	0.03	0.02	0.02	0.01	0.20		0.01	$107 \rightarrow 105 + 2$	103.04
105.8					0.04			0.01	$134 \rightarrow 119 + 15$	105.68
107		0.03								
113				0.01			0.25	0.06	$117 \rightarrow 115 + 2$	113.03
115							0.10	0.04	$119 \rightarrow 117 + 2$	115.03
119.5				0.01					$148 \rightarrow 133 + 15$	119.52
121.5		0.02	0.15						$150 \rightarrow 135 + 15$	121.50
127.1					0.02	0.08		0.14	$204 \rightarrow 161 + 43$	127.06
129.4						0.04				
130.7			0.14							
135.1	0.01		0.03							
175.1					0.05	0.03			$204 \rightarrow 189 + 15$	175.10
177.1	0.05								$206 \rightarrow 191 + 15$	177.09

I = Patchulane; II = Ledane; III = Clovane; IV = Caryophyllene; V = β- Selenene; VI = Humulene;
VII = β -Gurjunene; VIII = Clovene

TABLE VIII

M^* bserved	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	Transition	M^* Calculat
24.4	0.01	0.02	0.03	0.05	0.03	0.01	0.03	0.02	0.02	0.02	0.30	0.08	69→41 + 28	24.36
25.1				0.02							0.02	0.01	29→27 + 2	25.14
27.7		0.01	0.01	0.01	0.01	0.01	0.01						55→39 + 16	27.65
29.5		0.01					0.05				0.02	0.01		
31.2							0.02							
36.5	0.01	0.01	0.02	0.05	0.03	0.02	0.05	0.02	0.01	0.02	0.05	0.01	123→67 + 56	36.50
37.1	0.01	0.02	0.02	0.04	0.02	0.02	0.04	0.01	0.01	0.01	0.05	0.02	41→39 + 2	37.09
39.1	0.02	0.03	0.02	0.05	0.03	0.02	0.09	0.02	0.03	0.01	0.05	0.02	43→41 + 2	39.09
40.7									0.04					
41.1		0.01	0.02	0.03	0.03	0.01		0.02		0.02	0.03	0.02	109→67 + 42	41.18
43.3			0.06	0.05									222→98 +124	43.26
46.5		0.02	0.01			0.01	0.01	0.01			0.02	0.01	91→65 + 26	46.43
47.3			0.01		0.02		0.02					0.01	95→67 + 28	47.25
49.1											0.02	0.01	53→51 + 2	49.07
51.1											0.02	0.01	55→53 + 2	51.07
51.6		0.03		0.02					0.01			0.01	121→79 + 42	51.58
52.9				0.04									80→65 + 15	52.81
53.5							0.04	0.02	0.01				161→93 + 68	53.72
54.8			0.03	0.05	0.06	0.02					0.07	0.01	82→67 + 15	54.74
56.7				0.02										
57.3	0.18												151→93 + 58	57.28
58.2		0.02	0.01		0.02	0.03								
58.4								0.03			0.05	0.01	107→79 + 28	58.33
59.5		0.02							0.01				105→79 + 26	59.44
59.8			0.19						0.01				151→95 + 56	59.77
63.1	0.01	0.04	0.02	0.05	0.03	0.02	0.01	0.02	0.02	0.01	0.08	0.02	67→65 + 2	63.06
63.7	0.01	0.07	0.02		0.02	0.02			0.02		0.13	0.03	136→93 + 43	63.60
65.2											0.03	0.02		
66.4	0.01	0.05	0.03	0.05	0.06	0.09		0.03	0.06	0.02	0.14	0.05	94→79 + 15	66.39
68.5			0.02	0.10	0.09	0.06	0.04	0.03	0.12	0.01	0.03		161→105 + 56	68.48
69.2		0.02												
69.5									0.06				119→91 + 28	69.59
70.3				0.50									98→83 + 15	70.29

TABLE VIII (Cont'd)

M^* bserved	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	Transition	M^* Calculat
71.1								0.06					164→108 + 56	71.12
71.5		0.33		0.05		0.04					0.03	0.02	121→93 + 28	71.48
72.5		0.12											122→94 + 28	72.43
72.8										0.02				
75.1	0.01	0.02	0.03	0.05	0.01	0.04	0.03	0.02	0.04	0.03	0.02	0.01	79→77 + 2	75.05
75.5											0.03			
77.1	0.04	0.05	0.08	0.12	0.09	0.10	0.13	0.05	0.06	0.04	0.20	0.04	81→79 + 2	77.05
78.1		0.04												
79.2						0.02								
80.1	0.02													
84.9											0.14	0.02	135→107 + 28	84.81
85.8				0.06									222→138 + 84	85.78
88.0											0.03			
88.2									0.06				161→119 + 42	87.96
89.1	0.03	0.25	0.08	0.06	0.05	0.09	0.06	0.06	0.06	0.03	0.26	0.06	93→91 + 2	89.04
91.1		0.10		0.05		0.03			0.02			0.01	95→93 + 2	91.04
91.8				0.05					0.02				120→105 + 15	91.87
92.8					0.05								121→106 + 15	92.86
93.8					0.27	0.02	0.05	0.04	0.01		0.05	0.08	122→107 + 15	93.84
95.4	0.05												194→136 + 58	95.34
95.8										0.33			124→109 + 15	95.81
98.5								0.02					149→121 + 28	98.26
101.3		0.03	0.02			0.01			0.01				222→150 + 72	101.35
103.1												0.02	107→105 + 2	103.04
105.5	0.01													
105.8						0.01			0.03			0.01	134→119 + 15	105.68
107.5	0.03					0.02						0.03	136→121 + 15	107.37
107.7							0.15						204→148 + 56	107.65
110.									0.03					
111.1								0.02					164→135 + 29	111.13
116.2	0.01												150→132 + 18	116.16
117.2	0.75												151→133 + 18	117.15

