1129. *Electron Impact and Molecular Dissociation. Part IX.*[1] *The Mass Spectra of some Malonic Acids and Furan Compounds.*

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The mass spectra of some substituted malonic acids and furan compounds have been obtained. Many fragments have been correlated with the probable structures and the known modes of fission of typical compounds.

Malonic Acids.—The mass spectra of some substituted malonic acids have already been reported briefly,[1] and these measurements have now been repeated and extended. The main fragment ions are included in Table 1. These spectra show that even when the parent molecular ion (P^+) is absent there is an ion $(P + 1)^+$. The latter ion may be produced by an ion–molecule interaction or by the ionization and subsequent fragmentation of a dimer of the particular compound. However produced, this ion is of great value in determining the molecular weight of a malonic acid. The $(P + 1)^+$ ion is readily recognized since its abundance is proportional to the second power of the sample pressure. It has previously been employed in the analysis of a variety of compounds, including amines, ethers, glycols, and nitriles,[2] and, by an extension of the method, to amino-alcohols,[3] carbonates,[4] esters,[4,5] and sulphones.[3]

The acids here dealt with are methyl-, hept-6-ynyl-, ethylmethyl-, methyl-n-propyl-, n-butyl-ethyl-, di-n-propyl-, and di-n-octadecyl-malonic acid. These can be divided into

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[1] Reed, Reid, and Wilson, Symposium on Mass Spectrometry, Oxford, 1961, p. 175.
[2] McLafferty, *Analyt. Chem.*, 1957, **29**, 1782.
[3] Biemann, Gapp, and Seibl, *J. Amer. Chem. Soc.*, 1959, **81**, 2274.
[4] Quayle, 8th International Spectroscopic Conference, Lucerne, 1959.
[5] Ryhage and Stenhagen, *Arkiv. Kemi*, 1959, **13**, 523.

TABLE 1.

Mass-spectra of substituted malonic acids.

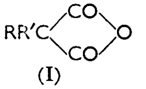
Substituents: A, methyl; B, hept-6-yryl; C, ethylmethyl; D, methyl-n-propyl; E, n-butylethyl; F, di-n-propyl; G, di-n-octadecyl.

m/e	A	B	C	D	E	F
40	2·6		6·7			
41	13·3		65·0			
42	5·1		13·4	13·0		
43	10·5	36·1	32·5	30·0	18·9	
44	16·7	36·0	22·4	16·5	41·6	
45	63·3	35·2	79·5	27·0	13·0	
46	6·8	3·4	5·6	3·5	1·6	
47	3·3	2·1	2·5	3·0		
48		1·7				
49		3·5				
50		15·2	4·1	3·5		0·6
51		23·0	7·5	4·2		1·1
52	0·8	19·3	4·1	3·5		1·1
53	5·3	34·4	22·4	9·1	6·5	11·3
54	3·5	54·0	14·5	5·3	5·2	8·5
55	55·6	92·5	85·0	26·5	*100·0*	68·2
56	61·0	13·8	22·0	11·5	28·2	18·2
57	10·3	20·5	17·5	14·5	33·6	36·7
58	1·5	5·8	5·9	4·5	3·2	3·4
59	2·5	14·2	52·1	23·5	6·4	2·8
60	1·3	19·2	4·9	4·0	3·2	3·1
61		3·8			3·2	0·7
62		3·5				
63	1·0	9·2		3·0		
64		3·4		2·5	3·1	0·7
65	0·9	19·3		5·0	1·2	1·9
66	0·7	18·6		3·5	2·1	1·6
67	2·5	75·1	3·4			
68	1·5	29·6	5·2	7·8	6·2	5·2
69	6·0	45·2	76·5	54·5	33·5	*100·0*
70	4·3	13·0	16·0	13·0	12·5	11·6
71	3·6	21·4	7·5	11·5	6·9	5·5
72	11·6	58·5	78·0	40·5	2·8	2·7
73	76·0	42·3	66·5	16·0	75·6	99·1
74	*100·0*	9·6	25·6	32·0	7·7	7·5
75	7·3	4·6	1·5	3·5	1·6	1·1
76	1·0	6·4		3·0	2·0	
77	1·1	45·1		5·0	2·1	0·9
78	0·8	89·9	2·5	3·5	1·6	0·9
79	1·5	*100·0*		5·0	2·8	1·6
80	0·8	40·0		3·4	2·0	0·9
81	3·1	51·1	4·1	8·5	8·5	5·4
82	1·6	22·6	17·5	5·5	5·7	4·7
83	3·3	17·6	20·6	9·0	69·2	7·8
84	1·1	14·3	40·6	4·2	8·5	7·7
85	1·6	12·2	23·1	7·1	5·3	4·8
86	1·3	54·0	14·6	7·6	31·5	2·7
87	2·8	23·2	94·0	90·5	40·8	4·8
88	3·5	2·5	24·2	11·5	58·5	1·2
89		3·3	3·7	3·5	4·7	
90		2·5			1·2	
91	1·6	32·5		4·5	2·0	0·7
92	1·0	17·2		3·0	1·6	
93	1·3	41·0		3·5	2·4	
94	1·0	94·3		3·0	1·8	
95	3·2	79·9	3·7	8·0	5·6	7·3
96	2·0	15·9		6·1	7·3	1·9
97	2·3	30·2		8·0	14·6	70·1
98	1·6	11·8		11·2	42·7	7·2
99	1·7	27·6	17·9	11·0	31·9	58·5
100	10·0	9·2	*100·0*	*100·0*	5·7	14·7
101	13·6	3·3	37·4	11·6	96·2	15·1
102	2·0	2·1	46·6	3·4	7·3	50·9
103	1·0	3·8	5·6	2·3	1·2	3·9
104	0·8	76·1	5·2	9·2	1·5	0·7
105	1·3	26·0		3·6	1·7	
106	0·8	15·1		2·4	1·7	
107	1·1	31·5		3·0	1·7	
108	1·0	21·7		2·9	1·6	0·7
109	1·8	19·4		5·4	5·8	4·6
110	1·1	17·6		3·2	5·6	34·9
111	1·1	18·4		4·0	15·3	3·9
112	0·8	22·7		3·5	10·4	1·4
113	0·6	15·0	5·9	7·0	13·7	16·4
114	0·6	8·7	3·7	19·5	91·6	3·2
115	1·2	9·3		8·5	22·6	91·2
116	0·8	4·2		15·5	25·9	9·2
117	0·6	23·6	3·7	5·5	25·0	72·1
118	3·0(P)	4·6	92·0	91·3	2·4	5·3
119	3·5(P + 1)	9·4	18·4	11·5	1·6	1·1
120		4·9	3·4	3·8		
121		9·9		3·0		
122		9·9		2·5		
123		34·5		3·8	3·6	0·8
124		16·8		3·0	12·2	1·1
125		11·1		3·2	4·5	1·9
126		8·3		2·4	37·5	49·6
127		8·9		4·2	20·6	11·4
128		7·5	1·9	3·0	3·2	45·5
129		4·4	5·6	2·8	20·6	4·9
130		3·1			2·8	0·8
131		3·7		3·5	1·6	
132		2·9	2·2	3·0	35·6	
133		6·9			3·9	
134		39·0			1·2	
135		19·0	1·5	3·8	1·5	
136		8·0		3·0		
137		16·4		2·8	1·5	
138		9·5		3·0	1·5	
139		8·2		3·0	1·1	
140		7·0		2·2		
141		9·8		3·0	10·9	5·3
142		3·7		2·8	19·5	9·1
143		2·8		4·4	6·7	5·9
144		3·5			11·7	9·3
145		3·7			3·2	4·0
146		2·4			1·2	26·0
147		6·0	3·0(P + 1)			
148		3·5				0·7
149		3·3			1·3	
150		2·4				
151		5·3				
152		23·0				
153		11·5				
154		5·2			8·5	
155		3·8			2·8	0·8
156		4·1			1·2	0·7
157		3·3			1·6	
158		4·2				
159		5·8			1·8	
160		2·6			6·7	
161		3·1		3·9 (P + 1)	1·2	
162		12·3				
163		4·5				
164		2·8				
165		2·9			1·5	
166		2·9			1·2	
167		2·4			1·2	
168		2·5			1·2	
169		2·3			2·4	0·6
170		2·6			2·3	0·6
171		3·8			2·6	6·8
172		4·2			3·6	1·3
173		2·9			2·0	
174		2·5				
179		2·9				0·6
180		3·4				
181		6·5				
183						0·9
184		2·5				
189		2·6			10·5 (P + 1)	3·7(P + 1)
190		2·6			1·2	0·9
198		2·4(P)				
199		2·5				

