1131. *Electron Impact and Molecular Dissociation. Part XII.*[1] *The Cracking Patterns of some Rotenoids and Flavones.*

By R. I. REED and J. M. WILSON.

The mass spectra of some rotenoids and flavones have been obtained. The cracking patterns show good correlation with the known structure.

MUCH of this work has been carried out in collaboration with Dr. D. Ollis, the University, Bristol. The mass spectra of the rotenoids (II)—(XI) are included in Table 1. All contain the chromanochromanone ring system and, with the exception of pachyrrhizone (II), they all have methoxyl groups at the 2- and the 3-position. These similarities in structure are reflected in the spectra, and become marked at mass numbers below $m/e = 193$. It is almost certain that in these ions [$m/e = 192$, 191, 177, 163·2 (metastable), 161, 149, 134, 121, and 106] we are observing fragmentations of the dimethoxychroman group which is common to them all. The most abundant ion of the series, excluding pachyrrhizone, is at $m/e = 192$, and must arise as shown in Scheme 1. The two bonds are both readily broken; one is α to a carbonyl group [2a] and benzylic, and the other α to an ether oxygen.[2b] The double bond formed on fragmentation presumably conjugates with the benzene ring. The formation of the other ions is shown in Scheme 2. The relatively unusual loss of a single hydrogen from the ion $m/e = 192$ is confirmed by the metastable ion at $m/e = 190·0$. The ion $m/e = 177$ is derived from the ion $m/e = 192$ also. This is confirmed by the

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[1] Part XI, *J. Sci. Instr.*, **40**, 259; Part X, preceding paper.

[2] Beynon, " Mass Spectrometry and its Application to Organic Chemistry," Elsevier, London, 1960, (*a*) p. 354; (*b*) p. 363.

TABLE 1.

Mass spectra (relative intensities) of some rotenoids.

m/e	(III)	(IV)	(V)	(VI)
359		18·4		
358		58·9(P)		
357		3·7		
356		5·6		
355		0·7		
353			22·2	11·9
352			77·6(P)	24·8(P)
351			1·2	0·7
350			1·2	0·9
344		0·6		
343	9·3	1·3		
342	34·3(P)	0·8		
341	0·5	0·9		
340	0·8			
338			0·5	
337			1·0	1·0
329		0·6		
328	0·6	0·6		
327	0·8	0·9		
323			0·5	
313	0·7	0·8		
312	0·5			
311	0·5			
307			0·5	
215		0·6		
214		0·4		
195	0·5	0·7	0·06	1·5
194	1·9	4·0	2·2	4·4
193	15·8	30·6	18·1	26·2
192	*100·0*	*100·0*	*100·0*	*100·0*
191	36·2	37·2	38·8	42·7
190	3·2	5·3	4·5	6·7
189		1·4	0·5	1·6
183				0·6
180		0·6		1·6
179	0·8	2·5	1·5	4·8
178	4·8	5·1	5·2	6·2
177	26·4	22·9	29·6	27·7
176	1·9	2·2	2·7	2·9
175	1·8	1·5	1·8	2·8
168		0·7		
167		2·5		0·6
166		1·6		1·0
165		1·3	0·8	2·2
164	0·6	2·4	2·2	3·2
163·2(m)	2·4	3·1	2·9	4·4
162	1·6	1·8	2·1	3·1
161	1·8	1·8	4·3	7·5
160		0·4	11·4	16·3
159		0·5		1·1
153		0·5		1·3
152	0·5	0·6	0·5	1·7
151	3·1	1·3	0·8	3·4
150	6·2	1·0	0·8	2·3
149	6·0	3·7	5·2	8·3
148	1·2	1·1	1·0	2·5
147	3·8	2·8	3·4	5·6
146	1·4	1·0	1·3	2·3
145		0·6	0·5	1·8
139		0·8		1·3
138		1·4		1·0
137		1·0		1·9
136		0·7		1·2
135	0·8	1·1	0·8	2·2
134	3·2	1·7	2·9	4·5
133	0·6	0·8	1·1	3·4
132		0·4	2·6	12·2
131	1·8	1·5	1·7	3·4
130	0·9	0·5	0·7	1·6
125		1·2		2·8
124		0·7		1·7
123	0·5	1·4		3·5
122	3·8	1·0	0·6	2·2
121	5·9	3·7	4·4	8·3
120	0·5			1·2
119	1·1	1·2	0·9	2·8
118	0·8	0·8	1·1	1·1
115	0·5			1·0
109			0·6	
108	1·2			
107	4·4		1·0	
106	6·2		3·8	
105	2·0		2·9	
104	0·5		1·2	
103	3·0		1·9	
102	0·8		0·5	
97			0·6	
95	1·1		0·9	
94	1·2		0·6	
93	5·9		4·7	
92	1·2		0·6	
91	3·1		2·7	
90	1·4		1·1	
89	1·4		1·2	