TABLE VIII (Cont'd)

M^* served	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	Transition	M^* Calculate
118.2	0.18												193→151 + 42	118.14
119.5					0.03	0.01	0.05	0.05			0.03		148→133 + 15	119.52
121.5			0.25										150→135 + 15	121.50
127.1			0.05	0.03	0.03	0.05		0.08	0.16		0.05	0.01	204→161 + 43	127.06
135.3			0.05					0.16					164→149 + 15	135.37
136.2								0.02					165→150 + 15	136.36
144.7				0.06								0.01	179→161 + 18	144.81
158.1	0.03												238→194 + 44	158.13
158.7	0.08												193→175 + 18	158.68
159.7	0.24												194→176 + 18	159.67
160.7	0.05												195→177 + 18	160.66
164.3										0.02			222→191 + 31	164.33
170.6	0.01	0.01											205→187 + 18	170.58
172.7			0.08	0.15	0.04	0.01	0.10	0.06	0.02	0.03	0.02	0.01	207→189 + 18	172.56
173.1		0.05											202→187 + 15	173.11
175.1				0.04	0.05	0.03	0.15	0.05	0.03		0.02	0.01	204→189 + 15	175.10
187.5			0.01	0.10	0.18		0.50	0.10	0.01	0.04		0.01	222→204 + 18	187.46
188.5	0.02												223→205 + 18	188.45
193				0.03									222→207 + 15	193.01
203.4	0.06												238→220 + 18	203.36

N.B. Peaks recorded as 0.01% abundance indicate a barely visible metastable ion.

IX = Daucol; X = Santalol; XI = Cedrol; XII = Patchouli Alcohol; XIII = Ledol; XIV = Elemol;

XV = α Caryophylene Alcohol; XVI = Eudesmol; XVII = δ-Cadinol; XVIII= Driminol; XIX = Nerolidol;

XX = Farnesol.

CHAPTER IV.

In mass spectrometry as in other spectroscopic techniques a great amount of information can be obtained concerning a compound in a high state of purity. Some of the most difficult problems in chemistry are related to the separation and purification of mixtures obtained from natural or synthetic sources. This investigation has been undertaken to find a method of analysing an essential oil using an M.S.9. general purpose mass spectrometer. The essential oil, chosen at random, was Leptospermum scoparium.

The mass spectrometer was used in the following way. A spectrum was obtained of the complete mixture at low electron energies (≈ 5 ev.). This yielded the parent ions of the molecules present and some fragments which were formed by facile processes. A 70 ev. spectrum was also obtained to facilitate the counting of the low ev. spectrum. See Table IX.

The parent ions were then mass measured to derive their molecular formulae. It was found that the parent ions of very low abundance could not be satisfactorily mass measured owing to the ragged peak shape at the high amplification needed. The molecular weights and molecular formulae of the parent ions measured were as follows.

Molecular Weight.	Molecular Formula.
132	$C_{10} H_{12}$
134	$C_{10} H_{14}$
136	$C_{10} H_{16}$
154	$C_{10} H_{18}O$
198	$C_{15} H_{18}$
200	$C_{15} H_{20}$
202	$C_{15} H_{22}$
204	$C_{15} H_{24}$

Several abundant fragment ions were also measured.

Mass.	Formula.
189	$C_{14} H_{21}$
161	$C_{12} H_{17}$
159	$C_{12} H_{15}$
157	$C_{12} H_{13}$
121	$C_{9} H_{13}$

The next step was to get the mass spectrum of each component at 70 ev. so that the customary analysis could be carried out.

Methods of Mixture, separation and examination.

Several techniques have been established for the mass spectrometric examination of mixtures. A comprehensive survey of these is contained in Beynon's textbook(29) and later developments have been dealt with by Biemann(30).

Two approaches are possible. One depends upon complete separation of the mixture into its individual components by chromatography and the other requires less exacting separation so that binary or ternary mixtures are produced. In the latter case comparison of a range of spectra obtained by varying the composition allows the assignment of ions to the spectra of individual components. Recognition of a component enables its contribution to each peak in the spectrum to be subtracted. This process can be repeated until each compound in the mixture has been found. For this method to be effective one peak must be found which is unique to each component. For qualitative recognition of a component the ions particular to one spectrum can be found by plotting the abundance of the major ions throughout the range of simple mixture compositions sampled. All peaks due to one component vary in abundance in the same manner and can be picked out by finding the slope of each curve.

Several methods of producing a range of simple mixtures are available.

Fractionation.

This method employs the difference in boiling points of the components in a mixture.

A Vigreux column was modified to fit the heated inlet system of the mass-spectrometer. It was loosely packed with glass wool to increase the effective surface area. The essential oil was introduced and twelve spectra obtained by sampling over a wide temperature range. Although some separation was achieved fragmentation of many components gave rise to ions at the same mass numbers. The possibility of producing a eutectic mixture could not be discounted because sesquiterpene fragments were present in every spectrum. These spectra are not included as tables because they were of little use. The experiment indicated that a more efficient separation was necessary. Preparitive gas-liquid chromatography was then tried.

Gas-Liquid Chromatography.

