STUDIES ON THE ELECTRON IMPACT INDUCED DISSOCIATION OF SOME ORGANIC COMPOUNDS.

Thesis presented for the degree
of Doctor of Philosophy
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by

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C O N T E N T S

A C K N O W L E D G M E N T S.

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S U M M A R Y.

The work discussed in the thesis can be considered in three separate sections:

Part I: The Mass Spectra of some Diaryl Ethers.

Part II: The Mass Spectra of some Naturally Occurring Phenolic Compounds.

Part III: The Mass Spectra of some Carbohydrate Derivatives.

Part I:

The ethers used in this section are compounds containing fused aromatic rings and homologues of diphenyl ether with methyl substituents on the aromatic nuclei. The spectra of these compounds have been compared with that of diphenyl ether. The degradation of diphenyl ether by loss of carbon monoxide has been noted previously and the extent to which the corresponding reaction takes place in other ethers has been correlated with the structures of these compounds. Other correlations have been made in an attempt to explain the presence of rearranged ions which appear in the ortho-methyl ether spectra.

Part II:

Some derivatives of tubaic acid were investigated. It was found that mass spectrometric methods can identify or help to identify the isoprenoid groups present in such molecules. This was confirmed by an examination of the rotenoids. The

2:3-dihydroxyrotenoids can be easily identified by their mass spectra. Two examples are given of the partial determination of the structure of compounds of this class. An analysis has been made of the spectra of some flavonoid compounds.

Part III:

A preliminary examination has been made of the mass spectra of some glycosides and sugar alcohols. Correlations have been made between spectra and structures in each case. Differences in the spectra of two methyl glycosides have been related to differences in the stereochemistry of the compounds. The spectra of all the isomeric inositols are recorded. Proposals have been made for the mechanism of degradation of these compounds.

P A R T I.

The Mass Spectra of some Diaryl Ethers.

Introduction:

The behaviour on electron impact of a wide variety of organic compounds has been reported. Of these the n- paraffins have the simplest structure. An examination of the mass spectra of these compounds will demonstrate the difficulties involved in correlations of spectra and structures.

Viallard and Magat [1] reported the mass spectra of some n- paraffins. They showed that as the molecular weight increases, the number of fragments due solely to cleavage at carbon-hydrogen bonds decreases. The extent of this decrease (from 84% of all fragment ions in ethane to 0.008% in n-octane) shows that fragmentation is determined to some extent by the strength of the bond broken. Bond strength alone does not entirely control the process as can be seen by an examination of the mass spectrum of n-eicosane (Fig.1).

The intense ions in the spectrum are mostly of the type $C_nH_{2n+1}^+$ and these could be produced by simple carbon-carbon bond fission. The relative intensities of ions of varying carbon number are, however, more difficult to explain. In the most recent work on this subject, Beynon and his collaborators[2] have shown that the prominent ions in the

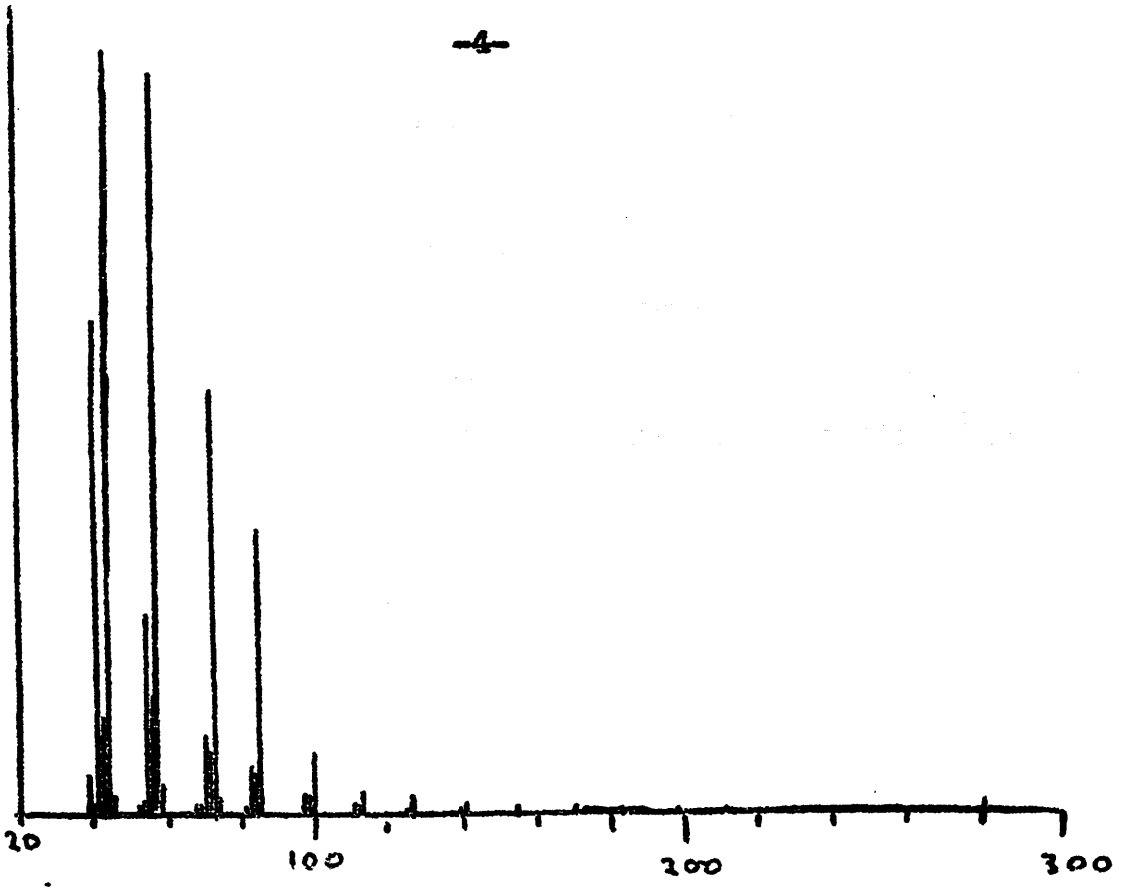


Fig. I.

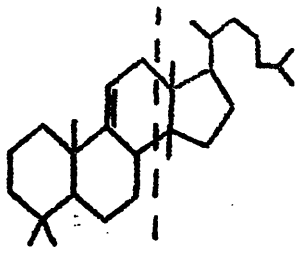
spectrum cannot be produced by simple carbon-carbon bond fission: they postulate a cyclic intermediate. The quasi-equilibrium theory of Eyring, Rosenstock and Wahrhaftig[10] has been used to calculate the mass spectra of small molecules. The method is too complex to be employed with the larger molecules which are of interest to the organic chemist. It has therefore been found that empirical and semi-empirical correlations are of value in the study of mass spectra and this has been the subject of two comprehensive reviews.[3,4].

It will be noticed in the spectrum of n-eicosane that all the prominent ions have an odd mass number. This is

consistent with the observation that ions having an even number of electrons are more stable than those having an odd number[5]. The general nature of the mass spectrum of n-eicosane is typical of the n-paraffin spectra.

Branched hydrocarbons show distinct differences. In a study of the octanes Mohler and his collaborators[6] have shown that the branched octanes have less abundant molecular ions. Compounds with quaternary centres usually have extremely small molecular ions. Fragmentation takes place predominantly at branch centres.

Acyclic olefins present difficulties in interpretation which probably arise from rearrangements. Four of the five isomeric pentenes have very similar spectra[3]. Cyclic olefins, however, fragment in a more predictable manner. Reed[7] has shown that lanost-9(11)-ene fragments in the following manner, i.e. cleavage takes place at the allylic bonds:-

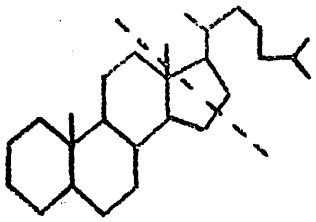


$\longrightarrow$ $C_{15}H_{28}^{+}$ $\frac{m}{e} = 208$ + neutral product

$C_{15}H_{24}^{+}$ $\frac{m}{e} = 204$ + neutral product

The presence of an alicyclic ring in a molecule can confer great stability on the molecular ion. Beynon[8] finds that a

compound having an intense molecular ion will probably contain a ring system, although the reverse does not necessarily hold true. In the spectra of ethylcyclopentane and ethylcyclohexane[9] the most abundant ions are the unsubstituted cycloalkyl ions. This behaviour is typical of monosubstituted cycloalkanes. More complicated cyclic systems do not necessarily follow this rule. In the steroids[7,11] one of the most common processes involves the loss of the side chain and a C_3 fragment. Friedland and his collaborators suggest that the fragmentation is of the form:-



$\longrightarrow$ $C_{16}H_{25}^{+}$ $\frac{m}{e} = 217$

in cholestane.

The introduction of atoms other than carbon and hydrogen raises the problem of assigning formulae to ions of a given nominal mass. The most common hetero atoms in organic chemistry are oxygen and nitrogen and the presence of isobaric doublets such as O : CH_4 and N : CH_2 does cause difficulties. The first method used to tackle this problem was the use of compounds specifically labelled with stable isotopes, the most common being ^{13}C, ^{15}N, ^{18}O and D. The method has been

successful in several cases, but the work involved in preparing labelled compounds is considerable. The use of the high resolution mass spectrometer has superceded the labelling method to some extent. Beynon[12] has described the use of a double-focussing mass spectrometer for the resolution of ions with the same nominal mass but different packing fractions. High resolution mass spectra have been obtained for some esters[13] and cyclic ketones[14]. In these two cases difficulty in interpretation is due to the presence of the doublet CH_4:O which involves a mass difference of 36.39×10^{-3} mass units. Therefore at $\frac{m}{e} = 100$,

$$\frac{\Delta M}{M} = 36.39 \times 10^{-5}$$

Resolution of this order is outside the scope of a conventional single-focussing mass spectrometer, but quite possible with a double-focussing instrument.

There are two main difficulties in the study of the mass spectra of alcohols. The first is the ease of thermal degradation in the inlet system before the molecule reaches the ionization chamber. With alcohols of high molecular weight this can be avoided by using a suitably volatile derivative of the alcohol. Trimethylsilyl ethers have been used very effectively[13]. Because of their greater volatility the inlet system can be used at a lower temperature than that

required for the corresponding alcohols. Trimethylsilyl ethers do not have a significant parent molecular ion $(P)^+$ but there is always an abundant $(P-15)^+$ ion. Formates[4] can also be used as derivatives of alcohols for mass spectrometry. In the spectra of the alcohols there is often a $(P-18)^+$ ion. Water is probably formed as the neutral fragment. The $(P-18)^+$ ion appears to fragment in a similar manner to the corresponding olefin. Cyclic alcohols usually have significant molecular ions. In most of these cases the $(P-18)^+$ ion is abundant, as can be seen in the mass spectra of some sterols[11]. Biemann and Seibl[14] have examined some naturally occurring epimeric alcohols, and find that the more crowded epimer has the more abundant $(P-18)^+$ ion.

In the spectra of oxygenated compounds there are often found ions which cannot be produced by simple bond fission. The presence of these can only be explained by invoking a mechanism involving formation of new bonds. McLafferty[15] considers such rearrangements to be of two main types: random and specific. The former involves random migration of various groups within the ion. This is most commonly observed as the migration of hydrogen and deuterium atoms within hydrocarbon ions. A family of ions, generally of low abundance is usually produced.

Specific rearrangements produce ions of greater abundance. The driving force for their formation is usually either a low-energy degradation route or the production of very stable intermediates and fragments. This type of ion is found most often in polar compounds, especially oxygen and nitrogen containing compounds.

Specific rearrangements are classified into five main types, according to whether the ions and neutral products concerned contain an odd (O.E.) or even (E.E.) number of electrons.