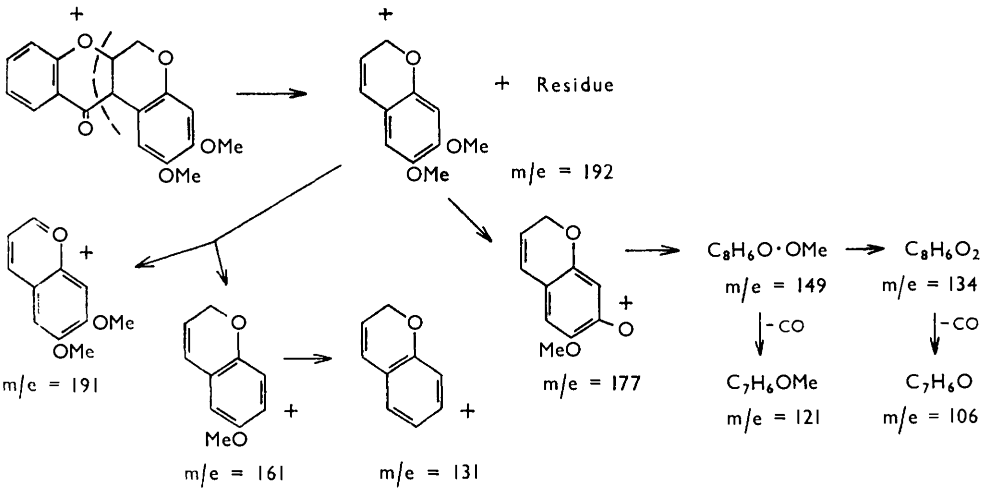
m/e	(VII)	(VIII)	(IX)	(XI)
397		5·9		4·6
396		23·7(P)		18·7(P)
395	10·9	1·0	9·5	0·7
394	38·0(P)	1·6	29·7(P)	0·8
393	2·0		1·1	
392	2·9		1·8	
381		0·6		0·5
380	0·6			
379	1·6	0·5	0·8	
378			0·5	
366	0·5			
365	1·0	0·5	0·5	
364	0·7		0·6	
363	0·9		1·0	
351	0·5			
349	0·6		0·8	0·5
341		0·6		
219			0·7	
217			0·7	
208	0·5		1·3	
207			1·3	
206			0·8	
205		1·4	0·7	0·8
204	0·6	0·5	0·5	1·0
203	2·7	0·5	2·0	1·2
202	0·4		0·8	
201	0·4		0·5	
196				0·5
195			0·5	2·5
194	1·7	1·6	1·0	7·7
193	14·2	15·7	16·3	38·6
192	*100·0*	*100·0*	*100·0*	*100·0*
191	23·5	23·3	24·3	30·3
190	4·8	1·6	2·6	7·8
189	0·7	0·8	1·0	3·3
188			0·5	0·8
187	1·2		2·0	0·6
181			0·9	
180			0·6	0·8
179	0·7	0·8	2·2	3·1
178	2·0	2·4	1·8	7·3
177	12·5	14·6	16·1	15·7
176	1·0	1·3	1·3	3·1
175	1·2	0·8	1·0	1·9
174	0·9		0·6	
173	0·6		0·8	
167			0·5	
166			0·5	0·5
165	0·8	0·5	1·4	1·5
164	1·9	0·7	2·4	3·3
163·2(m)	2·7	1·2	3·9	4·4
162	1·3	0·7	1·9	2·8
161	1·6	1·9	2·5	3·7
160	0·7		1·1	0·7
159	0·6		0·9	0·4
153			0·5	
152			0·5	0·5
151		0·7	1·7	1·3
150		0·7	0·6	3·4
149	2·4	5·2	4·2	9·6
148	0·6	1·0	1·1	1·9
147	2·0	2·1	2·7	3·3
146	1·1	0·8	1·0	1·3
145	0·6	0·5	0·8	0·6
143			0·7	
141			0·6	
139			0·5	
137		0·5	1·2	
136			0·7	0·5
135	0·6	0·8	1·6	1·2
134	1·4	1·5	2·1	2·6
133	0·7	0·8	1·1	1·0
132		0·4	0·7	0·8
131	1·4	1·3	2·5	2·0
130		0·5	0·5	0·7
129		0·6	0·6	
128	0·5		0·5	
127			0·5	
126			0·5	
125		0·5	1·4	
124			0·8	
123	0·5	0·8	2·5	0·7