This method has been developed over many years and has been used to separate mixtures for subsequent mass-spectrometric examination(31). Mass spectrometers have also been developed with gas-liquid chromatography units directly attached to them. The principle involved was to perform a rough separation using a 0.5% Apezion filled column to produce simple mixtures. A good separation would have required too long a period of gas-liquid chromatographic investigation and special columns which were not available.

Samples were collected in small U tubes which fitted inside the mass spectrometer heated inlet system sampling tube. The best separation achieved resulted in most of the mixture being concentrated around five large peaks which were poorly resolved on the gas-liquid chromatogram. Sampling was done at the tops of the peaks. Table number IX shows the mass spectra of five adjacent fractions which were cut from the above five peaks.

By using metastable transitions (Table X) in conjunction with the comparison of the abundances of ions in the spectra of adjacent fractions it was possible to assign the following groups of ions to spectra of separate hydrocarbons.

m/e = 204, 189, 175, 161, 147, 133, 119, 105.
m/e = 202, 187, 173, 159, 145, 131, 117, 103.
m/e = 200, 185, 171, 157, 143, 121, 115.
m/e = 198, 183.

Exact abundance values, which are necessary to recognize a component by comparison with a reference spectrum, could not be found. This is a result of the composition of the mixture. Alcohols and esters are decomposed to hydrocarbons and isomerism is possible with many of the components.

As the temperature of the column is increasing from fraction to fraction so is the degree of decomposition. This makes subtraction of one component very difficult and introduces uncertainty because the mistaken identity of one component renders the complete analysis futile. Trace components are also easily missed because their contributions to the spectra are so small.

The only way to obviate this difficulty is to improve the separation of the original mixture. This was not possible with the gas-liquid chromatography equipment available. However, thin-layer chromatography has been achieving some very encouraging results and it was decided to investigate its potential use as an auxiliary technique.

TABLE IX

	Total Mixture		Five Adjacent G.L.C. Fractions				
M/e	5ev	70ev	70ev				
39		33.4	57	24	17	11	35
41		66.6	41	64	45	26	77
43		5.3	39	25	18	11	38
45		0.7	61		1	1	
51			22	9	6	5	16
53		24.3	36	19	15	10	24
55		29.3	59	35	26	13	42
57			18	8	8	3	11
65			17	15	11	7	19
67		29.1	48	22	18	9	26
68		36.1	46	5	4	2	7
69		30.4	35	20	14	9	27
77		32.0	40	30	20	14	39
79		36.4	47	32	23	12	37
81		31.4	88	47	28	15	40
82			65	7	5	4	15
91		43.2	60	61	38	20	58
92			22	21	11	5	15
93		100.0	100	64	40	17	50
94			50	35	16	6	19
95		3.6	32	28	21	10	31
105		47.6	69	76	57	24	17
107		27.2	72	39	29	15	38
109			18	18	14	7	26
115			7	13	11	14	33
117			8	16	11	8	22
119		36.1	49	60	30	16	38
121			62	29	21	10	30
122			19	18	13	8	16
132	3.1	2.3	32	8	7	7	24
133			18	39	28	10	30
134	7.5	11.2	18	18	10	5	14
135		6.4	26	14	10	7	20
136	100.	23.8	25	10	5	3	12
141			3	5	7	17	31
143				7	10	21	33
145			7	20	16	11	37
147			35	30	20	8	29
148	1.2	6.4	20	13	8	3	12
149			11	9	8	4	15
152	0.6	0.7					
154	1.2	2.1					
157		6.2	3	7	12	83	100
159		29.7	11	32	100	100	93
161		41.2	66	100	49	21	39
163			7	5	43	2	12

TABLE IX (Cont'd)

	Total Mixture		Five adjacent G.L.C. Fractions				
M/e	5ev	70ev			70ev		
165			1	1	1	3	22
167					1	2	12
173			2	5	4	3	31
175			6	8	11	4	23
177			1	1	3	2	18
179							
183		0.7	2	1	1	8	92
185		0.5		1	2	4	37
187		0.2	2	12	9	7	20
189		14.4	40	50	40	11	21
191			1	2	2	1	6
198	5.0	0.5	1	1	1	5	50
200	12.5	1.4	2	2	3	21	41
202	18.7	4.1	5	20	20	13	25
204	87.5	24.3	62	75	46	15	24
205			11	14	9	4	9
207		0.2	4				
216					1	1	12
218	4.1	0.2		1	2	1	11
220	0.8	0.2		1	2	3	17
222	0.8	0.3		1	1		1

TABLE X

M/e		
Observed	Calculated	Process
175.1	175.10	$\overset{+}{204} \longrightarrow \overset{+}{189}$ + 15
173.1	173.11	$\overset{+}{202} \longrightarrow \overset{+}{187}$ + 15
171.1	171.12	$\overset{+}{200} \longrightarrow \overset{+}{185}$ + 15
169.1	169.13	$\overset{+}{198} \longrightarrow \overset{+}{183}$ + 15
127.1	127.06	$\overset{+}{204} \longrightarrow \overset{+}{161}$ + 43
125.2	125.15	$\overset{+}{202} \longrightarrow \overset{+}{159}$ + 43
123.3	123.24	$\overset{+}{200} \longrightarrow \overset{+}{157}$ + 43
107.7	107.65	$\overset{+}{136} \longrightarrow \overset{+}{121}$ + 15
105.7	105.68	$\overset{+}{134} \longrightarrow \overset{+}{119}$ + 15
89.1	89.09	$\overset{+}{93} \longrightarrow \overset{+}{91}$ + 2
69.6	69.59	$\overset{+}{119} \longrightarrow \overset{+}{91}$ + 28

Thin-Layer Chromatography.