m/e	G
70	5·13
71	8·09
72	1·76
73	5·73
74	3·60
77	3·51
78	1·62
79	2·36
80	1·62
81	5·50
185	1·52
213	5·17
214	1·43
227	3·23
228	1·80
241	2·82
242	1·39
250	1·71
251	1·20
252	1·80
253	1·43
254	0·69
255	3·23
256	2·40
269	15·01
270	5·91
271	1·43
276	1·16
277	1·16
278	1·16
279	1·16
280	1·02
281	1·16
282	0·92
283	8·27
284	5·87
285	2·08
292	1·43
293	1·39
294	3·65
295	2·08
296	1·11
297	2·59
298	3·47
299	1·16
311	7·85
312	*100·0*
313	30·68
314	5·31
325	29·61
326	10·12
327	2·31
339	5·50
340	2·13
350	1·62
351	1·16
352	0·69
353	2·35
354	1·80
367	6·05
368	2·86
381	7·99
382	3·42
383	1·29
395	2·08
396	1·16
409	1·52
410	1·16
423	2·82
424	1·62
437	2·77
438	1·62
451	1·48
452	1·16
465	1·39
466	1·16
480	1·57
481	1·11
493	1·20
536	3·88
537	2·08
538	1·39
544	1·85
545	1·66
546	1·80
547	1·20
550	3·47
551	1·85
552	1·16
564	72·44
565	35·99
566	12·94
567	4·34
568	1·43
578	1·34
593	1·16

two classes; the first and second possess a tertiary carbon atom and the remainder a quaternary one. Notwithstanding that some thermal decarboxylation may occur under the conditions of experiment it is significant that there is a parent molecular ion present in the spectra of methyl- and hept-6-ynyl-malonic acid. There are many examples from the alkanes which show that the parent molecular ion is small when a tertiary centre is present in the molecule. Equally, many examples possessing a quaternary centre do not have a parent molecular ion,[6] and the absence of such an ion in the malonic acid does not imply that one carboxy group has been eliminated thermally under the conditions of experiment.

The spectra show two main fragmentation processes of the molecular ion. First, there is the loss of 44 mass units, corresponding to the removal of carbon dioxide; this may be partly due to thermal decomposition. Secondly, there is the loss of 18 mass units; the elimination of a water molecule. Gohlke and McLafferty[7] have remarked that *o*-aromatic dibasic acids yield an ion which corresponds to anhydride formation and one may therefore suppose that a similar reaction occurs in the malonic acids. Some rearrangement might occur simultaneously but, since there is no direct evidence for this, and to simplify this discussion, the anhydride has been considered to have a four-membered ring structure (I). Table 2 shows the abundance of the ion formed by dehydration as a percentage of the most abundant, the base peak, of the spectrum. The results indicate that the elision of water is often a significant reaction. Of greater interest is the formation of the anhydride with simultaneous removal of the longer alkyl group and concomitant hydrogen migration. It is well established that in fragmentation at a centre of branching the longer alkyl chain is removed preferentially,[6,8] and if this principle is applied here the decomposition proceeds as shown in Scheme 1.



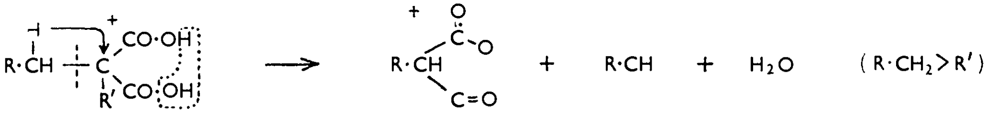
(I)

R, R' = H or alkyl

TABLE 2.

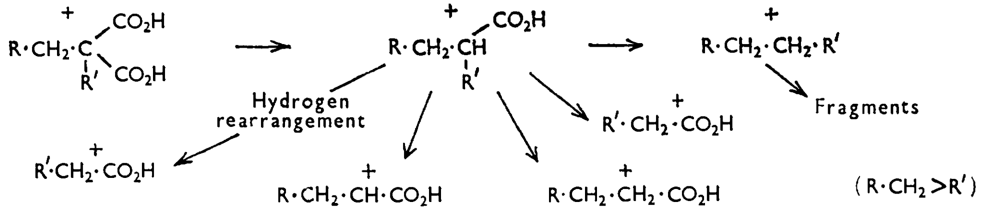
Substituted malonic anhydrides.

Substituents	Me	$Me\cdot[CH_2]_4\cdot C{\vdots}C$	Et, Me	Bu^n, Et	Me, Pr^n
m/e	100	180	128	170	142
% Abundance of base peak	100	3·4	1·9	2·6	2·8



SCHEME 1

The fragment ion obtained is often abundant (Table 3). The alternative fragmentation sequence, which involves decarboxylation with or without alkyl-group elimination, may be depicted as in Scheme 2, and leads to a series of ions many of which are very abundant. In the case of n-butylethylmalonic acid such a sequence should lead to the ions listed in Table 4. Ions of $m/e = 100$ can also arise by loss of two molecules of carbon dioxide from the heptane ion.



SCHEME 2

Direct comparison is, however, difficult since the intermediate concentration of the alkane ion is not known, and it is also possible that a rearrangement has occurred in fragmentation and that the molecular ion under consideration is not from n-heptane but from another isomer.

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[6] A.P.I. Research Project 44.

[7] Gohlke and McLafferty, A.S.T.M.E.-14 Meeting on Mass Spectrometry, San Francisco, 1955.

[8] A.P.I. Research Project 44.

TABLE 3.

Removal of larger alkyl groups on formation of malonic anhydrides.

Acid subst.	Me	$Me{\cdot}[CH_2]_4{\cdot}C{\vdots}C$	Et, Me	Bu^n, Et	Me, Pr^n	di-Pr^n
Ion anhydride subst.	Me	None	Me	Et	Me	Pr^n
m/e	100	86	118	132	118	146
% Abundance	10·0	54·0	92·0	35·6	91·3	26·0

TABLE 4.

Ions from fragmentation of n-butylethylmalonic acid as in Scheme 2.