TABLE 1. (*Continued.*)

m/e	(VII)	(VIII)	(IX)	(XI)
122		0·6	1·2	1·7
121	1·8	3·3	3·6	4·7
120			1·0	0·7
119	1·0	0·9	2·2	1·3
118	0·7	0·7	1·5	1·4
117	0·6		1·1	0·6
116			0·6	0·5
115	0·7	0·5	1·2	0·8
113			0·5	
111			2·4	
109			2·9	0·7
108			0·8	
107			2·3	1·5
106			3·9	3·6
105			2·2	1·9
104			0·9	0·7
103			3·6	2·1
102			0·5	0·6

m/e	(X)
411	6·4
410	28·1(P)
409	1·0
408	1·2
396	9·7
395	19·7
394	1·0
393	1·1
381	1·5
380	1·3
379	1·3
229	0·9
220	1·0
219	3·4
218	3·5
217	7·9
208	1·5
207	0·7
206	0·5
205	1·4
204	5·8
203	20·7
202	1·4
201	1·2
199	1·0
198	6·2
197	0·5
196	0·4
195	1·0
194	2·9
193	25·2
192	*100·0*
191	35·6
190	8·8
189	2·5
188	1·3
187	2·0
181	1·1
180	4·5
179	22·5
178	4·3
177	24·6
176	4·3
175	3·6
174	0·7
165	1·5
164	2·9
163·2(m)	4·1
162	3·1
161	3·7
160	1·2
159	1·6
152	1·0
151	4·3
150	1·7
149	7·1
148	3·6
147	6·4
146	2·3
145	1·0
136	1·1
135	3·9
134	3·9
133	4·3
132	1·0
131	2·5
130	1·1
123	0·7
122	1·3
121	7·7
120	1·1
119	3·2
118	2·6
117	0·8
116	0·5
115	1·2
111	0·6
110	0·4
109	1·1
108	0·9
107	3·5
106	6·5
105	3·2
104	0·9
103	3·7
102	1·2
101	0·3

m/e	(II)
367	10·5
366	36·5(P)
365	1·9
364	3·8
363	0·6
351	0·2
350	0·4
349	0·6
338	0·6
337	0·7
336	0·9
335	0·9
323	0·5
322	0·4
321	0·8
320	0·5
309	0·7
308	0·8
307	1·8
306	1·0
305	0·7
192	2·9
191	6·5
190	9·0
189	1·8
183	0·9
182	0·5
181	0·5
180	0·5
179	1·2
178	2·7
177	19·3
176	*100·0*
175	59·8
174	3·7
173	1·1
172	0·7
171	0·6
170	0·2
169	0·4
168	0·4
167	1·0
166	0·6
165	1·7
164	1·6
163	9·0
162	6·2
161	4·4
160	1·7
159	0·5
158	0·3
157	0·5
156	0·2
155	0·5
154	0·4
153	0·7
152	0·8
151	1·5
150	1·7
149	1·7
148	2·7
147	7·9
146	2·1
145	1·3
144	0·7
143	0·4
142	0·2
141	0·4
140	0·5
139	1·6
138	3·1
137	1·2
136	1·2
135	1·3
134	1·0
133	3·7
132	1·3
131	0·8
130	0·3
129	0·6
128	0·5
127	0·5
126	0·6
125	1·2
124	0·9
123	1·5
122	1·1
121	1·4
120	1·0
119	2·8
118	1·6
117	1·4
116	0·5
115	0·6
114	0·2