The use of this technique for separating a mixture before mass spectrometric examination has been mentioned by Biemann(32) and in a research note by Heyns and Grutzmacher(33). Both publications deal with thermal desorption of the material from the silica. In the latter case a small evaporating tube is situated close to the ion chamber in an Atlas-Werke CH_4 mass spectrometer. The spectra of a range of compound types have been obtained including acyclic acids, sugar derivatives, and peptides. However, no spectra were shown. Biemann points out the difficulty of locating the components on the thin plate chromatogram.

This technique has developed for several years and successful separations of a wide variety of mixtures have been reported. An example of its application to a terpenoid mixture which illustrates the separation and identification, by relative retention values, of some sesquiterpenoid olefins has been published by Gupta and Sukh Dev(34). The advantages of using this mode of separation lie in its economy and simplicity. Quantities of material in the order of microgrammes have thus been isolated and examined using the mass spectrometer e.g. prostaglandin $P.G.F._1$ trimethyl ether methyl ester(35). The mixture is applied to the plate in a line using a glass micro-pipette. When a range of components of different polarity is present in one mixture a suitable range of solvent polarities is used to effect optimum separation. A typical range is 100% Petrol-ether, 100% Benzene, 100% Chloroform and a separate plate must be used for each solvent or pair of solvents. Once elution has been completed each component can be located using a variety of sprays which includes ceric sulphate and ferric chloride. Placing the plate in iodine vapour also serves this purpose because the iodine becomes strongly absorbed onto the components present. These methods are chemically destructive, but are useful for finding relative retention values. One limited non-destructive method uses the fluorescence of a chromophere-containing component under U.V. light. A new method is now available which uses Rhodamine 6. G. dye mixed with the silica. Presence of a component is indicated by the quenching of the U.V. fluorescence of the dye. Because this method is independent of band linearity the compound bearing silica can be accurately located and removed.

Two methods of obtaining the spectra of the materials, absorbed on the silica scraped off the plate, are possible. One is thermal desorption in the heated inlet system. The other is isolating the compounds from the silica and introducing them pure by the normal methods. This, however, is well established and the investigation was restricted to the first method which if successful would be much faster in dealing with a multicomponent mixture.

Discussion.

The complete separation involved the use of four plates eluted with petrol-benzene, chloroform, chloroform - 10% methanol, and methanol respectively. The petrol-benzene eluted plate was sampled in the positions shown in Fig. XXI. The spectra obtained are shown in Table XI. A clear area was left at the top of the plate and was sampled as well as spaces between the bands to obtain the background spectrum. This was of the order of abundance of trace components and did not affect the measurement of major components. Rhodamine 6. G. was not thermally desorbed from the silica. It was also too involatile to be introduced as a pure sample through the heated inlet system. The spectra obtained for samples 1. and 2. are the same. These were taken from either edge of the first band and prove it to be pure. The parent ion is at m/e = 204 and the base peak is at m/e = 105. This is a typical sesquiterpene hydrocarbon spectrum, but is not one for which a reference was available for comparison. The same sampling of the second band gave the spectra 3. and 4. proving this band to represent one compound. The parent ion is m/e = 202 and the base peak is at m/e = 159. This is also a sesquiterpene hydrocarbon. There was no cross contamination of these two bands. Both represent a high percentage of the mixture because they could be seen on the plate without the aid of U.V. light. They also produced a high sample pressure in the mass spectrometer. Samples 5. and 6. are of trace components and only the parent ion and base peak were unaffected by the background. 5 is a sesquiterpene hydrocarbon of mass 198 and