A. O.E. ion $\longrightarrow$ O.E. ion + E.E. molecule
(single rearrangement).

B. O.E. ion $\longrightarrow$ E.E. ion + O.E. radical
(double rearrangement).

C. cyclic O.E. ion $\longrightarrow$ E.E. ion + O.E. radical
(single rearrangement).

D. E.E. ion $\longrightarrow$ E.E. ion + E.E. molecule
(single rearrangement).

E. Ion $\longrightarrow$ E.E. ion + E.E. molecule + other products.
(multiple rearrangements and fissions).

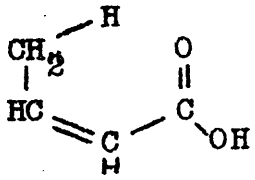
Of these the most easily recognised are the first group, since they are possible in the degradation of a molecular ion. A most common example of such a rearrangement is found in the spectra of aliphatic carbonyl compounds. It takes the form:

$$R - \overset{+}{C}O - CH_2.CH_2.CH_2R' \longrightarrow R\,C_2H_3O^+ + C_2H_3R' .$$

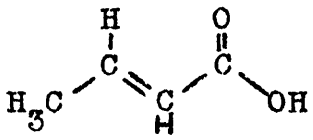
and is found in the spectra of aldehydes[16], ketones[17], amides[18], carboxylic acids(19) and esters(20).

It is considered that such a rearrangement takes place by means of a sterically favourable intermediate, e.g. in the case of n-butyraldehyde:

There is considerable evidence for the above mechanism. A similar double rearrangement is found in the isocrotonic acid spectrum with formation of an ion of $\frac{m}{e} = 60$. It is not found, however, in the spectrum of crotonic acid,



Isocrotonic Acid.



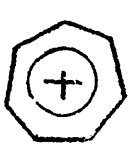
Crotonic Acid.

where a six-membered ring transition state is not possible. This type of rearrangement does not occur when there is no hydrogen atom γ to the carbonyl group, e.g. it is found in the n-butyric acid spectrum but not in the propionic acid spectrum. The structure proposed for the ion produced is not unlikely, since there is evidence[21] that such ions are present in the enol form.

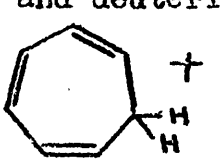
Purely aromatic compounds produce very simple mass spectra[22,23]. Benzene can lose C_2 fragments, resulting in the production of ions of $\frac{m}{e}$ = 52, 51 and 50. Almost half

the ionization produced consists of the molecular ion and doubly charged ions; the proportion of these in the spectrum increases as more fused rings are added. The loss of a C_2 fragment is still significant and the intensity of the ion $(P-26)^+$ has been used diagnostically by Reed[23] and treated theoretically by Lester[24]. Reed also noted the ready loss of two hydrogen atoms from the molecular ion in some cases.

Aromatic hydrocarbons with saturated substituents do not behave as the corresponding alicyclic compounds. The spectra of toluene, ethylbenzene and the xylenes all have the most intense ion at $\frac{m}{e} = 91$. The most obvious explanation is that of benzylic bond fission to give a resonance-stabilised benzyl ion, in the case of the first two compounds. The phenomenon is not so easily explained in the case of the xylenes. Meyerson and Rylander [25] have demonstrated that in the ion of $\frac{m}{e} = 91$, all the hydrogen atoms are equivalent and it must therefore be the tropylium ion (I). It has also been shown[25a.] that the hydrogen and deuterium atoms in the



I

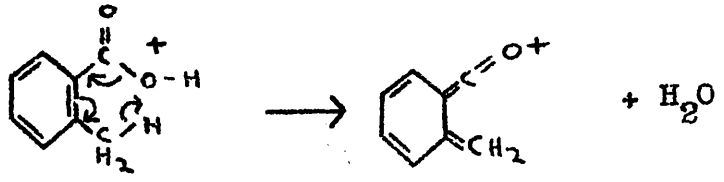


II

benzyl and α-$\underline{d}_2$-benzyl radicals are completely randomised on ionization.[26] In the formation of the tropylium ion from deuterated toluenes[25] the hydrogen atom lost from the molecular ion does not necessarily originate from the

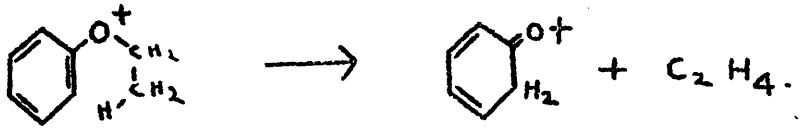
methyl group. This suggests that the molecular ion is involved in a skeletal rearrangement to the cycloheptatriene ion (II).

McLafferty[27] has reported the loss of water from aromatic carboxylic acids with α-hydrogen atoms in the ortho position. This would appear to be a specific rearrangement of type A[15] and the molecular geometry is suitable for a cyclic transition state, e.g. for o-toluic acid.



$\frac{m}{e}$ = 136 $\frac{m}{e}$ = 118

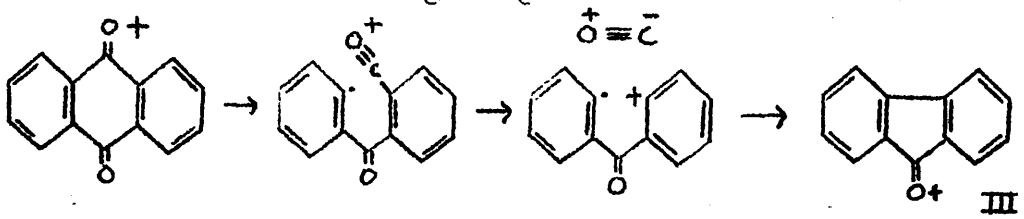
Similar behaviour was found in esters of salicylic acid[53]. The most abundant ion in the mass spectrum of phenetole has $\frac{m}{e}$ = 94. It is considered[28] to be formed by the following process which is similar to the behavious of vinyl ethers. The ion produced will probably rearrange to a completely conjugated form, e.g. phenol.



$\frac{m}{e}$ = 122 $\frac{m}{e}$ = 94

Some of the most interesting rearrangements of aromatic molecular ions have been reported by Beynon, Lester and Williams[29]. The compounds studied are phenol, anthraquinone and diphenyl ether. The process common to all three is the

elimination of carbon monoxide from the molecular ion. In the case of anthraquinone this could be considered as the simple fission of two bonds, but since a second molecule of carbon monoxide can be removed bond formation must be taking place. The mechanism proposed for the first loss of carbon monoxide is as follows giving a fluorene ion III. A similar



III

process will be involved in the further elimination of carbon monoxide from III. The ion produced will be the biphenylene ion. With the exception of its molecular ion, the mass spectrum of anthraquinone is very similar to that of fluorene.

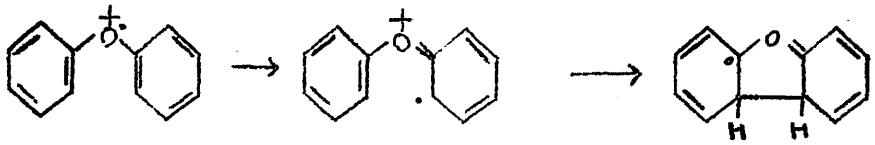
It is considered that phenol may rearrange to the cyclohexadienone form before losing carbon monoxide. If it does not do so, the expected fragment ion would be at $\frac{m}{e}$ = 65 with the loss of a formyl radical. This does occur but the $(P - CO)^+$ ion is the most intense fragment ion in the spectrum. Analogous to this is the behaviour of the mono-hydroxyanthraquinones[30]. In the spectra of these compounds there are the typical intense ions at $\frac{m}{e}$ = 224 (P), 196 (P-CO) and 168 (P-2CO) as found in anthraquinone. There is a further intense ion at $\frac{m}{e}$ = 139 with a corresponding doubly charged ion at $\frac{m}{e}$ = 69.5, which arises as follows:-

$$\underset{\frac{m}{e} = 168}{C_{12}H_8O^+} \longrightarrow \underset{\frac{m}{e} = 139}{C_{11}H_7^+} + CHO^{\cdot}$$

There is also an ion at $\frac{m}{e}$ = 140 which is produced by loss of three molecules of carbon monoxide from the molecular ion. This tendency is continued in the dihydroxy-anthraquinones where an ion of $\frac{m}{e}$ = 128 appears which can only be derived by loss of four molecules of carbon monoxide from the parent molecular ion. The authors note that the formula of this ion, $C_{10}H_8^+$, is the same as that of naphthalene, but one can only speculate as to the structure.

One of the main driving forces of this type of rearrangement appears to be the stability of the carbon monoxide molecule. Analogies can be found in the spectra of other aromatic compounds, e.g. the elimination of acetylene from hydrocarbons[23,24]. Nitrogen compounds behave similarly. The loss of HCN from indole derivatives and of both HCN and NO from nitroanilines[29] have been reported.

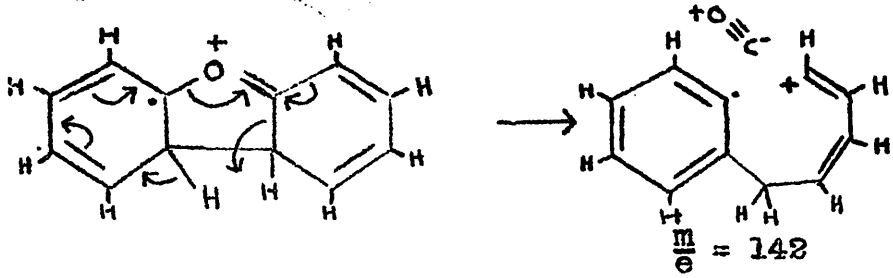
Beynon, Lester and Williams[29] also showed that diphenyl ether eliminated a molecule of carbon monoxide. This was confirmed by an accurate mass measurement of the ion of $\frac{m}{e}$ = 142. The following mechanism was proposed:-



IV V

IV is merely a mesomeric form of the molecular ion and the geometry of the molecule is such that a bond can easily be

formed between the two ortho positions. V can lose carbon monoxide by a series of electron shifts and a hydrogen migration. These are not necessarily concerted as shown.



$\frac{m}{e}$ = 142

The radical ion of $\frac{m}{e}$ = 142 can readily cyclise to the benzcycloheptatriene ion. The more abundant ion at $\frac{m}{e}$ = 141 may be formed in two ways: by loss of a hydrogen atom from $\frac{m}{e}$ = 142 or by elimination of a formyl radical from the molecular ion.

A series of diaryl ethers of higher molecular weight have been prepared and mass spectra have been obtained. The object of this study is to determine whether or not this rearrangement is common to diaryl ethers, and if its occurrence is compatible with the above mechanism. Attempts have been made to correlate the structures of these ethers with the cracking patterns obtained.

Experimental:

The mass spectra of the diaryl ethers were obtained using a Metropolitan Vickers Ltd., M.S.2 Mass Spectrometer employing an accelerating voltage of 2 KV and magnetic scanning. All spectra are run at an ionising voltage of 50 eV.