SCHEME I

observations: (i) that there is a metastable ion at *m/e* = 163·2 which corresponds to the transition $192^+ \rightarrow 177^+ + 15$; (ii) that there is no corresponding fragmentation in pachyrrhizone which does not possess the necessary methyl groups. The majority of the other ions are typical of a dimethoxy-aromatic compound such as veratrole,[3] with the

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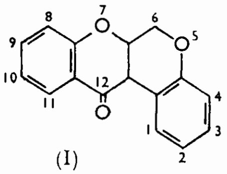
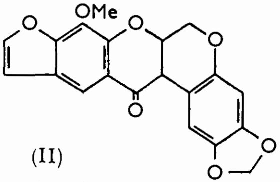
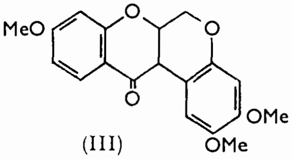
[3] A.S.T.M., uncertified spectra contributed by Phillip Morris Inc., Richmond, Virginia.



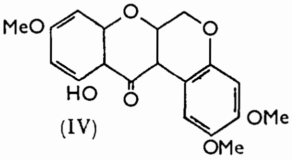
(I)



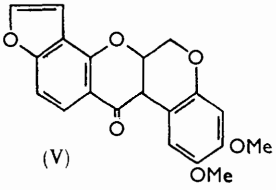
(II)
Pachyrrhizone



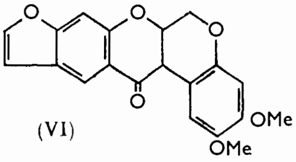
(III)
Munduserone



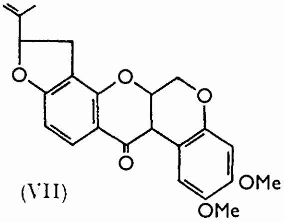
(IV)
Sermundone



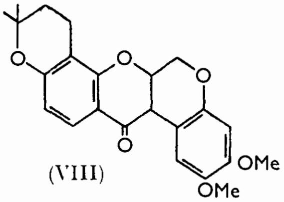
(V)
Elliptone



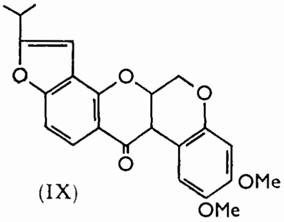
(VI)
Isoelliptone



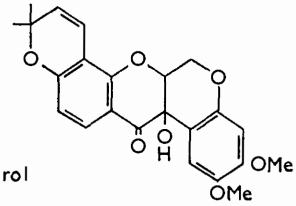
(VII)
Rotenone



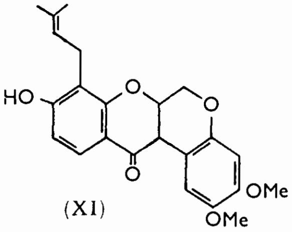
(VIII)
β-Dihydrorotenone



(IX)
Isorotenone

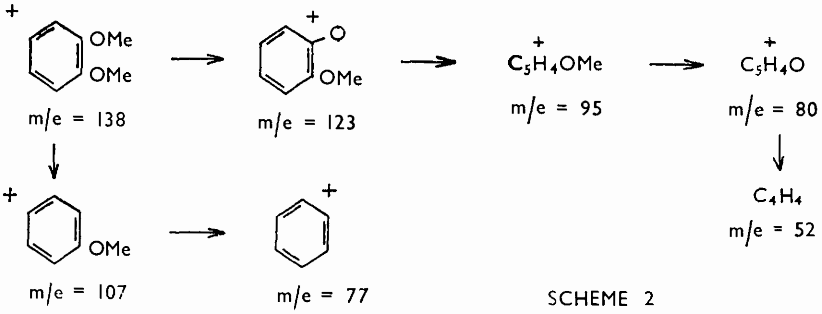


(X)
Toxicarol



(XI)
Rotenonic Acid ?

exception of the ion, *m*/*e* = 121, which could arise by the elimination of carbon monoxide from the ion with *m*/*e* = 149.