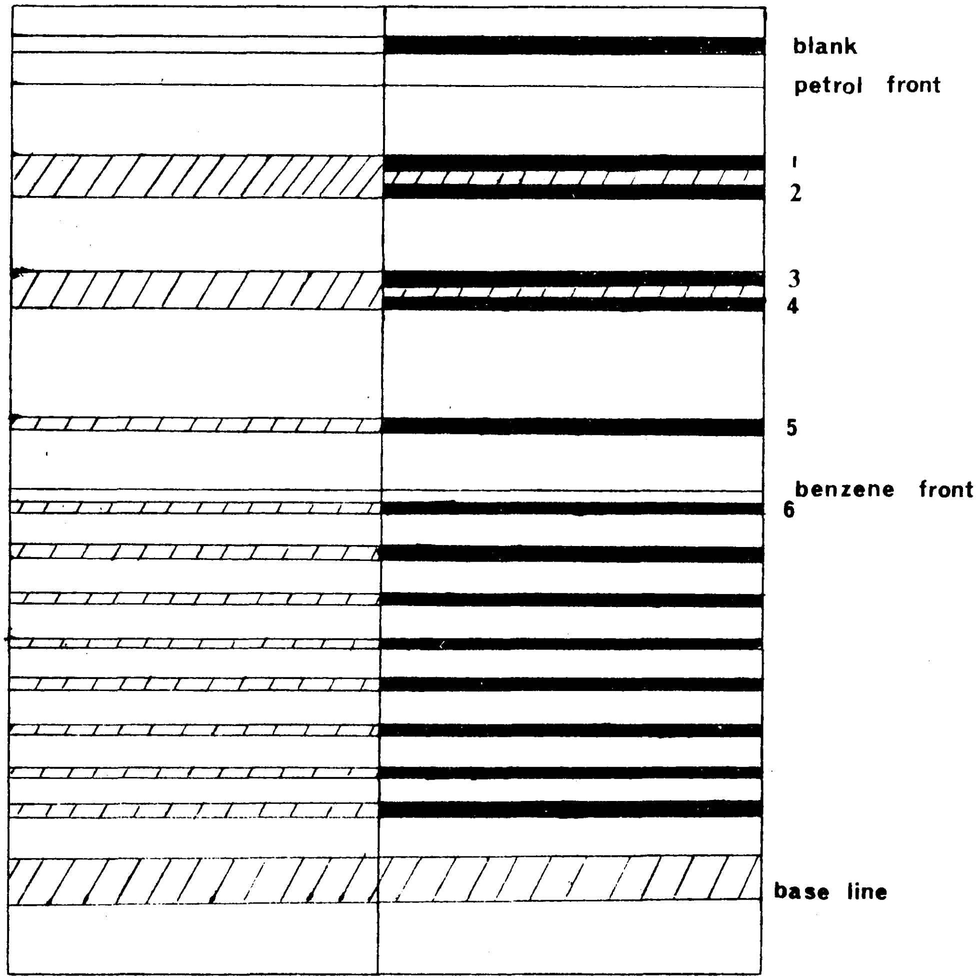


FIG XXI

TABLE XI

M/e	1	2	3	4	5	6
39	61.0	48.0	16.5	17.5		
41	93.0	97.0	16.4	22.5		
51	15.9	12.1	3.5	3.3		
53	35.0	35.3	4.0	4.1		
55	45.0	49.9	5.9	6.9		
65	21.8	20.7	3.7	3.3		
67	39.9	41.3	5.3	5.7		
68	11.7	11.8	2.6	2.2		
69	30.0	28.9	3.6	3.4		
71	7.9	7.5	3.0	2.8		
77	45.8	46.4	5.0	5.4		
78	13.8	13.5	2.5	2.9		
79	60.9	60.9	4.1	4.4		
81	57.4	65.1	3.4	3.0		
82	11.8	9.9				
91	72.8	77.0	8.1	8.9		
92	21.9	18.5				
93	78.5	76.4	3.4	2.6		
94	31.4	32.5				
95	28.8	27.8				
105	100.0	100.0	9.2	9.1		
106	23.1	21.5				
107	48.9	50.4	2.0	1.8		
108	21.8	21.9				
109	17.9	17.1				
115	15.4	13.3	8.5	8.2		
117	16.0	14.3	6.2	5.6		
119	57.6	52.8	4.3	5.4		100.0
121	32.2	32.5				
128			12.8	12.8		
133	43.4	44.9				
134						32.0
135	13.2	13.3				
143			7.1	7.4		
145	13.2	12.6	4.1	4.0		
147	28.1	28.5				
148	14.1	13.6				
157			3.6	5.9		
159	23.4	19.6	100.0	100.0		
161	70.6	64.5	2.2	1.8		
162	17.1	15.8				
175	11.7	12.5				
183					100.0	
189	41.0	41.7				
190	6.0	6.2				
198					37.5	
202	7.0	8.4	10.9	10.3		
204	48.4	46.3				
205	8.6	7.6				

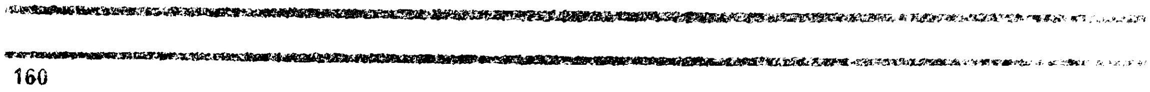
has a base peak at $m/e = 183$. It is highly unsaturated. 6 is a monoterpene hydrocarbon with a parent ion at $m/e = 134$ and a base peak at $m/e = 119$. It is probably p-cymene because it is highly unsaturated and easily loses fifteen mass units.

Another seven bands were removed from this plate. However, all were minor components and the spectra could not be normalized because of the background. The plates which were run using chloroform, chloroform - 10% methanol and methanol all had a wide range of components present in small amounts. The background was therefore considerable and made measurement of abundances impracticable. With the increase in polarity doubt arose about the consistent low abundance of the spectra. Two explanations are possible. The material may be present in too small an amount to give a sufficient sample pressure, or may be too polar or involatile to be thermally desorbed from the silica; the heat supplied to desorb materials could also cause decomposition.

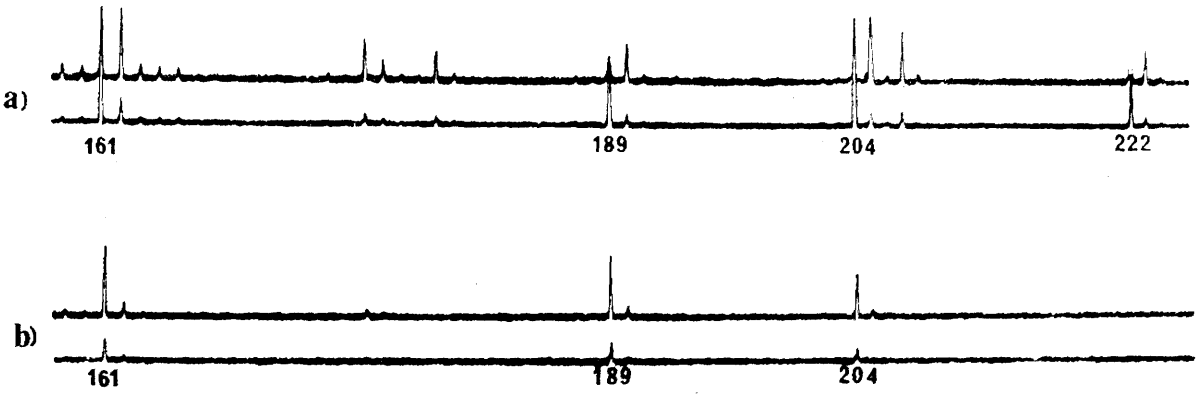
To resolve these difficulties a mixture was made up containing equal amounts of five compounds of different polarity. These were (1) citronellol, (2) patchouli-alcohol, (3) 20 keto pregnan-3-ol, (4) citronellyl acetate and (5) an unknown pure sesquiterpene hydrocarbon. This mixture was separated by a new technique using one plate 60 cms. long on which elution with all solvents was carried out. Excellent separation was achieved whereby each component was at least one inch from its nearest neighbour. The decreasing order of polarity was (3), (1), (2), (4) and (5). The bands of silica containing the components were scraped off along with blank samples. The spectra were obtained using thermal desorption to introduce them. The spectra of the pure compounds were run under the same conditions. To present the relevant data in a concise form the region of each spectrum containing the parent ion has been cut out. The data is set out in Figs. XXII and XXIII. (a) represents the pure compound and (b) the material thermally desorbed from the silica. The appropriate region of the blank has been placed at the top of each figure. The third galvanometer trace is nine times more sensitive than the second and it can be seen that the blank is very low in abundance.