Diphenyl, α-naphthyl phenyl, β-naphthyl phenyl, $\alpha:\alpha'$-dinaphthyl, $\beta:\beta'$-dinaphthyl, $\alpha:\beta'$-dinaphthyl, 9-phenanthryl phenyl and 9:9'-diphenanthryl ethers, o-phenoxybiphenyl and p-phenoxybiphenyl were introduced directly into the vaccuum system and allowed to evaporate continuously. The sample was introduced packed in the hollow at the end of a glass or copper rod which was inserted behind the ion source and sealed off with a screw cap and lead gasket. Reed and de Mayo[32] used a similar technique, but in this case no external heating was used. Reproducible spectra were obtained but since the compounds were polar there were pronounced "memory effects" which could not be quickly eradicated

For the other ether samples, some of which were liquid and not easily amenable to the above method, a heated inlet system was constructed (Fig. II). The samples are contained in small glass tubes and introduced at G while tap D is closed and tap C is in the position shown. Air is removed by opening tap D while the sample tube sits inside tap C. Tap C is then turned until the tube falls into the heated reservoir A, where the sample volatilises and is introduced

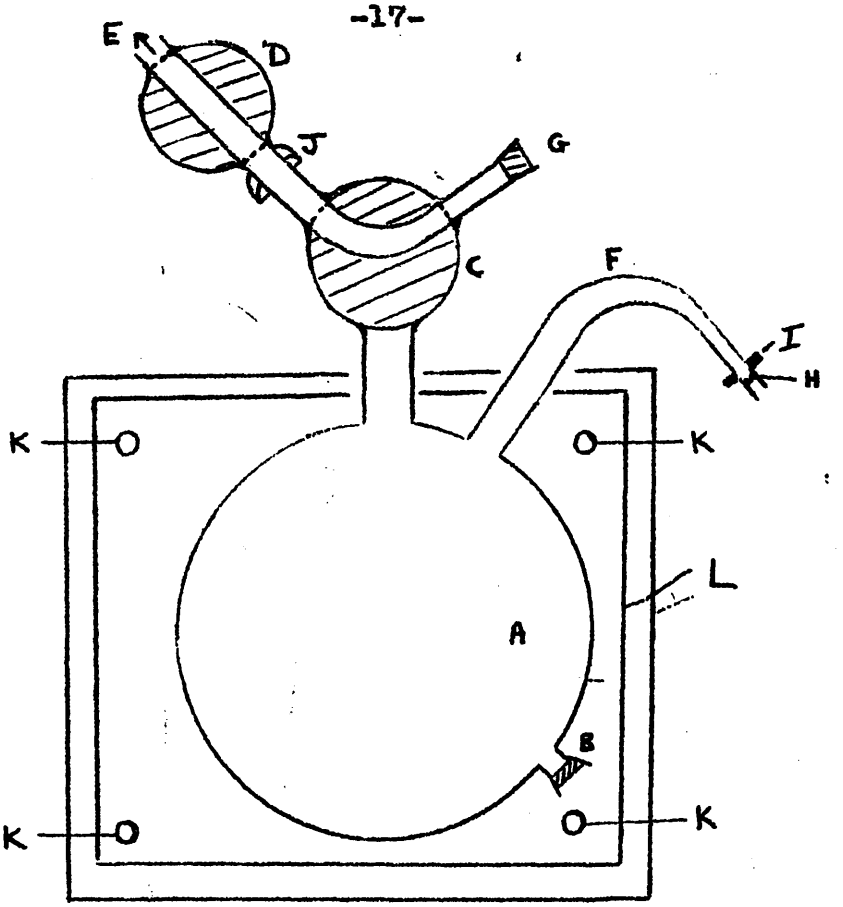


FIG. II.

A. 1 Litre spherical flask.
B. Outlet for removing used sample tubes.
C. 3-Way tap.
D. Open/close tap.
E. Outlet to second pumping system.
F. Heated and lagged copper tube.
G. Inlet for samples.
H. Leak.
I. Lead gasket.
J. Glass ball/socket joint.
K. Heating coils for hot air bath.
L. Insulated double jacket for hot air bath.

into the ion source through the sinter H. To remove the sample, the reservoir is opened to the second pumping system through taps C and D.

The reservoir is kept in an air bath heated by coils K. The copper tube F is directly heated by a winding. The temperature of the system is shown by a thermometer inside the air bath and a thermocouple on the tube F. The only possible "cold spot" is the tap C. This was so designed to make it possible to use lubricated taps. Edwards Silicone Grease was used. This was found to give no appreciable spectrum below 250°C. "Memory effects" were negligible.

The diphenyl ether used was commercial grade purified by crystallisation. α-naphthyl phenyl, β-naphthyl phenyl, $\alpha:\alpha'$-dinaphthyl, $\alpha:\beta'$-dinaphthyl[33], $\beta:\beta'$-dinaphthyl[34], 9-phenanthryl phenyl[35] and 9:9'-diphenanthryl[36] ethers were prepared by known methods. The phenoxybiphenyls were prepared by an adaptation of a known method[37].

p-phenoxybiphenyl: To a solution of 4.5 gm. sodium methoxide in 90 ml. methanol was added 14.2 gm. p-hydroxybiphenyl and 6.0 gm. diphenyliodonium bromide[38]. After the mixture had been refluxed for 24 hrs. the ether-soluble product was collected and distilled under reduced pressure. The solid distillate, recrystallised from benzene gave 1.37 gm. (48%) p-phenoxybiphenyl, m.pt. 136°C.

o-phenoxybiphenyl: The same method was used as above but light petroleum, b.pt. 60°-80°, was used to recrystallise the ether. This gave 0.91 gm. o-phenoxybiphenyl (35%) m.pt. 37°C.

The samples of the phenyl tolyl ethers, phenyl 2-m-xylyl, di-o-tolyl, o-tolyl 2-m-xylyl and di-2-m-xylyl ethers were prepared by Mr. G. Shearer of this department[39].

TABLES OF SPECTRA.

TABLE I: Diphenyl Ether.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
171	20.9	111	0.3	74	2.0
170	100.0	110	0.1	73	0.3
169	16.7	109	0.2	72	0.5
168	5.0	108	0.1	71.5	0.8
167	0.8	107	0.2	71	3.8
166	0.5	106	0.7	70.5	1.1
157	0.3	105	1.8	70	2.7
156	0.3	104	0.9	69	1.1
155	0.7	103	0.3	68	1.1
154	0.2	102	1.2	67	0.5
153	0.3	101	0.1	66	2.8
144	0.8	100	0.1	65	7.8
143	4.2	95	0.7	64	2.6
142	31.3	94	4.0	63	6.0
141	49.2	93	0.6	62	1.5
140	7.1	92	0.6	61	0.3
139	4.2	91	1.3	60	0.1
138	0.6	90	0.3	59	0.3
137	0.4	89	1.6	58.5	0.1
131	0.2	88	0.4	58	0.7
130	0.1	87	0.4	57.5	0.7
129	0.5	86	0.3	57	1.3
128	0.6	85.5	0.7	56	0.6
127	0.6	85	2.6	55	2.0
126	0.3	84.5	0.2	54	0.3
125	0.2	84	0.8	53	0.7
120	0.4	83	0.5	52	2.3
119	0.2	82	0.2	51	37.3
118	0.1	81	0.4	50	8.7
117	0.3	80	0.1	49	0.6
116	3.1	79	0.4		
115	17.2	78	3.7		
114	1.0	77	38.1		
113	0.8	76	2.9		
112	0.4	75	2.6		

TABLE II:

m/e	I	II	III	IV	V	VI	VII	VIII	IX
370	100.0(P)								
369	55.1								
368	13.7								
342	18.8								
341	16.5								
270		100.0(P)	100.0(P)	100.0(P)	100.0(P)				
269			80.5	77.0	69.4				
268			24.6	16.9	25.3				
246						100.0(P)	100.0(P)		
245						64.5	50.3		
244						16.6	30.7		
242		12.9	25.2	28.8	18.6				
241		20.6	22.3	17.8	15.7				
220								100.0(P)	100.0(P
219								61.1	63.5
218						10.1	7.8	22.3	20.3
217						5.3	8.0		
192								23.0	10.3
191								30.7	19.5
177	8.3	63.8							
165	18.3	35.1							
153						43.8	38.4		
141						44.4	10.9		
127			39.6	38.4	28.4			15.3	11.7
126				19.2	14.8				
115						12.6	9.5		
77	16.3					9.4	10.2		

I. 9:9'-diphenanthryl ether.
II. 9-phenanthryl phenyl ether.
III. β:β'-dinaphthyl ether.
IV. α:β'-dinaphthyl ether.
V. α:α'-dinaphthyl ether.
VI. p-phenoxybiphenyl.
VII. o-phenoxybiphenyl.
VIII. β-naphthyl phenyl ether.
IX. α-naphthyl phenyl ether.

TABLE III:

m/e	Relative intensity		
	Phenyl o-tolyl ether	Phenyl m-tolyl ether	Phenyl p-tolyl ether
184	100.0(P)	100.0(P)	100.0(P)
183	28.1	50.5	46.6
182	4.4	6.5	7.6
170	3.9	3.9	3.1
169	8.1	9.3	8.7
168	4.9	6.5	5.8
157	1.6	3.4	2.0
156	4.3	12.9	9.7
155	9.4	18.1	14.1
154	2.6	10.9	5.9
142	3.4	5.1	5.7
141	10.9	22.2	22.9
140	1.4	3.2	5.5
139	2.5	4.0	3.8
130	1.0	2.2	2.2
129	4.2	6.3	6.4
128	6.2	9.6	8.4
127	2.6	5.3	5.3
126	0.5	1.6	1.8
117	0.5	0.8	
116	1.9	0.6	2.5
115	8.1	13.3	10.9
114	0.4	2.1	2.0
109	1.4	0.6	0.5
108	2.3	4.0	4.2
107	11.5	6.5	10.0
106	25.9	2.5	2.4
105	2.3	0.8	1.2
104	1.0		0.5
94	1.9	3.7	2.5
93	0.8	1.9	1.9
92	4.7	9.5	11.5
91	39.5	69.4	84.5
90	6.1	7.3	8.4
89	7.4	12.2	9.9
88	0.3	1.8	1.5

TABLE III: (Cont'd)

m/e	Relative intensity		
	Phenyl o-tolyl ether	Phenyl m-tolyl ether	Phenyl p-tolyl ether
80	0.4	0.8	1.2
79	5.1	6.5	8.4
78	27.0	18.5	17.4
77	20.4	40.4	53.8
76	3.5	8.5	7.9
75	1.8	4.3	4.3
74	1.3	2.0	2.3
66	2.7	4.3	4.3
65	22.2	40.6	35.4
64	3.6	7.3	6.6
63	7.0	12.9	14.5
62	1.3	2.4	3.5
53	3.4	4.8	7.4
52	4.4	6.6	9.0
51	17.9	39.0	50.9
50	4.4	9.8	11.5

TABLE IV:

m/e	Relative Intensity			
	Phenyl 2-m-xylyl ether	Di-o-tolyl ether	o-tolyl 2-m-xylyl ether	Di-2-m-xylyl ether
226				100.0(P)
225				11.7
212			100.0(P)	6.8
211			14.5	25.2
210			1.1	9.7
209			2.6	12.2
208				2.3
199			3.0	
198	100.0(P)	100.0(P)	12.2	4.3
197	40.8	18.9	32.1	7.8
196	7.7		6.4	10.6
195	4.3		11.9	13.7
194			1.4	11.6
184	10.1	9.3	2.7	4.4
183	33.2	25.3	7.6	3.3
182	14.4	6.9	9.3	5.3
181	10.3	9.5	7.9	6.3
180	4.5	3.9	2.6	4.9
179			6.6	7.5
170	2.6	8.2	1.3	
169	5.0	14.3	5.5	3.1
168	4.5	10.6	4.1	2.7
167	3.5	2.9	3.8	3.9
166	1.2	4.5	3.1	4.5
165	2.3	11.5	6.1	8.4
155	8.5	9.4	2.8	2.2
154	5.8	6.3	4.0	1.7
153	6.8	7.2	4.9	3.2
152	6.3	6.9	4.7	4.0
151	4.0	3.0	2.5	1.8
143			1.4	1.1
142	1.6	1.3	1.8	1.6
141	3.8	3.6	3.5	3.0
139	1.0	1.4	2.9	
129	4.3	4.5	2.6	2.0
128	4.5	6.1	3.3	3.5
127	1.9	3.2	1.4	1.7
122	5.0		3.8	4.0
121	22.8		19.7	30.6
120	81.9	0.7	64.5	65.3
119	2.3	0.7	3.5	8.3

-Cont'd-

TABLE IV: (Cont'd)