SCHEME 2

In addition to these ions there are important fragments arising which preserve intact the tetracyclic system and those which also contain ring A. These ions occur at the high-mass end of the spectrum and, being different for each compound, are conveniently discussed separately.

In munduserone (III), the simplest known rotenoid, the parent molecular ion, *m*/*e* = 342, is the only abundant ion with *m*/*e* greater than 192. There is, however, present in this spectrum another ion, $m/e = 150$, which is the supplement of this and which presumably refers to the other part of the molecule which is formed when the dimethoxychromene grouping splits out. In some rotenoids there is a concomitant hydrogen shift in one direction or the other which gives rise to ions with $m/e = 151$ or 149.

The mass spectrum of elliptone is similar in appearance to that of munduserone. The ions resulting from the formation and decomposition of the dimethoxychromene ion are still abundant and the only other significant ions present are at $m/e = 352$ (parent ion) and $m/e = 160$ (analogous to $m/e = 150$ in munduserone). The ion of $m/e = 160$ degrades to $m/e = 132$ by loss of neutral carbon monoxide $C_9H_4O_3^+ \longrightarrow C_8H_4O_2^+ + CO$.

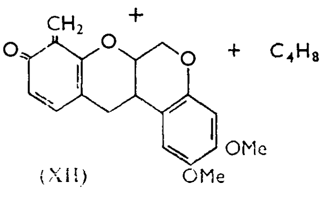
The great similarity in the spectra of isoelliptone (VI) and elliptone (V) suggests that the two compounds are isomeric. There are only minor differences in abundance between them and since both compounds contain a 2,3-dihydroxychroman grouping the differences in the fragment ions must arise in the remainder of the molecule. Since the only structural difference possible is in the position of fusion of the furan ring the structure follows.

The isomers rotenone (VII) and isorotenone (IX) differ only in the position of a double bond, and the spectra are very similar. The molecular ion with $m/e = 394$ is of greater abundance in rotenone than in isorotenone. The introduction of the isoprenoid group also results in an increase in the abundance of the $(P - 15)^+$ ion, although in neither case has it become an abundant ion.

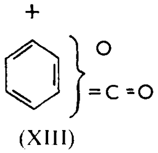
Two further compounds with the same molecular weight and similar spectra are β-dihydrorotenone (VIII) and rotenonic acid (XI). The parent molecular ions are at $m/e = 396$, and ions of low abundance at $(P - 15)^+$ occur. There are also fragment ions which correspond to the loss of a four-carbon grouping from the parent molecular ion. The ion with $m/e = 340$ in the mass-spectrum of β-dihydrorotenone probably has structure (XII). Rotenonic acid eliminates a C_4H_7 group by benzylic fission of the γγ-dimethylallyl group to yield the ion with $m/e = 341$. Other ions of low abundance are present in each mass spectrum but they do not justify a detailed analysis.

The spectrum of toxicarol (X) is again consistent with the known structure. In comparison with the other rotenones already discussed there is a more facile elimination of a methyl group and this results both in the comparatively high abundance of the $(P - 15)^+$ ion and also in the fact that the ion with $m/e = 203$ is more abundant than its higher homologue, $m/e = 218$, which is analogous to the ion of $m/e = 150$ in the munduserone spectrum.