The spectrum of pure patchouli alcohol has a significant parent molecular ion at m/e = 222. Thermal desorption results in complete dehydration and the spectrum (b) is that of a hydrocarbon. Citronellol shows the same effect. The steroid alcohol was in very short supply and the spectrum of the pure material (a) is one which was obtained at an earlier date(36). This alcohol was also dehydrated. The sesquiterpene hydrocarbon shows an increased amount of dehydrogenation on thermal desorption. Pure citronellyl acetate had an exceedingly weak parent ion at m/e = 198. No other ions were observed above m/e = 138. Spectrum (b) differs in that m/e = 198 is not present and the degree of dehydrogenation has increased.

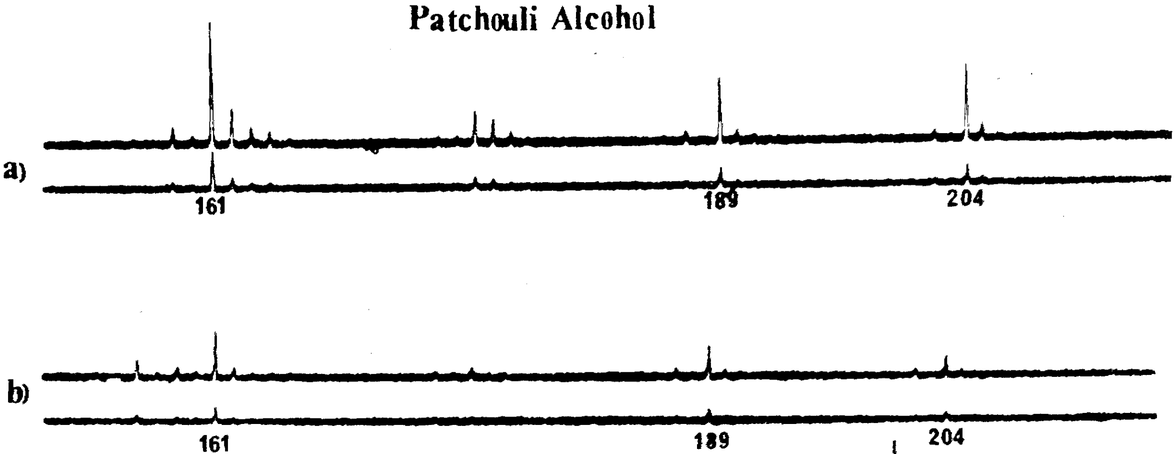
This proves that all the materials examined, which represented a