Ion	$P - CO_2$ $P - 44$	$P - CO_2 - C_4H_8$ $P - 100$	$P - CO_2 - C_4H_9$ $P - 101$	$P - CO_2 - C_2H_4$ $P - 72$	$P - CO_2 - C_2H_5$ $P - 73$	$P - 2CO_2$ $P - 88$
m/e	144	88	87	116	115	100
% Abundance	11·7	58·5	40·8	25·9	22·6	5·7

In addition to this general pattern there are two particular exceptions. The symmetrically substituted di-n-octadecylmalonic acid does not give a parent molecular ion or a $(P + 1)^+$ ion. This may be associated with the great size of the substituent groups, resulting in the loss of one so readily that the necessary ion–molecule interaction cannot occur, or it may be due to a drastic and facile decarboxylation during the measurement. A second exception is the loss of 55 mass units from n-butylethylmalonic acid, which is almost certainly due to the elimination of an n-butyl group; there is much evidence that this group is very readily eliminated when present in a molecular ion.[9]

Furancarboxylic Acids.—These, too, are thermally unstable, and the spectra were obtained by the technique used for the substituted malonic acids.

Oxygen-containing heterocyclic systems have previously been studied by several workers, who have reported the spectra of furan, tetrahydrofuran, 2,5-dimethylfuran, furfuryl alcohol, dibenzofuran,[10] some cyclic ethers,[11] and trioxolane.[12] More recently Collin has published a series of papers upon substituted furans, furan alcohols,[13] and some other oxygen-containing heterocycles.[14] This author comments upon the aromatic nature of the furan nucleus and contrasts it with the behaviour of tetrahydrofuran derivatives, which are not stabilized in this way [15,16] and which in consequence do not possess abundant parent molecular ions. He also shows that his fragmentation patterns are consistent with an initial fission at one of the carbon–oxygen bonds, followed by fission of the bond which is β to the now terminal oxygen. Thus for furan the products would be the $C_3H_3^+$ ion and presumably a formyl radical. The ion with $m/e = 39$ is the base peak of the spectrum. It has been discussed from a theoretical standpoint by Breslaw [17] who suggests that the predictions concerning aromatic-type molecules could be applied to three-membered ring systems containing two electrons. The cyclopropenyl cation, which has also been suggested by McLafferty,[16] could thus have an aromatic character. By using this structure for the $C_3H_3^+$ ion from the decomposition of the furan ion, the fragmentation can be represented as in Scheme 3. The spectra of some furan acids are given in Table 5.

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[9] A.P.I. Research Project 44.

[10] A.P.I. Research Project, 508, 545, 780, 397, 633.

[11] A.P.I. Research Project, 760, 768, 777, 778, 780, and 798.

[12] Friedel and Sharkey, *Analyt. Chem.*, 1956, **28**, 940.

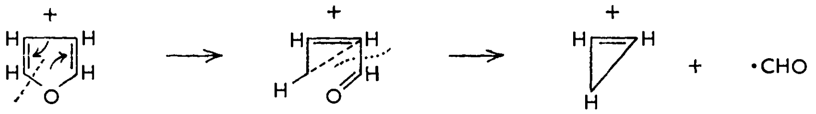
[13] Collin, *Bull. Soc. chim. belges*, 1960, **69**, 575.

[14] *Bull. Soc. chim. belges*, 1960, **69**, 585.

[15] *Bull. Soc. chim. belges*, 1960, **69**, 449.

[16] McLafferty, " Generalised relations of the mass spectra of molecules to the character of their functional groups," and " Driving forces for ion rearrangement processes," A.S.T.M.E.-14 Meeting on Mass Spectrometry, Atlantic City, 1960.

[17] Breslaw, *J. Amer. Chem. Soc.*, 1957, **79**, 5318.



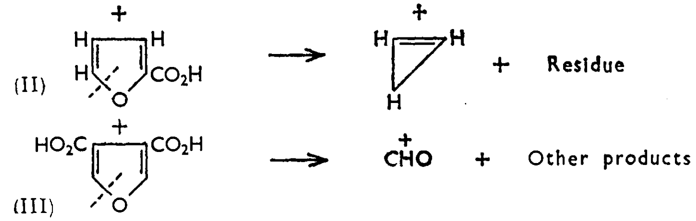
SCHEME 3

All the acids give rise to a parent molecular ion which is abundant in some cases. This suggests that even if thermal decarboxylation occurs under the conditions of experiment it is not complete. The monocarboxylic acids give rise to a base peak at $m/e = 39$ ($C_3H_3^+$) and following the fragmentation described for furan this implies that the carbon–oxygen bond remote from the carboxyl group is the one which is cleaved. The possibility that decarboxylation occurs before or after ring-opening and before the further fragmentation to yield the cyclopropenyl ion may be rejected by a consideration of the symmetrically substituted furandicarboxylic acids. In these there is evidence, provided the mechanisms remains the same, that the base peak, $m/e = 29$, is obtained by the elimination of the formyl ion after the ring-opening of the parent molecular ion. The suggested mechanisms for these four acids are shown for the cases of the 2- and 3,4-substituted furans, (II) and (III). In each case it is possible that the carboxyl group is not eliminated. This would

TABLE 5.

Mass-spectra of some furancarboxylic acids.

m/e	2	3	2,5	3,4	2,3:4,5	2-Me-3,4
25	3·5	4·3	5·1	5·4		
26	9·0	8·0	8·2	10·1	2·9	
27	6·4	10·3	22·1	18·9	11·4	
28	8·8	6·0	8·4	10·8	11·0	
29	47·7	46·3	*100·0*	*100·0*	21·6	
30	2·8	16·1	4·0	6·7	1·8	
31			9·6	16·9	17·3	3·2
32					2·9	
33			1·1		7·4	1·2
36	4·4	6·9	6·5	8·1	2·2	1·3
37	45·0	47·0	55·2	45·2	5·9	7·0
38	51·1	68·5	90·0	60·1	33·1	5·4
39	*100·0*	*100·0*	68·0	45·9	46·4	12·1
40	8·6	8·4	6·2	5·4	4·4	3·6
41	10·3	8·6	6·2	8·1	2·6	6·4
42	6·1	4·4	4·4	5·4	2·9	6·1
43	3·5	3·7	4·0	6·8	3·7	34·1
44	4·8	1·8	5·1	5·4	7·0	6·2
45	62·2	24·1	91·5	82·1	13·2	15·2
46	1·7		3·4	6·8	1·2	
47			2·6		1·8	
48						1·9
49	3·2	3·0	3·4			7·0
50	3·2	3·7	5·1	5·4	2·0	20·4
51	1·7	1·3				31·6
52	1·5	1·6	5·4	4·7		26·6
53	9·5	12·8		33·7	6·9	21·6
54	3·0	1·9	7·6	7·4	3·8	
55	12·2	19·9	30·0	25·7	14·3	7·0
56		4·2	4·5		1·2	
61					1·0	
62					1·2	1·1
64			2·0			
65	1·9	2·8	22·4	16·2	23·6	3·8
66	7·9	15·8	50·0	32·4	38·7	10·8
67	4·9	14·2	11·3	10·8	8·8	7·6
68	2·8	4·1	4·8	6·8	3·6	11·4
69	1·0		3·4	5·4	2·8	8·3
70						1·8
71			4·3	6·8	1·5	1·3
77			1·4	5·4		9·5
78						8·9
79			1·4	8·1		17·8
80					6·1	15·2
81		2·4	1·7		5·2	8·3
82			1·7		3·7	3·2
83	2·5		11·3	11·2	6·3	1·9
84	4·4	3·2	5·9	10·1	5·9	
85						1·4
86						1·0
91		3·5				
92	2·2		1·1	88·0		2·1
93					2·6	
94			2·6	10·8	15·8	
95	36·5	92·5	15·8	21·6	87·5	2·6
96			62·8	37·7	2·2	
97					2·0	
98						36·9
104						3·8
106				8·1		
108				12·8		
109				13·5		
110					1·8	10·2
111					4·8	8·3
112	40·7	58·2P	25·6	74·0	*100·0*	6·5
113					7·8	
114					3·3	
115						3·2
112					1·0	
123					1·6	
126						26·7
137						6·9
139			10·7	39·2	54·0	
140					7·4	1·5
155					9·0	*100·0*
156			9·0(P)	41·2(P)	21·9	
157					4·6	
170						17·7(P)
244					3·3(P)	