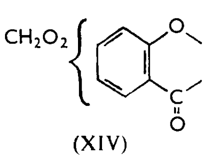
The cracking pattern of sermundone (IV) is so characteristic of the structure that there is no difficulty in identifying it completely. There is an abundant parent molecular ion, $m/e = 358$, with $m/e = 192$ as the base peak, and abundant ions of lower mass at $m/e = 191$, 177, 163·2 (metastable), 161, 149, 147, 134, and 121. These ions are characteristic of the mass spectrum of a 2,3-dimethoxy-rotenoid. From this it follows that the remainder of the molecule has a mass of 166 and gives rise to the other ions observed in



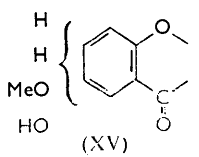
(XII)



(XIII)



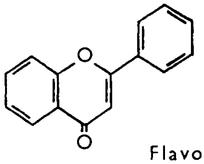
(XIV)

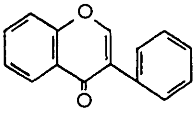


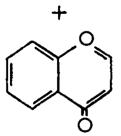
(XV)

the spectrum, namely $m/e = 167$, 166, and 165. By comparison with the spectra from rotenonic acid and toxicarol the ion of $m/e = 166$ would be of the form (XIII), with a further forty-six mass units. The only combination of carbon, hydrogen, and oxygen to satisfy these is CH_2O_2, and the above ring in the structure must be of the form (XIV). Now, the ion of $m/e = 166$ probably degrades further to give $m/e = 151$. This represents the loss of a methyl, and, since the loss of such a group from an aromatic ring is unlikely, the grouping is a methoxyl. The remaining oxygen will therefore be phenolic and one will arrive at a partial structure (XV).

Pachyrrhizone (II) has a methylenedioxy- instead of the more usual dimethoxy-system. The spectrum will therefore differ from all the others although the same fissions occur. Again the most abundant ion is a chromene ion formed by the same type of process as that shown in Scheme 1. This appears at $m/e = 176$ and is the methylenedioxychromene ion. However, since this is the only one of this series possessing a methylenedioxy-group that we have so far studied, it is not certain whether this is a property of the grouping or particular to this compound.


Flavone

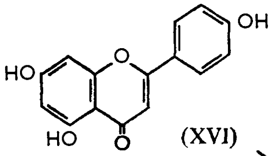

Isoflavone

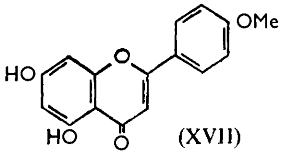

Ion

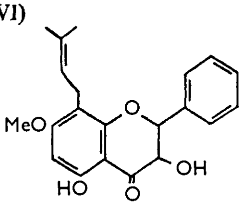
Flavones and isoflavones, all contain a chromenone ring system which may become completely aromatised on ionisation. Fissions across the heterocyclic ring will therefore be more difficult than in the rotenoids and, although the neutral product would not be stable, this type of fragmentation process will be much less abundant. This is confirmed by the mass spectra (Table 2).

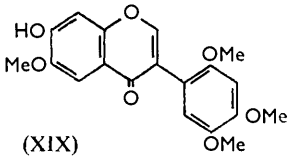
Apigenin (XVI) and acacetin (XVII) have the parent molecular ion as the base peak and an abundant fragment ion corresponding to the loss of carbon monoxide. Fragment ions of much less abundance correspond to fissions in the heterocyclic ring, to give (XX) or (XXI).

Leaserone (XVIII) is a hydroxyflavanone in which the heterocyclic ring resembles that of the rotenoids. Whilst the parent molecular ion is still the base peak there is more fragmentation than is usually observed in the flavones and isoflavones. The ions observed at the higher end of the mass spectrum are easily explained. $(P - 15)^+$, $(P - 18)^+$, $(P - 55)^+$, and $(P - 69)^+$ refer to the loss of a methyl group, water from the cyclic alcohol, a C_4H_7 fragment from the $\gamma\gamma$-dimethylallyl group, and C_5H_9 from the same grouping.