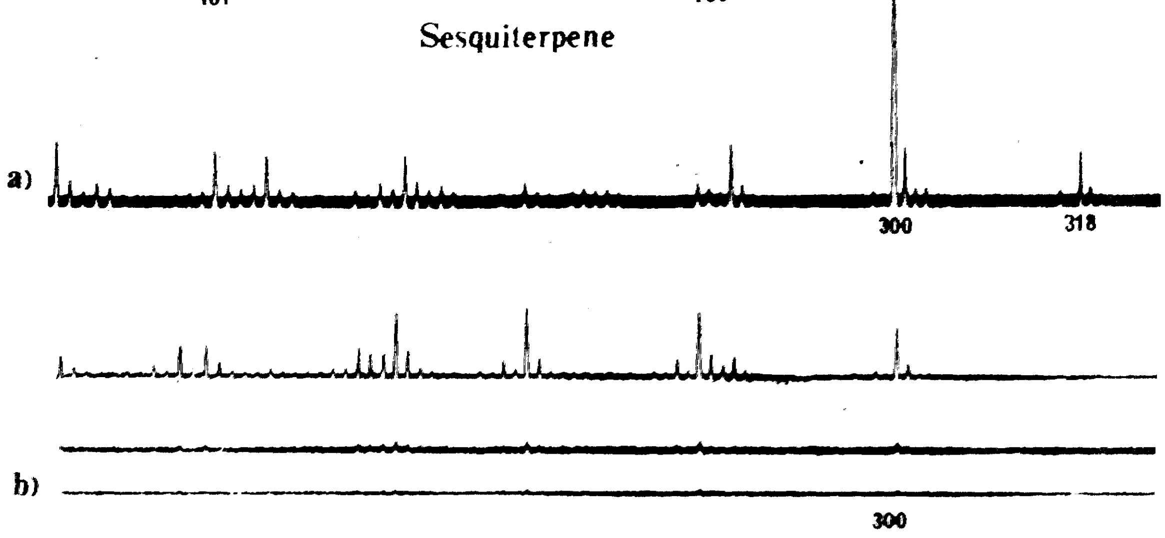
Blank



Patchouli Alcohol

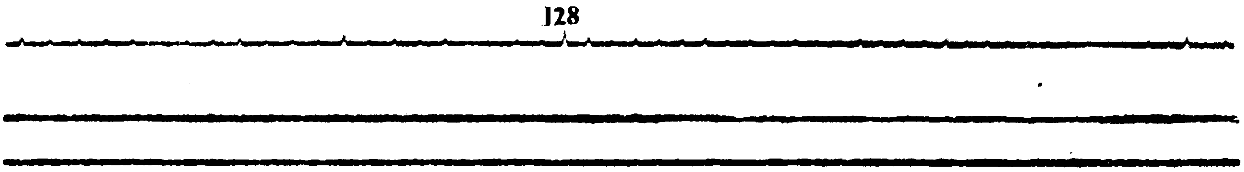


Sesquiterpene

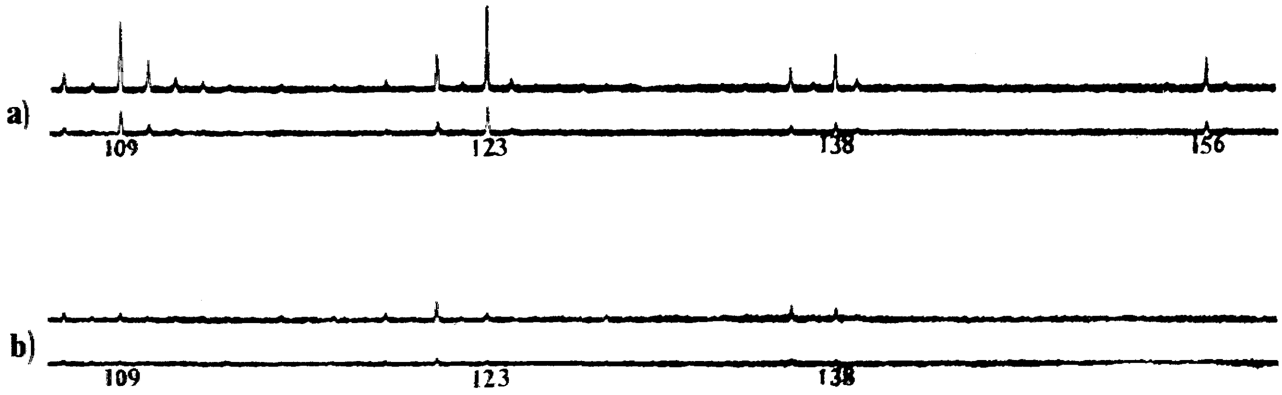


20 keto pregnan-3-ol

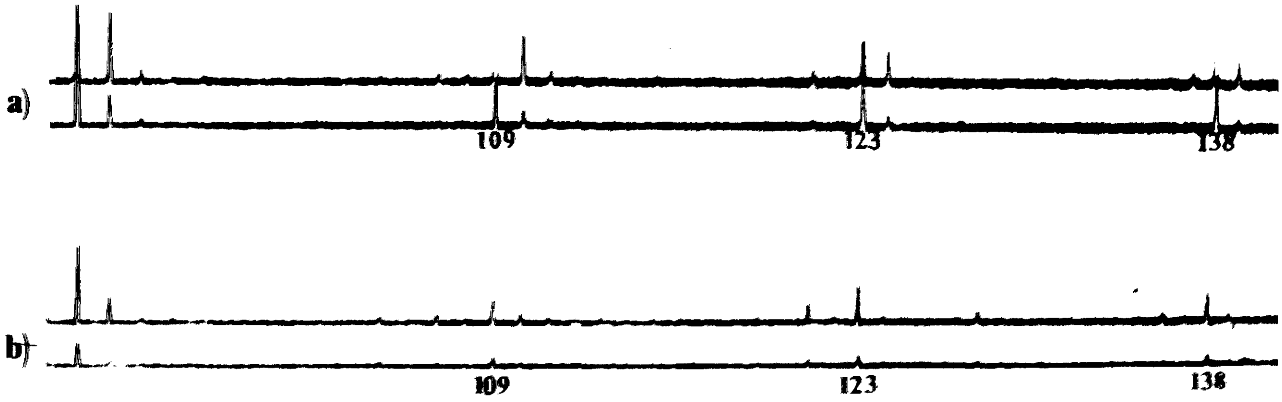
FIG XXII



Blank



Citronellol



Citronellyl Acetate

FIG XXIII

range of polarity and volatility, could be thermally desorbed from the silica. However, as has been shown all were decomposed to a certain extent. The blank was of low abundance and was consistent.

To use this method of obtaining the spectra of the components in a mixture the reference spectra would also have to be run on silica and volatilized in the same way. For mixtures which were known to contain very stable compounds this would not be necessary and thermal desorption could be used.

It has been established that an excellent separation of the complete essential oil was achieved using this technique. The five known compounds examined were at least one inch apart on the silica plate. The materials can be isolated pure from the silica by use of a suitable solvent and can be introduced into the mass spectrometer as normal samples. Components present in low quantities can be obtained in a workable amount by running several plates and concentrating the material from the corresponding band on each.