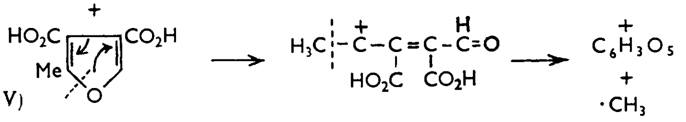
(II)

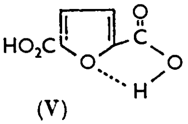
(III)

lead to ions of m/e = 83 and 127, respectively. In no instance is the relevant ion observed and it must be assumed that the elimination is complete.

The 2-methylfuran-3,4-dicarboxylic (IV) acid loses the methyl group to give a base peak of m/e = 155, and thereafter gives no very abundant ion. The presence of the methyl group, therefore, either reduces the likelihood of the breaking of the carbon–oxygen bond or, if this is broken, reduces the possibility of the formation of the cyclopropenyl ion. Since the presence of the carboxyl group appears to strengthen the adjacent carbon–oxygen bond, one may assume that the first bond fission would lead to an open-chain ion which, by electron migration, would lead to a conjugated ion having an allylic methyl group. The methyl group may now be fairly easily elided as it is known that allylically disposed groups in an ion are usually easily eliminated.[18] The remaining tetracarboxylic acid has the base peak at m/e = 112. This represents the loss of 132 mass units, presumably three molecules of carbon dioxide. This may be in part thermal and it is by no means certain which of the original substituents remains. However, the fact that the parent molecular ion is observed in the spectrum is an important demonstration that the present technique of inserting the sample directly into the ionization chamber of the mass spectrometer is successful for determining the molecular weight of even rather unstable compounds.

(IV)

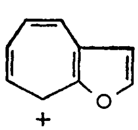




(V)

The loss of a hydroxyl group can also occur, as is shown in Table 5. The position of the carboxyl group obviously affects the ease of elimination, which is most marked in the 3- and 4-substituted furans, and least facile in the 2- and 2,5-substituted furans. This probably correlates with the ability of the acid group to hydrogen-bond to the oxygen of the ring as in (V).

Benzofurans.—Although there is evidently some aromatic character associated with furan and its derivatives, it is nowhere so marked in the furancarboxylic acid series here discussed as in aromatic compounds of the benzene type. Polycyclic hydrocarbons generally have the parent molecular ion as the base peak, and the ion of m/e = 39, when present, is seldom of great abundance.[19] Accordingly, a series of substituted benzofurans have been examined in order to discover if the extended conjugation formed by the added aromatic structure affected the cracking pattern in any way. Spectra of several benzofurans have already been reported, including benzofuran, 2-methyl- and 7-methyl-benzofuran, and also dibenzofuran and 4-methyldibenzofuran.[20] As may be expected, the extended conjugation increases the stability of the parent molecular ion, which is now the base peak in these spectra. Generally the spectra do not possess fragment ions of great abundance and most have a significant ion which corresponds to the doubly-charged parent molecular ion. However, the loss of 28 or 29 units from these compounds is observed. This represents the elimination of carbon monoxide or a formyl radical and is in keeping with the observations on simple furans. A further interesting feature is the loss of a single hydrogen from 7-methylbenzofuran to give an abundant ion, m/e = 131 (49%). A similar loss for toluene led Meyerson and Rylander to suggest that the tropylium ion is formed. By analogy, therefore, the ion formed from this substituted furan may be a tropylium derivative.



(VI)

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[18] Brown and Gillams, A.S.T.M.E.-14 Committee on Mass Spectrometry, New Orleans, 1954.

[19] A.P.I. Research Project 44.

[20] Carnegie Institute of Technology, Manufacturing Chemists Association Research Project Nos. 86, 89, 90, 101, 102.

Study of benzofurans has now been extended to include the 5-nitro-, 2-carboxy-5-nitro-, 5-acetamido-, and 5-acetamido-4-nitro-benzofuran. These contain substituents upon the aromatic ring and indeed their fragmentation patterns closely resemble those of the corresponding benzene compounds. The cracking patterns are reported in Table 6. The compounds containing nitro-substituents lose 30 (NO) and 46 mass units (NO_2). The acetylated amines have a rather facile fragmentation occurring on their grouping which tends to lower the stability of the parent molecular ion so that this is no longer the base peak. The fragments elided include a hydrogen atom, 42 mass units ($CH_2{\cdot}CO$), and, less readily, 71 units. In addition, 28 (CO) and 29 units (HCO) may be eliminated from the furan ring, and the possible combinations of these various occurrences make up much of the observed spectrum.

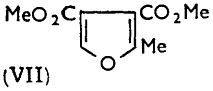
TABLE 6.

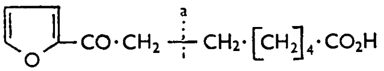
Mass-spectra of substituted benzofurans.