(XVI)
Apigenin


(XVII)
Acacetin


(XVIII)
Leaserone


(XIX)
Caviunin

The dissociation refers to the elimination of carbon monoxide from the ion of $m/e = 285$. to yield $m/e = 257$. A further consequence of the similarity of leaserone to rotenoids is the rather greater facility of fragmentation across the heterocyclic ring. The three rather abundant ions, $m/e = 235$, 234, and 233, as (XXII), may arise in this way. A concomitant hydrogen migration in either direction will yield the other ions. The ions of $m/e = 219$,

TABLE 2.

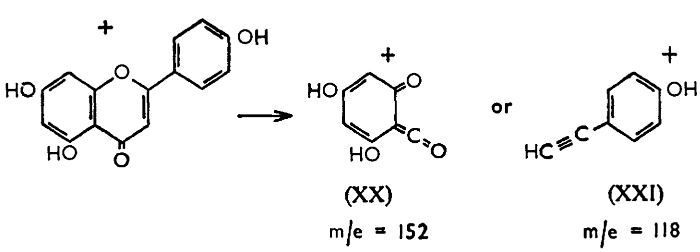
Mass spectra (relative intensities) of flavones and isoflavones.

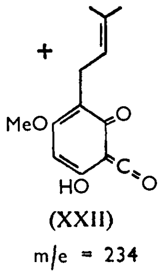
m/e	(XVI)	(XVII)	*m/e*	(XVI)	(XVII)	*m/e*	(XVI)	(XVII)	*m/e*	(XVI)	(XVII)
285		26·2	230	0·8		136		0·4	117	2·3	3·8
284		*100·0*	229	1·7		135		1·6	116	1·2	0·4
283		8·8	226·9(m)		1·0	134		0·6	115	5·0	0·9
282		4·5	215		0·2	133	3·9	4·2	114	0·4	0·1
271			214	1·4	0·6	132	1·1	15·0	112		0·2
270	*100·0*(P)	0·7	213	4·2	2·6	131	2·3	0·3	111		1·3
269	13·3	2·1	212		0·3	129	1·9	0·6	110		0·4
268	2·6	0·6	155	2·0	0·3	128·5		0·7	107		0·5
257		1·2	154	2·3	0·2	128	2·9	4·2	106		0·2
256		4·5	153	22·0	1·1	127	2·8	0·5	105		0·6
255		3·1	152	16·1	6·2	126	1·4	0·2	104		0·4
254		1·0	151	2·1	0·4	125	3·2	0·5	103		0·5
253		1·2	150		0·2	124	18·0	5·0	102		0·7
252		0·1	149	3·2	0·3	123	9·8	0·4	97		0·9
243	3·8	0·5	148	3·0	0·2	122	1·4	0·1	96		2·0
242	18·7	2·5	140		0·2	121	16·3	0·4	95		1·3
241	6·1	7·4	139		0·5	120	2·0	0·2	91		0·5
240	0·8	0·5	138		0·2	119	9·0	0·6	90		0·4
239	0·8		137		0·4	118	13·7	1·0	89		3·2
230·8(m)		0·7									

m/e	(XVIII)	*m/e*	(XVIII)	*m/e*	(XVIII)	*m/e*	(XVIII)	*m/e*	(XVIII)	*m/e*	(XVIII)
355	39·2	308	2·3	248	4·1	205	3·6	166	2·6	139	2·3
354	*100·0*(P)	307	2·8	247	4·0	204	2·1	165	4·5	136	2·9
353	3·4	299	4·9	241	4·6	203	3·2	164	3·0	135	4·6
352	3·6	298	3·5	236	6·5	193	8·4	163	5·7	123	4·2
340	7·1	297	2·7	235	25·1	192	9·9	162	2·5	121	8·7
339	18·4	295	4·1	234	6·9	191	45·2	153	8·1	120	11·6
338	5·2	294	2·3	233	11·6	190	3·7	152	3·9	119	6·6
337	5·5	293	4·3	222	1·1	181	2·5	151	4·0	118	5·7
336	4·2	286	3·6	221	3·6	180	9·7	150	2·1	117	4·5
327	2·5	285	10·8	220	13·5	179	53·0	149	9·6	115	7·8
326	7·8	280	2·3	219	51·4	178	3·1	148	3·9	108	4·1
325	17·9	269	2·9	218	3·8	177	7·3	147	4·6	107	5·8
324	4·1	268	2·3	217	6·4	176	12·9	146	2·0	106	2·9
323	4·7	267	2·5	209	2·1	175	2·9	145	5·3	105	13·0
322	6·1	258	3·4	208	4·7	168	2·5	141	2·3	104	2·3
321	14·8	257	13·0	207	5·1	167	12·7	140	4·7	103	7·9
309	3·1	249	2·0	206	23·5						