An additional advantage of using this technique is that the polarity is qualitatively found from the position of the material on the plate. Hence, if a band gives a hydrocarbon spectrum but requires chloroform to elute it, it must contain a polar group and could for example be an alcohol or acetate. If a trace component does not produce sufficient sample pressure to give a spectrum , its type can be guessed from its position on the plate.

By using thin-layer chromatography and isolating the pure material, thermal decomposition outwith the mass spectrometer is avoided. Gas-liquid chromatography does not have this advantage.

Conclusions.

For a mixture as complicated as an essential oil the most promising method of approach using an M. S. 9. mass spectrometer is as follows:-

a) Obtain 5 and 70 ev. spectra of the complete mixture at a heated inlet system temperature of about 190°C.

b) Mass measure all possible parent molecular ions observed.

c) Separate the mixture using thin-layer chromatography and isolate each compound pure from the chromatogram. Blank samples must be taken to ensure background consistency and purity of close bands.

d) Obtain the mass spectrum of each pure compound thus isolated and attempt to find its structure by customary analysis.

REFERENCES.

(1) Beynon, J. H., Saunders, R. A., Williams A. E., *Appl. Spectroscopy*, **17**, 63 (1963).

(2) Linstead, R. P., *J. Chem. Soc.*, **2**, 1016 (1934).

(3) O'Neal, M. J. Jr., "*Applied Mass Spectrometry. The Institute of Petroleum*", London, (1954), p.27.

(4) Reed, R. I., *Fuel*, **39**, 341 (1960).

(5) Beynon, J. H., "*Mass Spectrometry and its applications to Organic Chemistry*", Elsevier, London, (1960), pp. 546-53.

(6) Varadi, P. F., Sebestyon, L. G., Rieger, E.,
Vacuumtecknik **7**, 13 (1958).
ibid **7**, 46 (1958).

(7) Ruf, J., "*Technologie der Vakruumrohren*", Hamburg, **20**, 11 (1958).

(8) Diels, K., Moesta, H., "*Vacuum Symposium Transactions*", Pergamon Press, London, (1958) pp. 115-17.

(9) Ehlbeck, H. W., Locherer, K. H., Ruf, J., Schutz, H. J., "*Vacuum Symposium Transactions*", Pergamon Press, Oxford, (1961), pp. 407-16.

(10) Redhead, P. A., *Can. J. Phys.*, **30**, 1 (1952).
J. Appl. Phys., **24**, 331 (1953).

(11) Bennett, W. H., J. Appl. Phys., 21, 143 (1950).

(12) Hill, H. C., Reed, R. I., J. Sci. Instru., 40, 259 (1963).

(13) Jersey Production Research Company, A.S.T.M. Nos. 1446, 1447, 1448, and 1449.

(14) Beynon, J. H., "Mass Spectrometry and its applications to Organic Chemistry", Elsevier, London, (1960), pp. 325-40.

(15) Biemann, K., "Mass Spectrometry. Organic Chemical Applications", McGraw-Hill, New York, (1962), pp. 74,78,81.

(16) McLafferty, F. W., "Mass Spectrometry of Organic Ions", Academic Press, London, (1963), pp. 599-601.

(17) Gilchrist, T., Reed, R. I., Experientia, 16, 134 (1960).

(18) Von Sydow, E., Acta. Chem. Scand., 17, 2504, (1963). Ibid 2025.

(19) Thomas, A. F., Willhalm, B., Helv. Chem. Acta., 47, 487 (1964).

(20) Beynon, J. H., "Mass Spectrometry and its applications to Organic Chemistry", Elsevier, London, (1960), pp. 345-352.

(21) Reed, R. I., "Ion Production by Electron Impact", Academic Press, London, (1962).

(22) Biemann, K., "Mass Spectrometry. Organic Chemical Applications", McGraw-Hill, New York, (1962), pp. 93-96.

(23) Budziekiewicz, H., Djerassi, C., Williams, D. H., "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco, (1964), pp. 28-49.

(24) MacDonald, C.G., Shannon, J. S., Sugowitz, G., Tetrahedron Letters, 807 (1963).

(25) Sharkey, A. G., Jr., Shultz, J. L., Friedel, R. A., *Anal. Chem.*, **28**, 926 (1956).

(26) Gemmel, K. W., Parker, W., Roberts, J. S., Sim, G. A., *J. Amer. Chem. Soc.*, **86**, 1438 (1964).

(27) Sharkey, A. G., Jr., Shultz, J. L., Fieldel, R. A., *Anal. Chem.*, **28**, 934 (1956).

(28) Biemann, K., "*Mass Spectrometry. Organic Chemical Applications*", McGraw-Hill, New York, (1962) p.146.

(29) Beynon, J. H., "*Mass Spectrometry and its applications to Organic Chemistry*", Elsevier, London, (1960).

(30) Biemann, K., "*Mass Spectrometry. Organic Chemical Applications*", McGraw-Hill, New York, (1962).

(31) Beynon, J. H., "*Mass Spectrometry and its applications to Organic Chemistry*", Elsevier, London, (1960), pp. 187-191.

(32) Biemann, K., "*Mass Spectrometry. Organic Chemical Applications*", McGraw-Hill, New York, (1962), p. 192.

(33) Heyns, K. U., Grutzmacher, H. F., *Angew. Chem.*, **74**, 387 (1962).

(34) Gupta, A. S., Sukh Dev, *J. Chromatog.*, **12**, 189 (1963).

(35) Eglinton, G., Raphael, R. A., Smith, G. N., Hall, N. J., Pickles, V. R., *Nature*, **200**, 960 & 993 (1963).

(36) Clayton, E., Personal Communication.