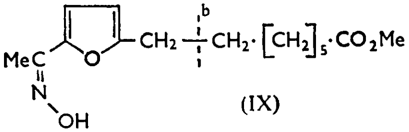
m/e	5-NO_2	5-AcNH	5-AcNH-4-NO_2	2-CO_2H-5-NO_2
27		0·9		
28		2·8	5·0	
29		1·8		0·7
30				1·1
31		3·4	2·4	3·3
32		0·6	0·7	0·8
33		0·9	0·8	1·1
36				0·5
38				0·3
39	5·6	4·2	0·4	1·9
40	1·3	1·1	0·2	
41	2·3	1·6	1·1	
42	2·0	0·7	6·3	
43	5·9	9·1	7·4	1·4
44	6·3	1·3	1·5	3·9
45	2·3	0·6		1·8
49	2·4			
50	2·3			0·7
51	2·1	3·3	0·8	0·5
52	2·2	1·1		0·7
53	2·2	1·0		1·1
55	3·3	2·5	1·5	0·7
56		1·1	0·8	
57	4·0	2·5	2·2	0·7
58		1·1	0·4	
60				0·7
62	5·3	0·4	0·3	3·1
63	26·4	1·0	0·6	7·8
64	2·7	0·3	0·4	0·7
65		0·8	0·6	2·8
66		0·6		0·7
67	1·7	1·1		0·6
68	1·3	0·7	0·5	0·3
69	3·6	2·1	1·2	4·0
70	2·3	1·0	0·6	0·4
71	3·0	1·6	1·1	0·5
75	2·0	0·4	0·5	1·0
76	2·3	1·9	2·4	2·2
77	14·1	7·3	3·7	11·1
78	7·3	5·2	1·1	1·7
79	2·3	2·0	0·4	1·7
80	2·3	1·6	0·9	0·4
81	3·0	2·7		5·3
82	2·0	1·4		0·4
83	2·3	1·4		0·5
84		0·7		
85		1·3	0·7	0·4
86		0·9		
87	2·6	1·7		2·2
88	3·6	0·5		1·3
89	49·8		0·7	17·2
90	5·9	0·5	0·9	1·7
91		1·7	1·1	0·5
92		0·5	5·3	
93		1·5		0·9
94		5·8		
95	2·7	3·4	7·9	0·6
96	1·3	1·0		
97	2·3	1·6	0·7	0·4
98		0·6		
99		0·3		
102		0·8	1·5	0·4
103		3·4	2·2	0·7
104	2·0	13·9	2·7	0·6
105	14·0	8·4	6·9	11·0
106	2·6	2·3	1·5	1·4
107		2·2		2·4
108		1·6		0·4
109		1·8	7·9	0·5
110		1·0		
111	1·7	0·9	0·7	
112		0·7		
115	41·6		0·9	
116			0·9	3·3
117		1·3	2·0	3·7
118	8·6	1·0	1·6	0·6
119	4·4	2·0	1·6	2·1
120		0·9	4·6	
121		1·7	7·9	1·1
122		0·7		
123		0·9		0·4
128		0·7		
129		0·6		
130		0·6	0·4	0·6
131		2·4	2·7	1·4
132		11·3	46·6	1·1
133	19·6	*100·0*	11·8	5·7
134	25·0	21·0	1·5	4·1
135		3·0		0·7
137		0·9		
143				1·3
144		0·9	13·0	3·4
145		2·3	3·6	0·8
146		2·0	1·9	
147		1·0	2·2	0·7
148		1·0	29·8	
149			3·9	4·0
150				0·6
152		1·1		
158		2·1		
159		1·0	1·1	0·7
160		0·9	2·2	2·5
161		0·6	4·8	38·8
162	11·1	0·7	4·9	5·7
163	*100·0*(P)		0·7	7·4
164	13·9			0·7
170		0·5		
171			1·0	
172		0·7	2·0	
173		1·0	2·9	
174		52·1	63·9	
175		10·4(P)	7·6	0·5
176			1·5	0·5
177			1·7	15·4
178			*100·0*	3·5
179			21·4	0·9
188			1·9	
190			0·9	3·9
191				5·7
192				1·0
204			1·1	
205			0·9	
206				7·6
207				*100·0*(P)
208				18·1
220			63·0(P)	
221			13·1	

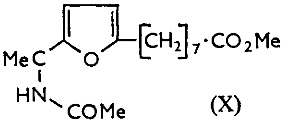
It is of interest to observe that 5-nitrobenzofuran-2-carboxylic acid does not show an abundant ion which might arise by the breaking of one of the carbon–oxygen bonds in the furan ring, and that, in fact, there is little evidence even for the loss of the carboxyl group.

Furan-substituted Acid Derivatives.—A further characteristic of the fragmentation of alkylated aromatic hydrocarbons is the facility of fission of the bond which is β to the aromatic nucleus. It is of interest therefore to compare the cracking patterns of some substituted furans, to see if this property appears there also. Moreover, in order to continue an examination of the technique of sample introduction, some rather elaborate compounds were chosen. The compounds (VII)—(X) were employed and their cracking patterns are contained in Table 7.


(VII)


(VIII)


(IX)


(X)

The main fragmentation in the molecular ion from compound (VII) is the elimination of the methoxyl group from the ester. This is well known to occur in carboxylic esters,[21] and in the present instance is accompanied by the elimination of 43 mass units (CH_3·CO) from the furan ring. Compound (VIII) has a weak spectrum with few abundant ions, the base peak of which occurs at $m/e = 110$ ($C_6H_6O_2$) and probably refers to fission at a. This is in agreement with the known centres of fission of carbonyl compounds [22] in which a β-bond is broken with a concomitant hydrogen shift. A further ion, $m/e = 81$, is probably derived from this fragment ion by the further loss of a formyl group. In compound (IX) the base peak arises from the elimination of a hydroxyl group and the other abundant ion, $m/e = 138$ ($C_7H_8NO_2$), by fragmentation at b.

It is usually the case that an ion with an even number of electrons is more stable than one with an odd number.[23] Thus a fragment ion with an even number and an even mass must contain nitrogen. This is the first reason for assigning the above ion to the known mass. The second reason is that this fission is consistent with the aromatic nature of the furan nucleus, a property obscured in the decomposition of compounds (VII) and (VIII).

The base peak, $m/e = 265$, in compound (X) results in the loss of 44 units (CH_3·CO,H) from the parent molecular ion, and this is assumed to be the loss of the acetyl group with a further hydrogen atom, which is in agreement with the facile loss of acetyl from compounds of this type.[24] The next abundant ion, $m/e = 251$ (44·5%), most likely refers to the removal of the complete group (CH_3·CO·NH).

One must conclude, therefore, that whilst the β-fission, which is the usual mode of fragmentation in the aromatic hydrocarbons, does occur in the furans it is by no means as powerful a driving force.

Complex Furan Compounds.—The spectra of marrubiin (XI), colubin (XII), isocolumbin (XIII), and certain derivatives of the last two are listed in Table 8. All these spectra show many abundant fragment ions which are, however, mainly associated with the bulk of the molecule and are not concerned with the furan nucleus. The loss of the furan group does not seem to occur to any great extent and thus its detection is not easy. Some evidence exists, moreover, to support the view that, when fragmentation does occur, the furan separates with part of the molecule. The particular ion, $m/e = 81$, which is

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[21] Ryhage and Stenhagen, *Arkiv. Kemi*, 1959, **13**, 523.

[22] Beynon, " Mass Spectrometry and its Application to Organic Compounds," Elsevier, London, 1960, p. 354.

[23] Delfosse and Bleakney, *Phys. Rev.*, 1939, **56**, 256.

[24] Clayton, personal communication.

TABLE 7.

Mass-spectra of some furan-substituted acid derivatives.