m/e	(XIX)	*m/e*	(XIX)	*m/e*	(XIX)	*m/e*	(XIX)	*m/e*	(XIX)	*m/e*	(XIX)
375	50·5	330	5·5	299	3·8	246	2·0	187·5	1·4	151	2·9
374	*100·0*(P)	329	7·6	298	2·6	245	2·7	187	3·1	150	3·9
373	6·4	328	7·8	288	2·1	244	1·7	183	2·2	149	7·8
372	2·2	327	4·5	287	2·5	243	2·0	180	2·4	148	1·5
360	17·9	326	3·0	286	2·9	242	1·7	179·5	3·5	147	1·9
359	34·5	325	2·2	285	3·3	231	2·3	179	3·0	145	2·1
358	5·1	318	1·8	284	1·6	227	1·0	178	5·8	144	4·1
357	6·7	317	3·8	283	1·5	219	1·7	177	3·7	139	2·8
356	12·0	316	6·8	276	2·5	218	1·6	172	2·4	136	2·0
346	6·6	315	6·2	275	5·0	217	1·9	171·5	1·6	135	5·4
345	11·9	314	5·8	274	4·3	215	2·4	167	2·3	134	2·8
344	11·8	313	7·0	273	1·7	203	2·5	165·5	1·8	121	2·3
343	17·0	312	2·6	272	2·5	193	3·3	165	2·1	120	1·6
342	5·6	305·2(m)	4·4	271	1·9	192	6·8	164	2·1	119	3·2
341	9·6	303	4·8	260	1·8	191	6·3	163	3·2	107	2·9
338·8(m)	2·1	302	5·1	259	2·4	190	1·7	158	3·2	106	2·3
332	13·6	301	8·1	258	1·6	189	2·1	153	2·8	105	1·9
331	28·3	300	3·4	257	1·8	188	1·4	152	1·5		

206, and 179 result from the further loss of methyl, carbon monoxide, and a C_4H_7, respectively, from the γγ-dimethylallyl substituent. The ion with *m/e* = 191 may represent the further degradation of *m/e* = 206; the loss of a further methyl group.


(XX) m/e = 152
(XXI) m/e = 118


(XXII) m/e = 234

Caviunin (XIX) is a rather heavily substituted isoflavone, and, while the parent molecular ion is still the base peak, the ion resulting from the loss of methyl is 34·5% of it.

The ion of $m/e = 343$ refers to the loss of methoxyl, and $m/e = 331$ to the elimination of acetyl; the nature of this process is confirmed by the presence of a metastable ion of $m/e = 305{\cdot}2$, corresponding to the transition, $359^+ \rightarrow 331^+ + 28$. The elimination of molecular water from the parent molecular ion accounts for the abundant ion, $m/e = 356$, and it too is confirmed by the presence of a metastable ion, $m/e = 338{\cdot}9$, derived from the fission, $374^+ \rightarrow 356^+ + 18$. The ions whose masses lie immediately below $m/e = 351$ are derived by the degradation or elimination of the substituents in the ring. These ions are so numerous, and the possible routes to them are so varied, that a detailed discussion of them would be unprofitable. On the lower mass range too, it is possible to detect ions formed by the fragmentation of the heterocyclic ring. This region is, however, so complicated, and includes so many doubly-charged ions, that a detailed analysis would be quite unrewarding.

The spectra were obtained on a Metropolitan-Vickers Ltd. M.S.2 mass spectrometer used in conjunction with an N.E.P. 1050 ultra-violet recorder. The sampling system has already been described in Part IX.[1] The samples, kindly provided by Dr. Ollis, were used as obtained.

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