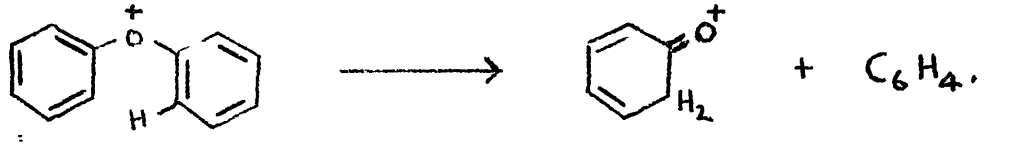
m/e	Relative Intensity			
	Phenyl 2-m-xylyl ether	Di-o-tolyl ether	o-tolyl 2-m-xylyl ether	Di-2-m-xylyl ether
118	1.5	0.5	4.0	14.7
115	3.8	5.4	3.1	3.4
107	7.1	39.1	13.9	9.7
106	7.5	22.0	25.5	71.5
105	33.7	11.2	21.8	75.7
104	11.6	24.9	30.7	19.0
103	22.0	2.7	11.1	30.1
94	3.7	0.5	2.1	2.2
93	5.7	5.5	4.4	4.7
92	35.0	54.4	30.9	20.8
91	43.5	61.7	44.6	48.4
90	3.9	13.9	4.9	6.3
89	2.9	15.1	6.9	8.5
79	16.8	8.1	13.8	35.8
78	18.4	28.8	11.6	28.0
77	46.8	20.9	28.0	71.8
76	3.1	4.2	2.1	5.3
75	2.6	3.0	1.7	4.9
65	14.8	53.1	21.7	18.6
64	2.3	6.6	2.8	4.0
63	5.1	15.3	5.2	12.6
53		6.6		15.4
52	5.6	7.8	2.8	8.9
51	21.9	19.5	6.0	25.0
50	4.7	4.5	1.5	6.7

DISCUSSION:

The simplest member of the diaryl ethers is diphenyl ether. In its mass spectrum (Table I) the most intense ion is the parent molecular ion. The most intense fragment ions are at $\frac{m}{e}$ = 142, 141, 115, 77 and 51. The ion of $\frac{m}{e}$ = 77 will be $C_6H_5^+$ arising from the simple fission:

$$C_6H_5\overset{+}{O}\,C_6H_5 \longrightarrow C_6H_5^+ + {}^{\cdot}O\,C_6H_5.$$

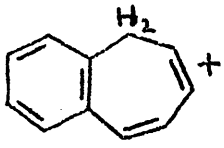
The phenoxy ion appears only in low abundance. There is, however, an ion at $\frac{m}{e}$ = 94 which must arise by rearrangement. It is commonly abundant in the spectra of other phenyl ethers where there is the possibility of formation by a six-membered ring transition state, e.g. from phenetole[28] as shown previously. In the latter case a stable neutral product, ethylene, is formed. In the case of diphenyl ether the neutral product must be C_6H_4. Assuming the same type of mechanism, the process will be as follows. The neutral product will not



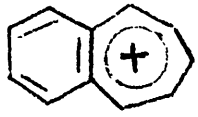
be stable in the cyclic form, and the ring may open. This is, however, not a predominant reaction in the degradation of the diphenyl ether molecular ion. Indeed the ion of $\frac{m}{e}$ = 94 has an abundance of 4% of that of the molecular ion.

The presence of the ions of $\frac{m}{e}$ = 142 and 141 has already

been discussed, and the structures proposed for these ions are VI and VII respectively. It is to be expected that VI



VI



VII

would lose a hydrogen atom readily to produce the completely aromatic ion VII, by analogy with cycloheptatriene[25]. This is confirmed by the presence of a metastable ion at $\frac{m}{e}$ = 140.0 which corresponds to the transition:-

$$142^{+} \longrightarrow 141^{+} + 1.$$

This analogy can be extended. It has been shown[25] that toluene and cycloheptatriene both form the tropylium ion of $\frac{m}{e}$ = 91 and they almost certainly form the same molecular ion. If 1-methylnaphthalene behaves analogously to toluene there should be some similarity in the spectra of 1-methylnaphthalene[40] and diphenyl ether at mass numbers less than 142. These two spectra (Figs. III and IV) have the following ions in common with some similarity in relative intensity:-

$\frac{m}{e}$ = 141, 115, 102, 91, 89, 75, 74, 71, 70.5, 70, 69.5, 69, 63 and 61. There is a significant difference in intensity in the ions at the following masses:

$\frac{m}{e}$ = 105, 94, 85½, 85, 84½, 78, 77, 76, 75, 65, 51. It should be possible to explain the formation of the latter group of ions in terms of mechanisms which do not involve the prior formation of $C_{11}H_{10}^{+}$.

Fig. III

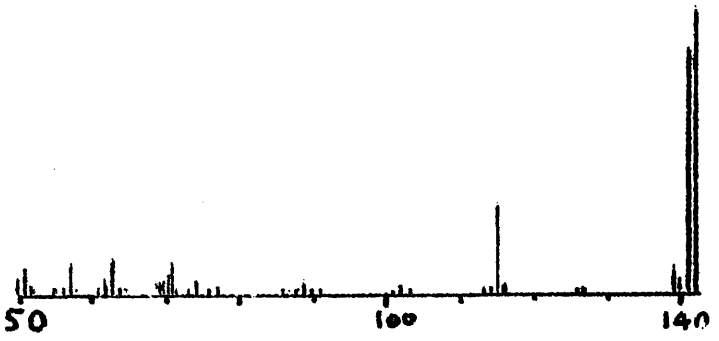
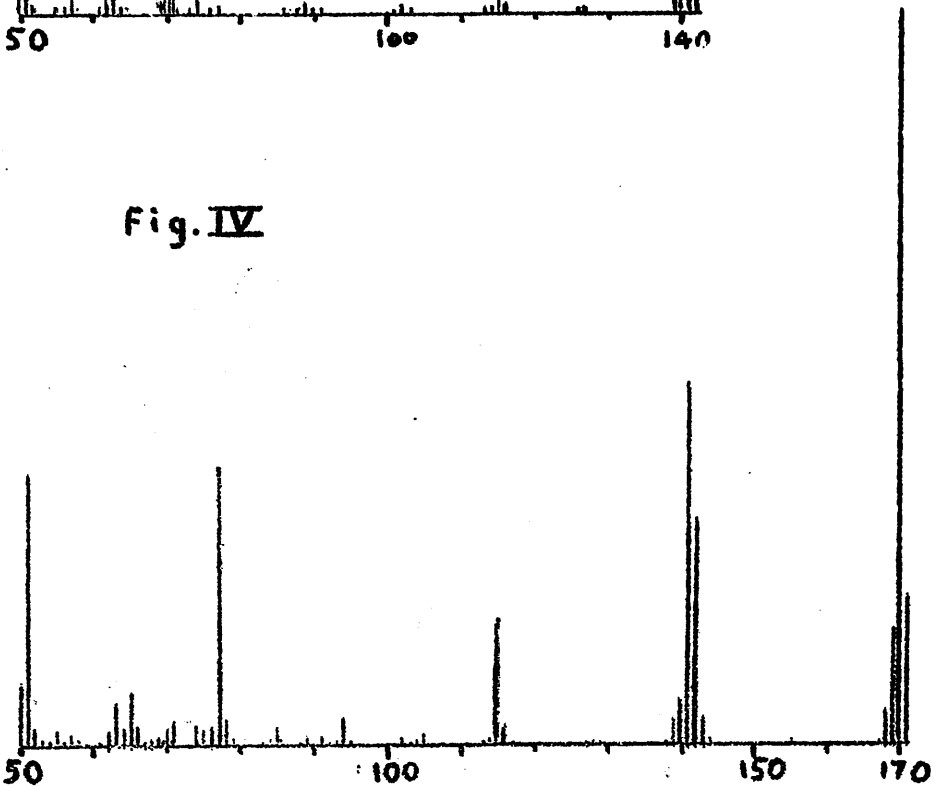


Fig. IV



The ions of $\frac{m}{e}$ = 94 and 77 have already been discussed. The ion of $\frac{m}{e}$ = 85 is the doubly charged molecular ion, $(P)^{2+}$. It will be noted that $\frac{m}{e}$ = 105 and 65 are complementary. They may be produced by the following type of fission:

$$C_{12}H_{10}O^{+} \longrightarrow C_7H_5O^{+} + C_5H_5$$

$$\frac{m}{e} = 105$$

or

$$C_5H_5^{+} + C_7H_5O.$$

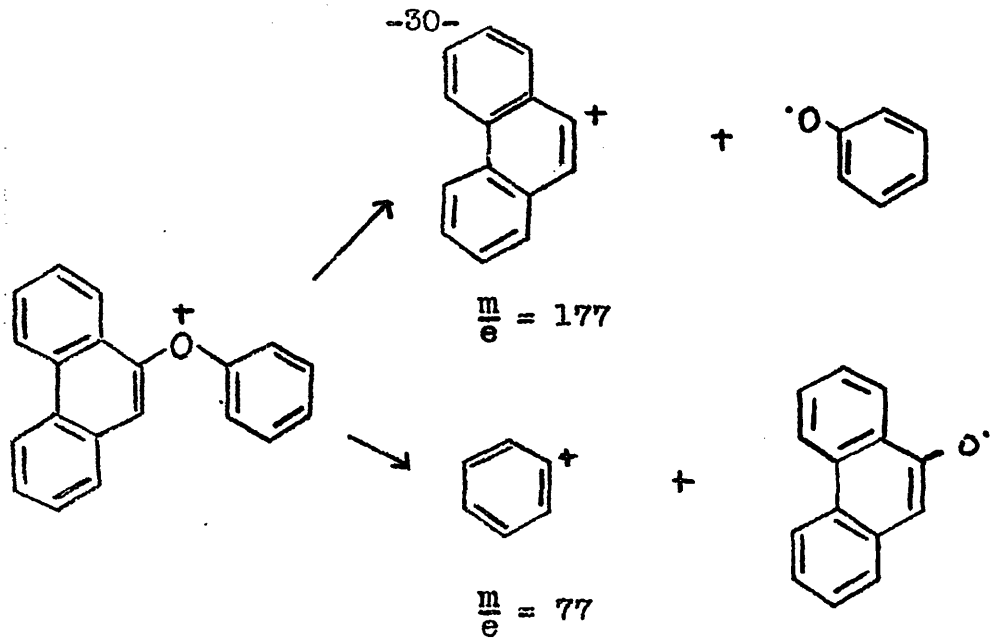
$$\frac{m}{e} = 65$$

The abundance of the ion of $\frac{m}{e}$ = 51 is typical of compounds which show an intense phenyl ion, e.g. bromobenzene[41]. It is probably produced by elimination of acetylene from the phenyl ion.

$$C_6H_5^{+} \longrightarrow C_4H_3^{+} + C_2H_2.$$

In the partial mass spectra of ethers with condensed aromatic rings, (Table II), The same processes are found. The predominant reactions are elimination of CO and CHO˙ and aryl oxygen fission. As with other purely aromatic compounds, the molecular ion is the most intense in the spectrum. As found in fused aromatic hydrocarbons, the stability of the molecular ion appears to increase as the number of fused rings increases.

In the unsymmetrical diaryl ethers both aryl groups appear as ions, e.g. in the spectrum of 9-phenanthryl phenyl ether,



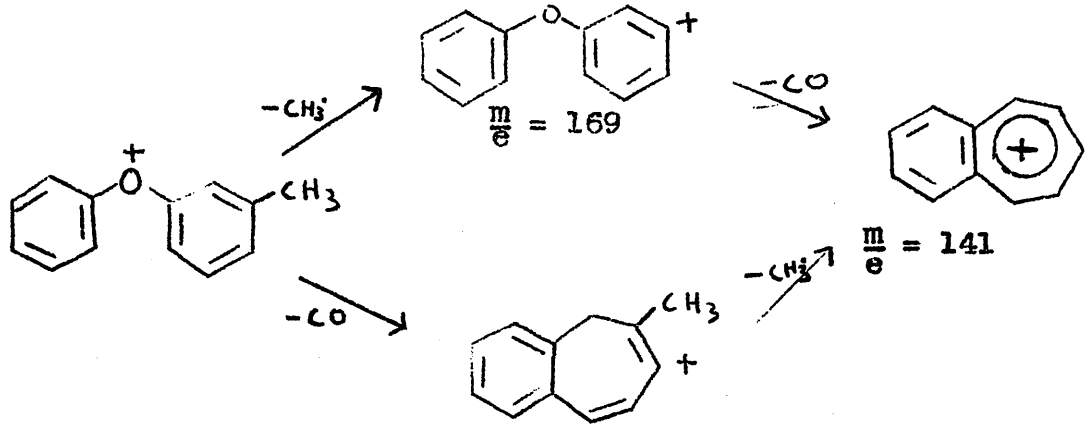
It is therefore possible to detect the individual groups present in an unsymmetrical ether. The problem is more difficult when one tries to make a distinction between isomeric groups, e.g. α- and β-naphthyl. In the spectra of the ethers the main difference between such isomeric compounds is in the loss of one or two hydrogen atoms from the molecular ion. There is, however, no empirical rule which can be used to determine the orientation of substitution in aromatic nuclei from the abundance of these ions.