m/e	(X)	(VIII)	(VII)	(IX)
26			10·2	
27		9·4	22·2	
28		30·7	17·6	16·1
29		10·6	32·4	7·3
30			10·7	1·4
31			16·2	9·8
32		6·7	5·1	4·4
33			2·8	3·7
37			9·3	
38			10·3	
39		20·4	33·3	6·5
40		5·8	10·2	1·9
41	25·5	16·9	19·5	11·1
42	14·1	5·2		6·7
43	56·0	10·3	*100·0*	9·4
44	42·0	7·3	9·3	6·3
45	10·7	6·2	8·3	
46			6·5	
47			3·7	
49			5·5	
50		0·8	22·2	
51		1·9	53·5	2·3
52			38·0	7·2
53	4·7	6·2	46·4	5·4
54	8·9	4·5	8·3	
55	32·0	17·2	7·4	11·2
56	11·4	1·7		2·4
57	20·3	2·4		5·0
58	7·3	3·1		2·7
59	17·8	2·0	40·8	6·1
60	8·7	0·9	17·6	9·6
61		3·1	4·6	
65	3·9		10·2	6·2
66	3·6	2·3	11·1	5·2
67	14·6	2·1	12·9	5·3
68	7·5	7·9	10·2	2·3
69	20·9	7·7	12·9	8·9
70	9·1	1·3		1·9
71	11·6	2·6		3·2
72	4·6			
73	6·4	1·3		9·6
74	21·8			2·2
77	14·2	3·3	10·2	4·1
78			5·5	2·3
79	8·4	4·1	27·8	8·5
80	4·7	1·6	34·3	11·6
81	21·7	10·3	18·5	8·9
82	14·5	5·0	5·4	3·3
83	8·8	3·2	15·7	3·6
84	8·7	1·6		
85	28·1	1·5		
86	10·2	2·1		
87	20·1			
91	9·1	4·2		3·5
92		1·1		
93	10·4	4·1	5·4	8·9
94	10·4	11·3	3·7	8·5
95	18·7	73·0	5·4	6·2
96	11·1	7·0		2·3
97	15·5	4·1		11·6
98	12·9			
99	5·9			2·8
101	4·5			
105	9·6	2·8		2·3
106	5·0	1·2		
107	18·2	3·7	16·6	
108	12·3	2·1	50·0	
109	24·1	2·9	20·4	
110	25·4	*100·0*	7·4	
111	16·8	12·2	10·2	
112	6·8	1·6	2·8	
113	5·5			
114		1·0		
115	4·3	1·0		
117	3·6	1·0		
119	5·2	2·7		3·6
120	4·8	1·2		6·0
121	12·2	3·9		7·6
122	13·2	1·4		14·7
123	18·9	13·8	6·6	8·1
124	20·6	2·3	2·8	
125	12·8			
127	8·4	1·2		
133	8·3	2·7		2·0
134	6·6	1·4		5·8
135	10·9	1·5		5·8
136	9·6			11·5
137	16·6	1·4	25·0	3·9
138			13·9	58·0
139			8·3	12·6
140			3·7	2·3
141	5·5			
145		1·7		
146		1·0		
147	6·8	3·5		
148	4·8	1·6		3·4
149	15·0	1·3		5·1
150	8·0			5·2
151	10·2	1·0		8·1
152	8·3			11·5
153		1·5	7·4	1·9
159	8·7	1·0		
161		1·2		1·6
162	10·2			7·2
163	9·5	1·4		3·5
164	10·4			5·6
165	13·9	1·7		1·7
166	8·2		60·2	
167			72·1	
169	12·0			
173		1·0		
175	3·9	1·0		
176	4·6			1·9
177	16·8	0·8		
178	10·5	1·4		2·9
179	7·1	0·7		1·5
180	4·6			
182	9·1			
185	5·7			
190	4·8			2·4
191	5·7	0·8		1·9
192	9·1	0·7		2·2
193	9·1	0·5		1·9
196	26·0		9·3	
197	5·5		6·5	
198			5·5(P)	
204				7·0
205				2·3
206	12·9	0·8		1·7
207	8·4	0·6		1·6
208		0·7		3·7
209				1·4
211	16·5			
212	5·7			
219	16·8			
220	13·2			
221	10·2			1·2
222				1·7
224		1·7(P)		
225		0·6		
227	17·7			
228	4·6			
232				7·1
233				1·9
234	8·2			1·5
235	4·4			
236	9·1			
237	9·1			
238	5·7			
243	6·6			
246				2·0
248	19·1			6·1
249	24·2			6·0
250	12·3			10·0
251	44·5			
252	11·8			
253	6·2			
262				2·0
264				*100·0*
265	*100·0*			
266	35·0			
267	14·5			
268	6·4			
280	10·0			
281				26·0(P)
282				8·9
294	8·3			
309	32·2(P)			
310	10·9			
311	10·2			
312	7·3			

TABLE 8.

Mass-spectra of: A, marrubiin (XI); B, columbin (XII); C, isocolumbin (XIII); D, decarboxycolumbin; E, decarboxyisocolumbin; F, dihydrocolumbin; G, dihydroisocolumbin; H, octahydrocolumbinic acid methyl ester (XIV); J, octahydroisocolumbinic acid methyl ester (XIV).

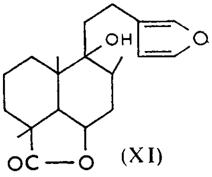
m/e	A	B	C	D	E	F	G	H	J
27		9·5	5·6	18·7		7·3	18·2		
28	35·5	15·8	25·4	30·1	18·8	57·1	75·5		
29	5·9	9·1	8·8	12·1	5·8	16·5	33·6		
30	2·5	1·2					3·7		
31	4·9	7·3	7·7	8·8	12·6	34·5	5·5		
32	6·6			1·8		11·2	46·5		
33	1·8					10·7			
34									
35									
36	1·8								
37		5·2					4·6		
38	1·2	1·4					5·9		
39	4·9	17·5	9·6	38·7	7·8		39·0		
40	2·9	6·0	4·0	13·2		5·1	18·2	56·4	31·6
41	13·3	29·8	26·7	85·5	16·8	19·6	78·0	27·0	33·5
42	6·6	3·5		7·7		7·3	19·1	6·7	7·3
43	19·0	27·0	23·3	35·7	11·4	35·5	54·5	35·8	37·9
44	16·5	62·5	67·0	12·1	7·1	19·6	53·5	27·5	16·5
45		15·1				6·9		7·1	16·0
46									6·3
51				4·4			6·8		4·9
52				2·6			4·1		3·9
53	4·5	8·4	12·2	11·1	7·3	7·9	14·6	9·2	18·7
54	2·9	4·6		6·3			5·9	4·4	6·8
55	16·5	8·1	35·4	33·5	18·0	31·0	59·9	46·0	74·9
56	8·6			3·7		9·0	16·4	7·7	10·2
57	14·9				3·7	20·7	37·0	15·8	21·4
58						14·0	16·0	12·2	17·5
59							3·6	10·7	18·0
60						7·3	2·7		
63							5·5		
65	4·1		8·2	1·8	4·7	6·2		5·1	7·3
66	2·9		6·5	1·8		5·1		4·1	5·8
67	14·9	14·8	18·2	3·4	12·0	16·2	26·4	21·4	36·4
68	5·9	4·7	20·3	2·8	31·2	23·0	11·8	7·7	11·7
69	14·9	10·5	21·0	2·9	14·4	25·8	32·3	27·5	43·2
70	7·4			2·6		6·7	12·7	10·7	17·7
71	10·8	5·6	6·6			15·7	18·2	10·2	14·6
72	2·5							2·6	2·9
73						23·0		3·1	3·9
74								2·6	3·4
76							5·5		
77	5·4	19·2	25·1		15·6	14·6	25·5	10·2	16·5
78	2·5	4·2		3·3			8·2	4·6	6·3
79	11·2	36·5	52·0		36·0	30·8	25·5	32·1	50·5
80	3·3	11·9	16·1	22·0	28·9	11·2	8·2	9·2	14·1
81	62·0	51·0	69·0	4·1	36·0	53·8	41·4	37·2	81·1
82	20·5	22·6	25·0	9·9	13·2	18·5	22·7	16·3	34·0
83	10·6	11·3	6·8	4·1	8·4	16·2	19·1	44·4	72·9
84	7·5	14·5	10·8			7·9	10·0	7·7	12·6
85	5·8	3·8			5·2	11·7	13·6	18·9	37·0
86						14·6	11·8	14·8	21·4
87								9·7	14·1
88								3·6	3·4
89								3·1	2·9
90									1·9
91	11·6	38·0	38·0	6·6	28·2	29·1	35·5	21·9	34·5
92	3·7	11·1	11·9	4·4	8·4	7·9	10·0	6·6	10·7
93	19·8	44·3	40·5	12·5	32·4	36·0	30·0	34·2	58·7
94	22·1	*100·0*	*100·0*	*100·0*	84·0	*100·0*	77·7	41·3	68·4
95	68·5	80·1	44·6	58·0	39·5	66·0	49·0	52·0	*100·0*
96	20·6	11·1	9·5	4·8	11·4	13·4	17·3	*100·0*	55·3
97	13·3	14·8	12·2	4·1		22·5	19·0	29·1	32·0
98	5·8							18·9	9·2
99	8·3							10·7	8·7
100		6·0						3·6	5·0
101								3·6	5·8
102								2·0	1·9
103		5·2		3·4	6·1		5·9	3·6	4·4
104		3·4					9·2	3·1	3·4
105	14·0	32·5	16·8	5·9	33·0	31·5	30·0	25·0	38·3
106	7·4	15·4	14·3	3·4	14·4	14·0	10·9	11·7	15·0
107	28·1	41·4	4·6	5·3	52·1	49·2	18·2	43·4	74·8
108	24·5	26·0	58·5	3·8	60·1	43·2	16·4	19·9	40·3
109		36·5	77·0	7·0	83·5	66·0	21·9	28·1	47·6
110	18·5	8·1	23·0	2·6	29·4	21·7	14·6	16·3	43·2
111	17·3					14·5	10·9	11·7	18·4
112		5·4	18·2					3·6	5·3
113								3·5	4·9
114							7·3	9·2	13·6
115		2·7	5·1	3·7	9·0		11·4	7·7	10·2
116		7·0	3·5	2·6			6·4	4·1	4·9
117		6·0	9·6	6·6	15·6		12·7	7·7	10·7
118		5·7	6·0	6·3	10·8		5·9	5·1	6·8
119	18·1	7·6	37·3	15·8	37·2	33·5	38·0	24·5	37·9
120	5·7	3·2	12·2	7·4	20·4	13·4	14·5	10·2	17·0
121	33·0	40·5	64·5	23·5	*100·0*	65·1	33·6	29·6	55·3
122	14·8	9·5	23·0	5·5	27·6	15·7	11·8	10·7	19·4
123	44·7	3·5	8·2	3·7	11·4	16·2	12·7	25·0	47·3
124	14·0	2·7					11·8	13·8	29·6
125	9·8	1·6				10·7	19·1	14·8	24·8
126							11·4	7·1	12·1
127		2·7			7·2		24·0	7·7	10·7
128		2·4			7·2		31·8	5·6	7·3
129		2·6	5·6	5·9	9·0		44·5	6·1	8·3
130			3·5	4·1			18·2	3·6	4·4
131	7·8	6·1	16·9	22·7	22·7	17·9	52·0	10·2	19·4
132	4·1	3·5	8·8	7·0	11·4	11·2	25·5	6·6	9·7
133	14·5	8·7	32·5	23·5	44·5	36·0	73·0	42·1	47·6
134	31·4	5·7	17·7	9·6	23·4	17·9	26·4	13·3	18·4
135	77·5		13·6	5·2	28·8	22·9	25·5	21·9	36·9
136	39·0		4·6	2·9	10·8		7·7	10·2	14·1
137	25·0	7·6	5·1			12·9	10·7	15·3	25·2
138			3·7		6·6			9·7	14·6
139	15·7							8·2	12·1
140								3·6	5·3
141		2·3					6·4	4·1	5·3
142		1·9						3·6	4·9
143		2·6	4·5	4·1	7·2			6·6	9·2
144								4·1	5·3
145		5·0	11·9	6·3	15·1	17·4	14·5	13·8	20·9
146			6·5	6·3		6·7	9·1	6·1	8·7
147	14·0	9·6	25·5	19·8	24·6	28·5	32·7	19·4	33·0
148	6·6	5·3	15·0	13·2	16·8	16·2	17·3	8·2	13·6
149	39·0	37·1	6·8	4·1	13·2	15·1	10·9	14·3	25·7
150	39·0		3·5				4·6	7·1	12·1
151	25·0		3·0			10·1		11·7	17·0
152	79·5	6·8	7·7		9·6	17·3	15·0	6·1	8·7
153	17·4	7·8	16·8			20·7		6·6	9·7
154								4·1	6·8
155								4·1	5·8
156								3·1	3·9
157								16·3	25·2
158			2·6					6·1	11·2
159	7·3	8·1	8·8	2·2	12·6	19·6	12·3	18·4	35·4
160		4·9	12·6	8·1	21·6	15·7	9·1	6·6	13·1
161	9·2	16·0	14·0	8·5	25·3	22·4	11·8	19·9	37·4
162		6·7	3·5	2·9			7·3	7·7	13·1
163	49·9		3·7			11·8	16·8	15·3	25·2
164	20·5		3·5					7·1	13·1
165	49·5		2·5					10·7	18·0
166			4·6		9·0			9·7	16·0
167								11·2	23·3
168								4·8	8·3
169								3·6	6·8
170								2·0	3·9
171		2·4	3·9			9·0	7·3	4·6	8·7
172		3·4						2·6	4·9
173	17·8	3·6	5·9		7·8	13·4	12·7	8·7	14·6
174	7·4						9·1	4·1	6·8
175	18·6		5·6		9·4	12·9	10·5	32·1	30·6
176	13·2	3·9	4·6		9·6		7·3	6·6	12·6
177	33·0	7·3	3·7	4·8	6·2		8·2	13·3	22·8
178	11·2	7·8	3·3			14·5	6·4	6·6	11·2
179	6·6	7·0	2·8				8·2	8·2	15·5
180	13·1							5·1	9·1
181	22·1	4·7						5·6	14·7
182								3·1	6·8
183			3·7				5·9	3·6	6·3
184								2·0	4·9
185			3·1	7·0	5·2		5·5	7·1	10·2
186			2·5	6·3				4·1	6·3
187			5·4		7·4		6·4	11·2	16·5
188			10·2		14·4			5·6	8·7
189	20·0	3·5	7·0		11·1	13·4	5·5	10·7	17·0
190	34·0		3·9		7·9	16·5		5·1	7·8
191	32·5		6·3	3·7	8·9	20·3	9·6	9·2	14·1
192	7·3				6·5			6·1	8·7
193								46·4	46·6
194								19·9	26·2
195								9·2	13·1
196								5·1	7·8
197								6·1	8·3
198								5·1	8·7
199								8·2	11·7
200								3·6	6·8
201				11·0				6·1	10·2
202					6·2			4·1	5·3
203		3·0		16·5	6·1	15·7	7·3	32·6	29·6
204		7·8	8·1	5·3	10·8	17·9	5·9	12·2	31·6
205	10·6	3·8	11·5	4·4	26·4	24·7		12·8	19·9
206			4·7		10·8	10·1		8·7	12·1

TABLE 8. (*Continued.*)