When a methyl group is introduced into the aromatic nucleus there is a considerable change in the appearance of the spectrum. In the spectrum of phenyl m-tolyl ether (Table III) the ions corresponding to the loss of CO and CHO are reduced in intensity, and the most intense fragment ion appears at $\frac{m}{e} = 91$. This ion, $C_7H_7^+$, could be obtained by simple fission:

$$C_7H_7\overset{+}{O}\,C_6H_5 \longrightarrow C_7H_7^{+} + C_6H_5O^{\cdot}$$

It is unlikely that it will be the m-tolyl ion. As is found with the xylenes[25] the $C_7H_7^+$ ion will rearrange to the more stable tropylium form.

As mentioned before there is only a moderate abundance of the ions of $\frac{m}{e}$ = 156 and 155 which are derived by elimination from the molecular ion of carbon monoxide and the formyl radical respectively. There is, however, a more intense ion at $\frac{m}{e}$ = 141 and an ion of low but significant intensity at $\frac{m}{e}$ = 169. The latter must result from the loss of the methyl group from the molecular ion. These two ions will be related as in the following scheme, with the production of the benztropylium ion. The ion of $\frac{m}{e}$ = 115



$\frac{m}{e}$ = 169

$\frac{m}{e}$ = 141

or other isomer

$\frac{m}{e}$ = 156

is also found, as it was in other spectra containing the benztropylium ion (Figs. III and IV).

In its other features the spectrum is similar to that of diphenyl ether. The other aryl group is present as an abundant ion at $\frac{m}{e} = 77$, with its expected degradation product at $\frac{m}{e} = 51$. The ion of $\frac{m}{e} = 65$ is intense as is usual in the spectra of compounds which degrade to the tropylium ion. It is derived from the latter by elimination of acetylene[25].

$$C_7H_7^+ \longrightarrow C_5H_5^+ + C_2H_2.$$

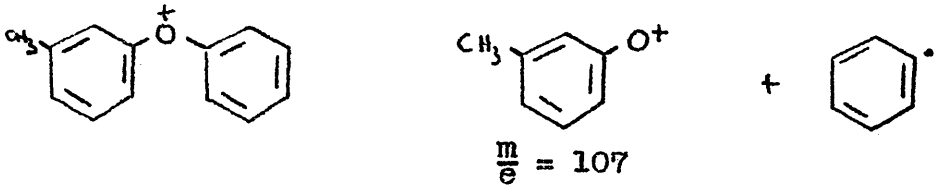
The ions of $\frac{m}{e} = 128$ and 129 can be produced by elimination of C_2 fragments from the $(P-CO)^+$ and $(P-CHO)^+$ ions, e.g.

$$C_{13}H_{12}O^+ \xrightarrow{-CO} C_{12}H_{12}^+ \xrightarrow{-C_2H_4} C_{10}H_8^+$$

$$\frac{m}{e} = 156 \qquad \frac{m}{e} = 128$$

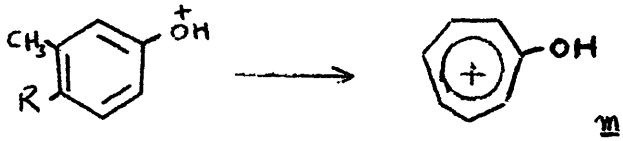
It has been suggested that the ion of $\frac{m}{e} = 128$ in the spectrum of 1:2-dihydroxyanthraquinone[30] may have the naphthalene structure, and the same structure may be possible in this case.

The ion of $\frac{m}{e} = 107$ could arise from the fission:



$$\frac{m}{e} = 107$$

It is present in greater abundance than the phenoxy ion. Similarly an ion of the same mass appears more abundantly in the spectra of the cresols and dimethyl phenols than the phenoxy ion in phenol. By analogy with toluene[25] it is to be expected that a hydroxytropylium ion will be formed.

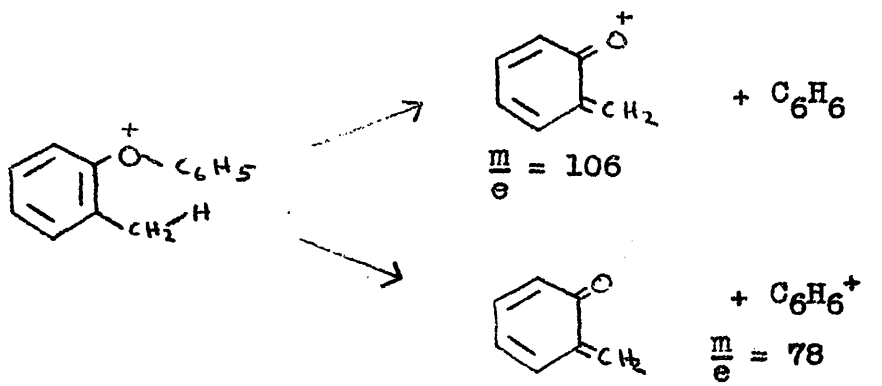


m-cresol R = H

3:4-dimethylphenol R = CH_3

Phenyl p-tolyl ether has a spectrum (Table III) very similar to that of phenyl m-tolyl ether. The fragmentation processes would appear to be the same and the only differences are in the relative intensity of the ions formed.

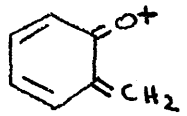
Phenyl o-tolyl ether shows some striking differences in fragmentation from its isomers. The most intense ion is still at $\frac{m}{e}$ = 91 but its intensity is reduced as is that of the phenyl ion ($\frac{m}{e}$ = 77). Two other ions appear with enhanced abundance at $\frac{m}{e}$ = 78 and 106. Both ions can be obtained by a rearrangement process involving a six-membered ring transition state, which is only possible where there is



$\frac{m}{e}$ = 106

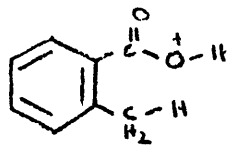
$\frac{m}{e}$ = 78

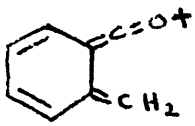
an α-hydrogen atom in a position ortho to the ether oxygen atom. The ion of $\frac{m}{e}$ = 78 may also be derived by the following fission:



$\longrightarrow$ $C_6H_6^+$ + CO.

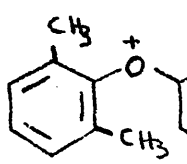
This is analogous to the behavious of o-toluic acid[27].



$\longrightarrow$  $\longrightarrow$ $C_7H_6^+$ + CO.

$\frac{m}{e}$ = 118 $\frac{m}{e}$ = 90

In the spectra of the two isomeric ethers (Table IV) with two ortho methyl groups the $(P - CH_3)^+$ ion is more intense, especially in phenyl 2-m-xylyl ether. This molecule contains a 1:2:3-trisubstituted benzene system. In the spectrum of this compound the most intense ions appear at $\frac{m}{e}$ = 120, 105, 92, 91 and 77. These ions can be obtained by simple aryl oxygen fission (Fig. V) and by α-hydrogen migration (Fig. VI).



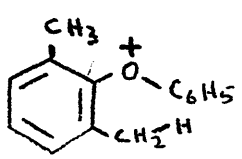
$\longrightarrow$ $C_8H_9^+$ + $C_6H_5O^\cdot$

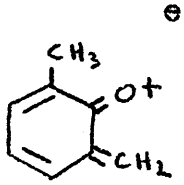
$\frac{m}{e}$ = 105

$\longrightarrow$ $C_6H_5^+$ + $C_8H_9O^\cdot$

$\frac{m}{e}$ = 77

FIG. V.



$\longrightarrow$  + C_6H_6

$\frac{m}{e}$ = 120

$C_7H_8^+$ + CO $C_7H_7^+$ + $CHO^\cdot$

$\frac{m}{e}$ = 92 $\frac{m}{e}$ = 91

FIG. VI.

The ion of $\frac{m}{e}$ = 105 (Fig. V) will probably be the methyltropylium ion rather than the 2-m-xylyl ion. The appearance of the ion of $\frac{m}{e}$ = 92 indicates that a similar process may be responsible for the production of the ion of $\frac{m}{e}$ = 78 from phenyl o-tolyl ether.

In the phenyl 2-m-xylyl ether spectrum the $(P - CO)^+$ and $(P - CHO)^+$ ions are noticeably less intense than the corresponding ions in the spectra previously discussed. The products in this case will be dimethylcycloheptatriene and dimethylbenztropylium ions, which will degrade more easily than more simply substituted ions. If the mechanism proposed[29] for the elimination of carbon monoxide is correct and applicable in this case, the process will be hindered. Since the first stage of this mechanism involves ortho-ortho coupling, the presence of substituents in the ortho positions will decrease the probability of this process.

As with phenyl o-tolyl ether the $(P - CH_3, CO)^+$ ion is more intense than the $(P - CHO)^+$ ion: the former appears at $\frac{m}{e}$ = 155. The benztropylium ion still appears at $\frac{m}{e}$ = 141. It is possible that it is derived from the $(P - CHO)^+$ ion in the following manner. The ions of $\frac{m}{e}$ = 155 and 141

$$\underset{\frac{m}{e} = 198}{C_{14}H_{14}O^+} \xrightarrow{-CHO} \underset{\frac{m}{e} = 169}{C_{13}H_{13}^+} \xrightarrow{-C_2H_4} \underset{\frac{m}{e} = 141}{C_{11}H_9^+}$$

degrade by loss of C_2 fragments to ions of $\frac{m}{e}$ = 128 and 115 respectively.

Di-o-tolyl ether is isomeric with phenyl 2-m-xylyl ether, but the methyl groups are in less sterically hindered positions. This difference is reflected in the lower abundance of the $(P - 15)^+$ ion. Again there is a stepwise degradation of the $(P)^+$ and $(P - 15)^+$ ions by loss of CO and C_2 fragments.

$$198^+ \xrightarrow{-CHO} 169^+ \xrightarrow{-C_2H_4} 141^+ \xrightarrow{-C_2H_2} 115^+.$$
$$\downarrow -CH_3$$
$$183^+ \xrightarrow{-CO} 155^+ \xrightarrow{-C_2H_3} 128^+.$$

The rearrangement involving fission at the ether link and transfer of an α-hydrogen atom again occurs. In this case the hydrocarbon fragment of $\frac{m}{e} = 92$ appears to be ionized more readily than the oxygenated fragment ($\frac{m}{e} = 106$), whereas the reverse is true of phenyl 2-m-xylyl ether. This may be due to the difference between the ionization potentials of the expected hydrocarbon fragments, toluene and benzene.

Toluene	C_7H_8	I.P. = 8.82eV.[43]
Benzene	C_6H_6	I.P. = 9.21eV.[43]

The difference is, however, rather small and comparative values are not known for the other fragments. In this case the hydroxytropylium ion at $\frac{m}{e} = 107$ is more intense than the ion at $\frac{m}{e} = 106$. The ions of $\frac{m}{e} = 79$, 78 and 77 will be produced by loss of CO and CHO from the ions of $\frac{m}{e} = 107$ and 106.

There are also in the spectra of both di-o-tolyl ether and phenyl 2-m-xylyl ether several ions which cannot be explained by invoking the conventional mechanisms so far used. These are at $\frac{m}{e}$ = 181, 165, 152 and 104. The last-mentioned is more intense in di-o-tolyl ether and the first three occur also in o-tolyl 2-m-xylyl and di-2-m-xylyl ethers. Such ions have not been so far reported in similar compounds and there is insufficient evidence to justify the postulation of structures for these ions.

In the spectrum of o-tolyl 2-m-xylyl ether (Table IV) one finds that the loss of 30 and 31 mass units is predominant over the loss of 28 and 29. This may be the successive removal of methyl groups. Similar behaviour is found in the polymethyl indoles[31]. It is, however, possible to observe the stepwise degradation of the $(P)^+$ and $(P - CH_3)^+$ ions which takes place in a manner similar to that of the two previously discussed compounds.

$$C_{15}H_{16}O^+ \longrightarrow C_{14}H_{13}O^+ \longrightarrow C_{13}H_{13}^+ \longrightarrow C_{11}H_9^+ \longrightarrow C_9H_7^+$$

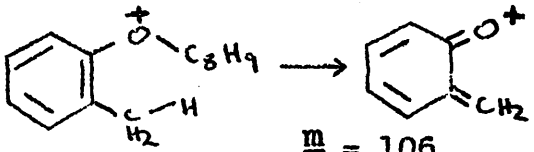
$\frac{m}{e}$ = 212 $\frac{m}{e}$ = 197 $\frac{m}{e}$ = 169 $\frac{m}{e}$ = 141 $\frac{m}{e}$ = 115

$$\downarrow$$

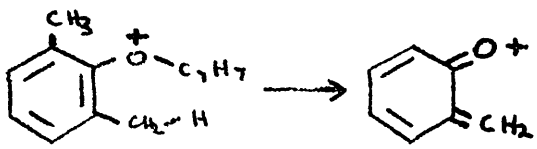
$$C_{14}H_{15}^+ \longrightarrow C_{12}H_{11}^+ \longrightarrow C_{10}H_8^+$$

$\frac{m}{e}$ = 183 $\frac{m}{e}$ = 155 $\frac{m}{e}$ = 128

With this compound there are two possible α-hydrogen rearrangements, VIII and IX. All the ions shown are

VIII  or $C_8H_{10}^+$

$\frac{m}{e} = 106$ $\frac{m}{e} = 106$

IX  or $C_7H_8^+$

$\frac{m}{e} = 120$ $\frac{m}{e} = 92$

abundant as are the simple fission products at $\frac{m}{e} = 105$ and 91. The unexplained rearrangement ion of $\frac{m}{e} = 104$ is, however, more intense than either of the ions at $\frac{m}{e} = 105$ and 106.

The mass spectrum of di-2-m-xylyl ether (Table IV) is even more complicated in the upper mass range. The $(P - CH_3)^+$ ion is intense as should be expected. The ions which constitute the typical stepwise degradation are all of low intensity. They appear at the following mass numbers:

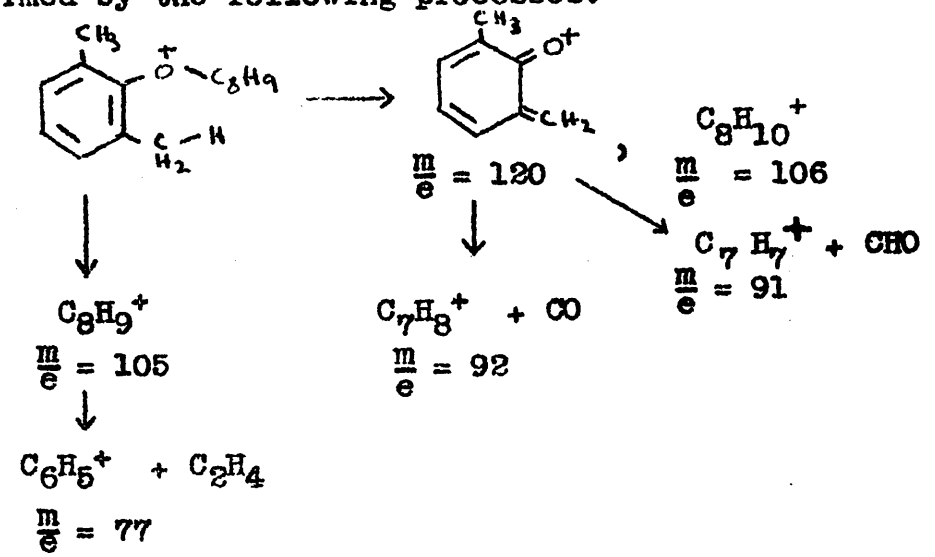
$226^+ \longrightarrow 197^+ \longrightarrow 169^+ \longrightarrow 141^+ \longrightarrow 115^+$

$\downarrow$

$211^+ \longrightarrow 183^+ \longrightarrow 155^+ \longrightarrow 128^+$

There are, however, equally or more intense ions appearing at $\frac{m}{e} = 195$, 179, 165 and 152. Similar behaviour is found with o-tolyl 2-m-xylyl ether. The persistent presence of ions at $\frac{m}{e} = 165$ and 152 suggests that there is a common process for their formation. The predominant

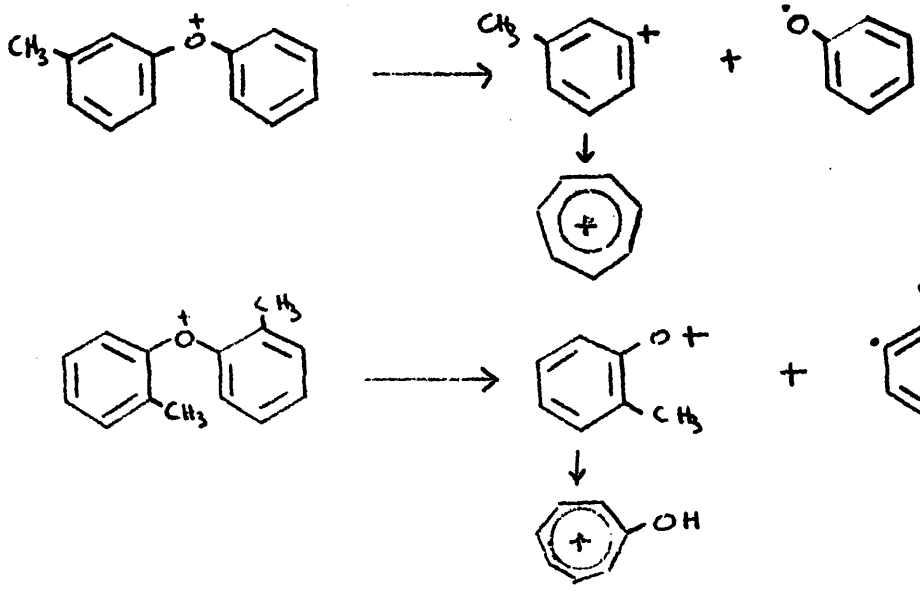
fission processes do, however, appear to be similar to those in the other ethers with ortho methyl groups, i.e. fission of the ether linkage with and without (α-hydrogen migration. The most abundant ions will probably be formed by the following processes:



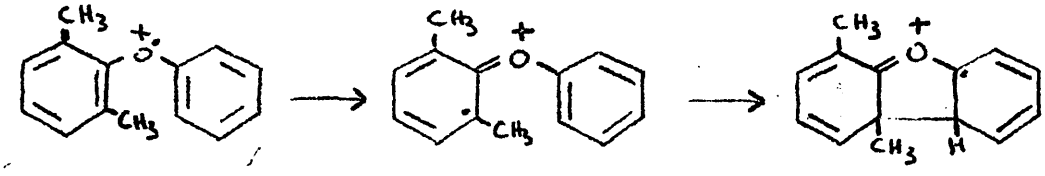
It will be noted that in all the diaryl ethers studied there occurs to some extent the rearrangements leading to the $(P - CO)^+$ and $(P - CHO)^+$ ions. In the series of polynuclear ethers the intensity of these ions decreased with increasing molecular weight. This is consistent with the opinion that fusion of extra aromatic rings stabilises the molecular ion by charge delocalisation.

The presence of methyl groups in the aromatic nucleus also decreases the intensity of these ions, the most marked effect being caused by the presence of methyl groups in the ortho position. Two reasons can be advanced for this.

Firstly, very stable ions can be formed by competing reactions involving much simpler mechanisms, e.g. formation of a potential tropylium ion by simple fission.



Secondly, the presence of ortho methyl groups will hinder the formation of a tricyclic intermediate. If the proposed mechanism[29] can be applied to phenyl 2-m-xylyl ether, the first step in the process will be as follows:



The approach of the ortho positions will be hindered by the presence of the o-methyl group. This effect should be greater in the above case than in di-o-tolyl ether where there is one unsubstituted ortho position in either ring.

It is indeed found that the $(P - CO)^+$ ion is more intense in the latter case than in the former. These facts do not constitute a proof of the mechanism proposed by Beynon, Lester and Williams but they are consistent with it.

PART II.

The Mass Spectra of some Naturally Occuring Phenolic Compounds.

Introduction:

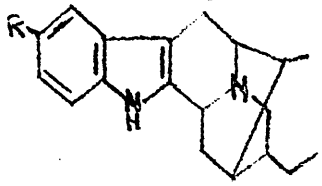
The mass spectra of naturally occurring phenolic compounds have not been obtained by any previous workers. This neglect is probably due to the low volatility of these compounds. Indeed this latter problem has been a stumbling block in the use of this method for the analysis of most classes of naturally occurring compounds.

Of the groups which have been studied the most obviously amenable to the method of mass spectrometry are the aliphatic compounds occurring in natural fats and plant waxes[44]. Saturated hydrocarbons were among the first compounds to be studied by this method. The mass spectrum alone can identify such compounds[45]. Using heated inlet systems hydrocarbons containing more than 40 carbon atoms can be studied. The mass spectra of esters of long chain acids obtained from natural fats have been the subject of extensive studies by Stenhagen and Ryhage[46].

Among the naturally occurring alicyclic compounds most attention has been focussed on the steroids but some studies have been made on the monoterpenes[47] and the diterpenoid resin acids[47a]. Some mass spectrometric studies in the protein

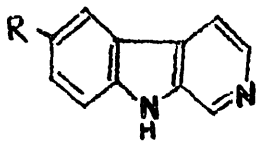
field have been carried out by Biemann and his collaborators but they were restricted to amino acid esters[48] and the reduction products of small peptides[49]. Both groups of compounds are fairly volatile. The other main group of high molecular weight compounds, the carbohydrates, are discussed in Part III of this work.

There is one group of natural products which bears some similarity to the compounds discussed in this section, in molecular size and in the presence of a partially aromatic cyclic structure. This is the indole group of alkaloids, and the mass spectra of several of these have been discussed by Biemann and his collaborators[50]. Typical examples of the type of compound studied are Ia and Ib, which are reduction products of sarpagine and ajmaline.



Ia R = OCH_3

Ib R = H



IIa R = OCH_3

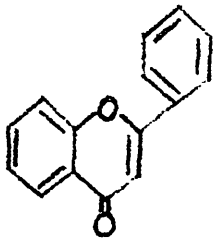
IIb R = H

In the spectrum of Ia the most intense ion is IIa. Similarly IIb is the most intense ion in the spectrum of Ib. In both spectra all ions of $\frac{m}{e}$ values higher than II will contain the intact aromatic ring system, since the alicyclic portion will fragment readily. The mass spectra of Ia and Ib in this region are almost superimposible, each ion from

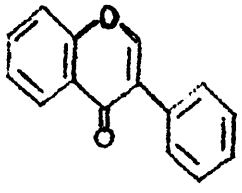
Ia having a mass to charge ratio 30 units greater than the corresponding ion from Ib.

None of the compounds studied in this section has an extensive alicyclic system as part of its structure.

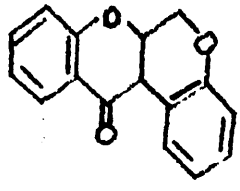
The majority of these possess one of the following ring systems, in which there are two benzene rings linked or fused



flavone



isoflavone



rotenoid

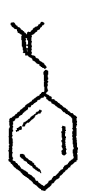
to a heterocyclic system. If these systems cleave in such a manner that the benzene rings remain intact it may be possible to obtain some information about the nature of the ring system and the positions of substituents on the benzene rings.