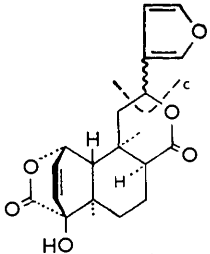
m/e	A	B	C	D	E	F	G	H	J
207								14·8	35·4
208							7·7	7·7	19·4
209	20·1							12·8	26·7
210	18·2							5·1	10·7
211								4·1	8·3
212								2·6	4·9
213								4·6	7·8
214								3·1	6·3
215								6·1	9·2
216								5·1	5·3
217								19·9	25·2
218					6·4			8·2	11·7
219	14·5			17·7	5·0			11·2	17·0
220	20·5	3·0		3·7	4·9			9·2	13·6
221	7·4							25·6	37·4
222							7·7	17·3	43·2
223								10·2	22·8
224								5·6	8·7
225								3·6	6·8
226								3·1	3·9
227								3·6	4·9
228								5·6	4·9
229								6·6	6·8
230								4·6	4·9
231		15·1			5·4	8·4		14·8	16·5
232					4·4			16·3	35·9
233								14·2	17·0
234								8·7	10·7
235								35·2	46·1
236							15·2	12·8	19·9
237	9·9						5·9	6·6	10·7
238								3·8	4·9
239			2·4					3·6	4·9
240								2·6	2·9
241								3·1	4·4
242								3·1	3·9
243								3·6	5·8
244								3·1	3·6
245		4·9	3·7	3·7				21·4	16·0
246	5·8	2·4	2·4		4·6			14·8	15·5
247						7·7	5·9	16·8	16·0
248								13·8	13·1
249							10·5	64·8	85·0
250								20·9	35·4
251								7·7	14·1
252		1·6	2·8	4·1	5·4			3·6	5·3
253		1·9		3·7	6·6			4·6	13·6
254								3·1	7·8
255								2·6	5·8
256								3·6	5·3
257		3·8						6·1	8·9
258		6·0						4·1	5·8
259		6·8				9·5		6·1	8·7
260		3·5						17·3	21·8
261		3·0						12·2	15·5
262			1·6					7·1	8·7
263								40·8	20·9
264								14·8	11·7
265								6·1	6·8
266								4·1	4·4
267								10·7	26·2
268		2·2		5·2	5·0			4·6	9·2
269			1·8	3·8	5·5			3·6	4·4
270			1·8		4·1			2·0	2·9
271		1·6		4·4	3·8			2·0	3·4
272						8·4	6·8	2·0	2·9
273							5·5	3·6	7·8
274								9·7	18·4
275		6·5						8·7	15·0
276		3·5						8·0	9·7
277								8·7	11·2
278								5·6	8·3
279			3·7				5·5	32·1	8·3
280								10·2	4·9
281			2·9					45·4	21·8
282								14·8	39·3
283								4·6	13·1
284								6·6	9·2
285								5·1	7·3
286		8·5		11·4	6·0			4·6	6·3
287				4·4				4·6	6·3
288								3·1	9·2
289								3·1	6·8
290								3·1	5·8
291								4·6	7·3
292								29·1	43·2
293								12·8	20·4
294								5·1	9·2
295		4·7	1·6					4·1	7·3
296				8·6	4·0			3·1	5·9
297				2·9				3·1	4·4
298			1·7						3·4
299				2·6	5·8				3·9
300									3·4
301							7·3	3·1	3·9
302								9·0	19·4
303								7·7	18·4
304								4·6	9·2
305								5·1	7·3
306								9·7	21·4
307								4·1	8·3
308								2·6	4·9
309								2·6	3·4
310			1·6						2·4
311						22·4			2·4
312						9·0		4·6	5·3
313		12·2	17·5						4·4
314			5·6	29·5(P)	50·5	21·8	12·7		2·4
315				9·6	14·4	8·4	6·4		4·9
316					4·0		9·6	5·1	18·4
317							9·2	3·1	10·7
318								5·1	12·1
319								8·2	18·4
320								20·4	36·0
321								16·8	25·2
322								6·1	8·7
323								3·1	4·4
324								2·6	3·9
329								3·1	3·9
330								7·7	14·1
331								6·6	6·8
332						6·7	23·6	3·6	3·4
333							8·7	5·6	7·3
334								10·2	10·2
335								4·9	5·8
336								2·6	3·4
337								2·6	4·9
338							4·6		2·9
342						3·9	9·1		
343		0·7					5·5		
344								16·8	11·2
345						3·4		7·1	8·3
346								3·9	5·3
347								4·6	5·8
348								50·0	91·3
349								27·5	40·8
350								9·7	13·1
351								3·6	
352								5·6	19·4
353									7·8
358		1·35(P)	4·2(P)						2·4
360						28·6(P)	*100·0*(P)		
361						8·4	30·1		
362								5·1	11·2
363								3·1	5·8
364								2·0	
365								3·6	
376									5·0
380								60·7(P)	93·7(P)
381								23·5	39·8

abundant in the spectra of columbin, isocolumbin, and the dihydro-derivatives, as well as the ion, *m/e* = 85, which is of some prominence in the methyl esters of octahydrocolumbinic and octahydroisocolumbinic acids (XIV), almost certainly arises by fission as at c in (XII).

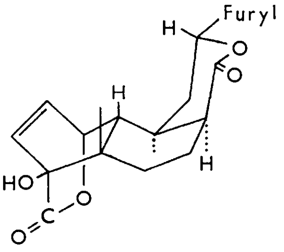
It is also of interest to compare the stability of the parent molecular ions in the columbin and isocolumbin series as a percentage of the total ion current (εI) present in each spectrum. Since the corresponding members of each series are epimers, the molecular crowding in one of them will be greater than in the other. Following the observations of Biemann and Seibl,[25] who correlated the abundance of the parent molecular ion with molecular configuration, it is here assumed that the least crowded epimer will have the more abundant parent ion.

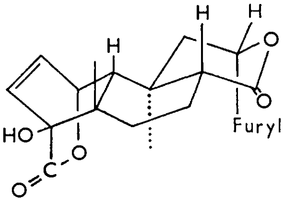


(XI)
Marrubiin

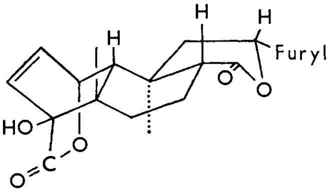


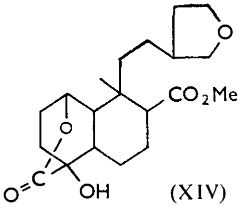
(XII)
Columbin





(XIII) Isocolumbin





(XIV)

Such a study amongst the present compounds supports the view that the isocolumbin series contains the less-crowded epimers, which is in agreement with the structures

TABLE 9.

Total ion current (ΣI) and stability of parent moleular ions.

Compound	B	C	D	E	F	G	H	J
ΣI	1317·0	1563·0	1018·8	1654·8	1926·9	2438·2	3301·5	4906·9
Parent (P)	1·35	4·20	29·5	50·5	28·6	100·0	60·7	93·7
$(P/\Sigma I) \times 100$	0·10	0·27	2·89	3·05	1·41	4·10	1·84	1·90

suggested by Overton, Weir, and Wylie.[26] The apparent exception, the similarity between the ratio observed in octahydrocolumbinic acid methyl ester and its isomer, is evidently related to the opening of the lactone ring in these molecules and the difference in crowding between the two epimers then disappears.

Experimental.—These experiments were carried out on a Metropolitan Vickers Ltd. M.S.2. mass spectrometer. The sample was introduced directly into the ion chamber, without vaporization, by a method already described.[27] The spectra were recorded on a N.E.P. 1050 ultra-violet recorder.

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