A difference in orientation of a substituent in an aromatic ring does not usually give rise to a substantial difference in the cracking pattern of the compound. In the spectra of the three isomeric xylenes[51] the greatest difference shown is one of 9% of the intensity of the ion ($\frac{m}{e}$ = 106) between o- and m-xylene. It is probable, however, that differences in the mass spectrum will be greater where there is the possibility of a facile rearrangement, as has been observed with the three phenyl tolyl ethers. Orientations which involve a high degree of steric crowding may also affect

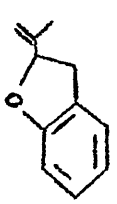
the spectrum. The effect of differences in electronic properties of different isomers (o, m and p effects) are more readily observed using the low-energy sensitivity method of Crable, Kearns and Norris[52]. Unfortunately the compounds being studied at present are not sufficiently volatile to allow sensitivity measurements to be made.

It is therefore probable that the information about substituents that can be most easily obtained by this study is their distribution between the two benzene rings. It may also be possible to detect the presence of identically orientated groups in different molecules by superposition of their mass spectra, as was shown for the alkaloids.

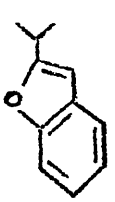
Another problem which has been attempted is the determination of the nature of the isoprenoid groups which are sometimes present as substituents in flavones and related compounds. The most common types of isoprenoid group are $\gamma:\gamma$-dimethyl-allyl (IIIa), 2-isopropenyl-2:3-dihydrobenzfuran (IIIb), 2-isopropylbenzfuran (IIIc), 2:2-dimethylchroman (IIId) and 2:2-dimethylchromene (IIIe).



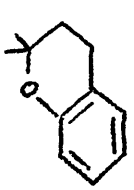
IIIa



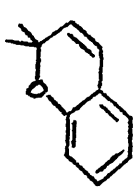
IIIb



IIIc



IIId



IIIe

As a preliminary study of the behaviour under electron

impact of these systems, mass spectra have been obtained for some salicylic acid derivatives which contain such isoprenoid groups.

Experimental:

Samples were obtained from Dr. W.D.Ollis, University of Bristol.

The spectra were run as in Part I. The samples used were less volatile and the method of continuous volatilisation was modified in the following manner. The sample, at the end of the glass rod, was held at a distance of 1.5 to 1 cm. from the repeller plate. The source filament was switched on 15 minutes before beginning measurements to allow equilibration of temperature in the region of the sample. When the run was completed, a section of the run was repeated as a check on the constancy of the sample pressure and to detect any decomposition of the sample.

Tables of Spectra.

TABLE I: Tubaic Acid.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
222	4.6	165	2.9	122	3.1	80	3.1
221	19.3	164	1.3	121	4.0	79	4.6
220	88.4(P)	163	4.0	120	2.0	78	3.8
219	2.7	162	6.6	119	4.3	77	6.8
218	2.2	161	38.3	118	9.5	76	2.8
217	1.9	160	19.0	117	12.4	75	0.5
207	1.3	159	27.6	116	4.8	74	0.4
206	3.5	158	4.1	115	11.6	73	0.5
205	11.2	157	6.0	114	0.9	72	0.5
204	3.8	156	2.0	113	2.2	71	2.5
203	11.1	155	1.9	112	2.2	70	1.7
202	40.9	154	0.9	111	7.3	69	3.4
201	7.4	153	1.3	110	3.9	68	1.4
200	1.8	152	1.3	109	7.7	67	2.5
194	0.9	151	3.2	108	4.8	66	1.7
193	2.1	150	2.3	107	8.3	65	4.4
192	2.6	149	9.5	106	3.4	64	2.5
191	3.6	148	3.8	105	8.9	63	2.5
190	2.1	147	11.5	104	4.7	62	0.6
189	4.7	146	35.6	103	8.2	61	0.3
188	17.8	145	17.6	102	2.7	60	0.6
187	100.0	144	4.2	101	2.0	59	0.6
186	11.4	143	4.4	100	0.3	58	1.0
(m)185.5	10.6	142	0.5	99	1.2	57	4.8
185	23.7	141	1.9	98	1.2	56	3.4
184	1.7	140	1.7	97	3.4	55	8.6
181	0.8	139	3.4	96	1.7	54	1.7
180	1.6	138	2.4	95	7.2	53	13.7
179	2.5	137	4.8	94	1.2	52	5.1
178	4.2	136	2.4	93.5	0.7	51	11.3
177	3.4	135	4.4	93	1.8	50	3.9
176	10.3	134	7.1	92	2.1		
175	15.1	133	8.6	91	5.2		
174	69.9	132	10.8	90	0.9		
(m)173.1	24.8	131	32.5	89	1.6		
173		130	2.6	88	0.8		
172	3.9	129	11.3	87	1.4		
171	1.4	128	11.3	86	1.3		
170	0.6	127	6.1	85	3.0		
169	0.6	126	2.1	84	2.6		
168	0.8	125	5.7	83	4.3		
167	1.7	124	3.9	82	3.0		
166	1.0	123	11.5	81	4.0		

TABLE II: Isotubaic Acid.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
221	12.0	130	0.9	76	2.1
220	35.9(P)	129	0.7	75	1.8
219	2.4	128	0.7	74	0.8
218	1.1	119	0.8	73	0.4
217	0.9	118	0.4	72.5	0.2
205	0.9	117	2.1	72	0.2
204	4.2	116	1.4	71	1.1
203	21.4	115	3.1	70	0.7
202	78.5	114	0.3	69	2.2
201	6.9	107	0.8	68	0.5
200	1.9	106	0.5	67	1.6
189	3.6	105	1.7	66	1.5
188	22.4	104	0.3	65.5	1.3
187	100.0	103	11.1	65	2.1
186	6.0	102	3.7	64.5	0.2
(m)185.5		101	1.8	64	0.8
185	0.55	100.5	0.2	63	2.8
177	1.1	100	0.4	62	0.6
176	2.8	97	1.1	59	0.3
175	2.1	96	0.5	58.5	0.1
174	4.0	95	1.9	58	0.4
(m)173.1		94	2.1	57.5	0.2
173	6.9	93.5	2.9	57	1.9
172	2.3	93	2.0	56	1.0
163	0.2	92	0.8	55	4.1
162	0.6	91	3.0	54	0.5
161	4.1	90	0.5	53	3.2
160	4.6	89	1.5	52.5	0.1
159	4.1	88	0.5	52	1.1
158	1.3	87	1.2	51.5	0.7
157	0.3	86.5	0.3	51	3.1
151	0.3	86	0.2	50.5	0.1
150	0.2	85	0.6	50	1.3
149	0.6	84	0.4		
148	0.2	83	1.3		
147	0.6	82	0.7		
145	1.1	81	1.5		
144	0.3	80.5	0.4		
143	0.3	80	1.6		
135	0.5	79.5	0.7		
134	0.4	79	2.0		
133	0.7	78.5	0.6		
132	1.7	78	2.1		
131	6.8	77	10.0		

TABLE III: β-dihydrotubaic acid methyl ether.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
237	23.9	164	2.6	109	5.8
236	92.5(P)	163	15.1	108	1.1
235	1.5	162	5.8	107	5.2
234	1.6	161	10.8	106	1.8
222	3.5	160	6.3	105	5.6
221	15.7	159	3.1	104	1.6
220	4.4	154	1.7	103	3.6
219	20.8	153	7.0	97	1.7
218	33.0	152	15.4	96	4.8
217	2.2	151	91.3	95	7.4
(m)206.9	2.0	150	6.4	94	6.2
205	5.7	149	19.4	93	3.3
204	23.6	148	6.1	92	4.6
203	100.0	147	18.3	91	7.6
202	3.8	146	2.4	90	1.3
(m)201.4	5.6	145	3.9	89	2.8
193	1.5	144	2.0	81	5.7
192	1.1	137	3.8	80	1.5
191	3.1	136	2.4	79	4.9
190	2.7	135	10.8	78	4.5
189	8.5	134	13.0	77	10.1
188	4.2	133	4.7	76	2.2
187	11.2	132	3.2	75	2.1
(m)186.6	6.4	131	3.6	69	4.1
185	1.9	123	3.6	68	1.5
182	8.5	122	5.1	67	5.6
181	55.0	121	5.5	66	3.5
180	7.7	120	2.6	65	6.2
179	1.9	119	3.0	63	3.6
177	1.6	118	1.6	55	7.6
176	7.4	117	2.5	54	0.9
175	30.5	116	1.6	53	6.7
174	2.2	115	3.8	52	1.9
173	2.9	110	1.4	51	5.3

TABLE IV: β-Tubaic acid methyl ether.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
235	3.6	149	0.7	89	1.8
234	13.9 (P)	148	0.3	88	0.6
233	0.8	147	0.9	87	1.2
221	8.8	146	9.9	86	2.0
220	37.0	145	2.4	83	0.6
219	100.0	144	3.3	82	0.3
218	8.8	143	1.0	81	0.7
217	12.7	135	0.4	80	0.5
216	0.9	134	0.6	79	1.8
(m)205.0	1.5	133	1.2	78	1.6
203	0.7	132	5.0	77	5.1
202	0.4	131	3.2	76	1.3
201	1.6	130	0.9	75	1.4
190	0.7	129	1.5	74	0.7
189	3.4	128	1.7	69	0.8
188	1.8	127	1.1	67	0.8
187	8.8	117	2.0	66	0.8
186	0.7	116	1.8	65	2.0
185	1.1	115	4.4	64	0.8
184	0.3	114	0.6	63	2.5
175	1.7	107	0.9	62	0.8
174	1.7	106	1.3	57	0.9
173	2.2	105	1.6	56	0.6
162	0.9	104	1.3	55	1.9
161	6.2	103	3.2	54	0.4
160	28.5	102	1.8	53	2.4
159	3.2	101	1.3	52	0.9
158	1.1	95	1.1	51	2.3
157	0.7	92	1.0	50	0.9
151	0.4	91	3.8		
150	0.2	90	0.7		

TABLE V.

m/e	Relative Intensity			
	Munduserone	Sermundone	Elliptone	Iso-elliptone
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	00.6	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

- Cont'd -

TABLE V. (Cont'd)

m/e	Relative Intensity			
	Munduserone	Sermundone	Elliptone	Iso-elliptone
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

- Cont'd -

TABLE V. (Cont'd)

m/e	Relative Intensity			
	Munduserone	Sermundone	Elliptone	Iso-elliptone
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	

TABLE VI.

m/e	Relative Intensity			
	Rotenone	Isorotenone	β-Dihydro-rotenone.	Rotenonic Acid
397			5.9	4.6
396			23.7(P)	18.7(P)
395	10.9	9.5	1.0	0.7
394	38.0(P)	29.7(P)	1.6	0.8
393	2.0	1.1		
392	2.9	1.8		
381			0.6	0.5
380	0.6			
379	1.6	0.8	0.5	
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		0.7	1.4	0.8
204	0.6	0.5	0.5	1.0
203	3.7	3.0	0.5	1.2
202	0.4	0.8		
201	0.4	0.5		
196				0.5
195		0.5		3.5
194	1.7	1.0	1.6	7.7
193	14.2	16.3	15.7	38.6
192	100.0	100.0	100.0	100.0
191	23.5	24.5	23.3	30.3
190	4.8	2.6	1.6	7.8
189	0.7	1.0	0.8	3.3
188		0.5		0.8
187	1.3	2.0		0.6

- Cont'd -

TABLE VI. (Cont'd)

m/e	Relative Intensity			
	Rotenone	Isorotenone	β-Dihydro-rotenone.	Rotenonic Acid.
181		0.9		
180		0.6		0.8
179	0.7	3.2	0.8	3.1
178	2.0	1.8	2.4	7.3
177	13.5	16.1	14.6	15.7
176	1.0	1.3	1.3	3.1
175	1.2	1.0	0.8	1.9
174	0.9	0.6		
173	0.6	0.8		
167		0.5		
166		0.5		0.5
165	0.8	1.4	0.5	1.5
164	1.9	2.4	0.7	3.3
163.2(m)	3.7	3.9	1.3	4.4
162	1.3	1.9	0.7	2.8
161	1.6	2.5	1.9	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		1.7	0.7	1.3
150		0.6	0.7	3.4
149	2.4	4.2	5.2	9.6
148	0.6	1.1	1.0	1.9
147	2.0	2.7	2.1	3.3
146	1.1	1.0	0.8	1.3
145	0.6	0.8	0.5	0.6
143		0.7		
141		0.6		
139		0.5		
137		1.2	0.5	
136		0.7		0.5
135	0.6	1.6	0.8	1.2
134	1.4	2.1	1.5	2.6
133	0.7	1.1	0.8	1.0
132		0.7	0.4	0.8
131	1.4	2.5	1.3	2.0
130		0.5	0.5	0.7

-Cont'd-

TABLE VI. (Cont'd)

m/e	Relative Intensity			
	Rotenone	Isorotenone	β-Dihydro rotenone.	Rotenonic Acid.
129		0.6	0.6	
128	0.5	0.5		
127		0.5		
126		0.5		
125		1.4	0.5	
124		0.8		
123	0.5	2.5	0.8	0.7
122		1.2	0.6	1.7
121	1.8	3.6	3.3	4.7
120		1.0		0.7
119	1.0	2.2	0.9	1.3
118	0.7	1.5	0.7	1.4
117	0.6	1.1		0.6
116		0.6		0.5
115	0.7	1.2	0.5	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

TABLE VII

Toxicarol.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
411	6.4	191	35.6	132	1.0
410	28.1(P)	190	8.8	131	2.5
409	1.0	189	2.5	130	1.1
408	1.2	188	1.3	123	0.7
396	9.7	187	3.0	122	1.3
395	19.7	181	1.1	121	7.7
394	1.0	180	4.5	120	1.1
393	1.1	179	22.5	119	3.3
381	1.5	178	4.3	118	2.6
380	1.3	177	24.6	117	0.8
379	1.3	176	4.3	116	0.5
229	0.9	175	3.6	115	1.2
220	1.0	174	0.7	111	0.6
219	3.4	165	1.5	110	0.4
218	3.5	164	2.9	109	1.1
217	7.9	163.2(m)	4.1	108	0.9
208	1.5	162	3.1	107	3.5
207	0.7	161	3.7	106	6.5
206	0.5	160	1.2	105	3.2
205	1.4	159	1.6	104	0.9
204	5.8	152	1.0	103	3.7
203	20.7	151	4.3	102	1.2
202	1.4	150	1.7	101	0.3
201	1.2	149	7.1		
199	1.0	148	3.6		
198	6.2	147	6.4		
197	0.5	146	2.3		
196	0.4	145	1.0		
195	1.0	136	1.1		
194	2.9	135	3.9		
193	25.2	134	3.9		
192	100.0	133	4.3		

TABLE VIII

Pachyrrhizone.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
367	10.5	176	100.0	144	0.7
366	36.5(P)	175	59.8	143	0.4
365	1.9	174	3.7	142	0.2
364	3.8	173	1.1	141	0.4
363	0.6	172	0.7	140	0.5
351	0.2	171	0.6	139	1.6
350	0.4	170	0.3	138	3.1
349	0.6	169	0.4	137	1.2
338	0.6	168	0.4	136	1.2
337	0.7	167	1.0	135	1.3
336	0.9	166	0.6	134	1.0
335	0.9	165	1.7	133	3.7
323	0.5	164	1.6	132	1.3
322	0.4	163	9.0	131	0.8
321	0.8	162	6.3	130	0.3
320	0.5	161	4.4	129	0.6
309	0.7	160	1.7	128	0.5
308	0.8	159	0.5	127	0.5
307	1.8	158	0.3	126	0.6
306	1.0	157	0.5	125	1.2
305	0.7	156	0.3	124	0.9
192	2.9	155	0.5	123	1.5
191	6.5	154	0.4	122	1.1
190	9.0	153	0.7	121	1.4
189	1.8	152	0.8	120	1.0
183	0.9	151	1.5	119	2.8
182	0.5	150	1.7	118	1.6
181	0.5	149	1.7	117	1.4
180	0.5	148	2.7	116	0.5
179	1.2	147	7.9	115	0.6
178	2.7	146	2.1	114	0.2
177	19.3	145	1.3		

TABLE IX.

m/e	Relative Intensity		m/e	Relative Intensity	
	Apigenin	Acacetin		Apigenin	Acacetin
285		26.2	137		0.4
284		100.0	136		0.4
283		8.8	135		1.6
282		4.5	134		0.6
271			133	3.9	4.2
270	100.0(P)	0.7	132	1.1	15.0
269	13.3	2.1	131	2.3	0.3
268	2.6	0.6	129	1.9	0.6
257		1.2	128.5		0.7
256		4.5	128	2.9	4.2
255		3.1	127	2.8	0.5
254		1.0	126	1.4	0.2
253		1.2	125	3.2	0.5
252		0.1	124	18.0	5.0
243	3.8	0.5	123	9.8	0.4
242	18.7	2.5	122	1.4	0.1
241	6.1	7.4	121	16.3	0.4
240	0.8	0.5	120	2.0	0.2
239	0.8		119	9.0	0.6
230.8(m)		0.7	118	13.7	1.0
230	0.8		117	2.3	3.8
229	1.7		116	1.2	0.4
226.9(m)		1.0	115	5.0	0.9
215		0.2	114	0.4	0.1
214	1.4	0.6	112		0.2
213	4.2	2.6	111		1.3
212		0.3	110		0.4
155	2.0	0.3	107		0.5
154	2.3	0.2	106		0.2
153	22.0	1.1	105		0.6
152	16.1	6.2	104		0.4
151	2.1	0.4	103		0.5
150		0.2	102		0.7
149	3.2	0.3	97		0.9
148	3.0	0.2	96		2.0
140		0.2	95		1.3
139		0.5	91		0.5
138		0.2	90		0.4
			89		3.2

TABLE X.

Caviunin.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
375	50.5	299	3.8	187.5	1.4
374	100.0(P)	298	2.6	187	3.1
373	6.4	288	3.1	183	2.2
372	2.2	287	2.5	180	2.4
360	17.9	286	2.9	179.5	3.5
359	34.5	285	3.3	179	3.0
358	5.1	284	1.6	178	5.8
357	6.7	283	1.5	177	3.7
356	13.0	276	2.5	172	2.4
346	6.6	275	5.0	171.5	1.6
345	11.9	274	4.3	167	2.3
344	11.8	273	1.7	165.5	1.8
343	17.0	272	2.5	165	2.1
342	5.6	271	1.9	164	2.1
341	9.6	260	1.8	163	3.2
338.8(m)	2.1	259	2.4	158	3.2
332	13.6	258	1.6	153	2.8
331	28.3	257	1.8	152	1.5
330	5.5	246	2.0	151	2.9
329	7.6	245	2.7	150	3.9
328	7.8	244	1.7	149	7.8
327	4.5	243	2.0	148	1.5
326	3.0	242	1.7	147	1.9
325	2.2	231	2.3	145	2.1
318	1.8	227	1.0	144	4.1
317	3.8	219	1.7	139	2.8
316	6.8	218	1.6	136	2.0
315	6.2	217	1.9	135	5.4
314	5.8	215	2.4	134	2.8
313	7.0	203	2.5	121	2.3
312	2.6	193	3.3	120	1.6
305.2(m)	4.4	192	6.8	119	3.2
303	4.8	191	6.3	107	2.9
302	5.1	190	1.7	106	2.3
301	8.1	189	2.1	105	1.9
300	3.4	188	1.4		

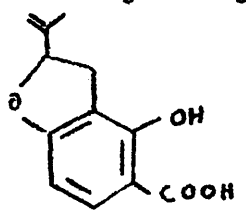
TABLE XI.

Leaserone.

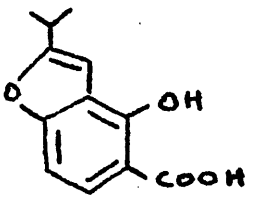
m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
355	39.2	249	2.0	167	12.7
354	100.0(P)	248	4.1	166	2.6
353	3.4	247	4.0	165	4.5
352	3.6	241	4.6	164	3.0
340	7.1	236	6.5	163	5.7
339	18.4	235	25.1	162	2.5
338	5.2	234	6.9	153	8.1
337	5.5	233	11.6	152	3.9
336	4.2	232	1.1	151	4.0
327	2.5	221	3.6	150	2.1
326	7.8	220	13.5	149	9.6
325	17.9	219	51.4	148	3.9
324	4.1	218	3.8	147	4.6
323	4.7	217	6.4	146	2.0
322	6.1	209	2.1	145	5.3
321	14.8	208	4.7	141	2.3
309	3.1	207	5.1	140	4.7
308	2.3	206	23.5	139	2.3
307	2.8	205	3.6	136	2.9
299	4.9	204	2.1	135	4.6
298	3.5	203	3.2	133	4.2
297	2.7	193	8.4	121	8.7
295	4.1	192	9.9	120	11.6
294	2.3	191	45.2	119	6.6
293	4.3	190	3.7	118	5.7
286	3.6	181	2.5	117	4.5
285	10.8	180	9.7	115	7.8
280	2.3	179	53.0	108	4.1
269	2.9	178	3.1	107	5.8
268	2.3	177	7.3	106	2.9
267	2.5	176	12.9	105	13.0
258	3.4	175	2.9	104	2.3
257	13.0	168	2.5	103	7.9

DISCUSSION:

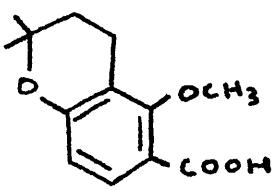
The following tubaic acid derivatives were chosen for a preliminary study of the behaviour of isoprenoid groups:



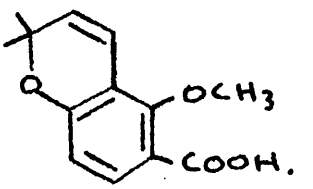
Tubaic acid.



Isotubaic acid.



β-Dihydrotubaic acid methyl ether.



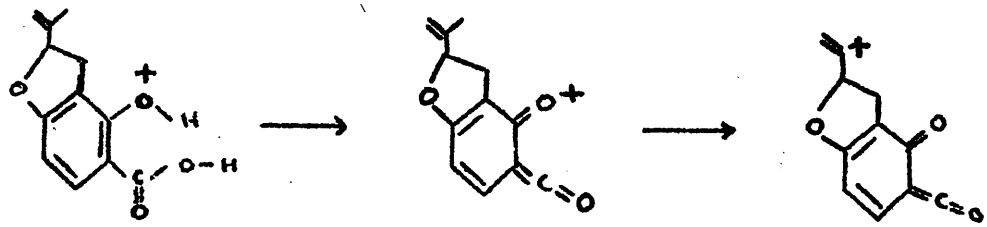
β-Tubaic Acid methyl ether.

In the spectrum of tubaic acid (Table I) the most intense ion appears at $\frac{m}{e}$ = 187, 33 mass units less than the molecular ion ($\frac{m}{e}$ = 229). This is a secondary ion resulting from the consecutive loss of 18 and 15 units, as is shown by the presence of two metastable ions which confirm the transitions:

$$220^+ \longrightarrow 202^+ + 18 \qquad \frac{m}{e} = 185.5$$

$$202^+ \longrightarrow 187^+ + 15 \qquad \frac{m}{e} = 173.1$$

The neutral fragments will be water and a methyl radical (which can also be lost from the molecular ion giving the ion of $\frac{m}{e}$ = 205). The transitions can be represented as follows:



$\frac{m}{e}$ = 220 I $\frac{m}{e}$ = 202 II $\frac{m}{e}$ = 187

The loss of water is to be expected from a salicylic acid. Emery[53] has shown that salicylate esters, on electron impact, form salicylic acid ions which then lose water. This is an α-hydrogen rearrangement similar to that of o-toluic acid[27].

The further degradations of the ions I and II appear to proceed by loss of carbon monoxide. The presence of the ions at $\frac{m}{e}$ = 131 and 146 suggests both carbonyl groups shown

$202^+ \longrightarrow 174^+ + 28$

$187^+ \longrightarrow 159^+ + 28$

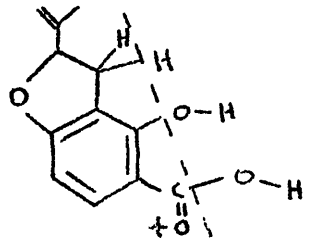
$174^+ \longrightarrow 146^+ + 28$

$159^+ \longrightarrow 131^+ + 28$

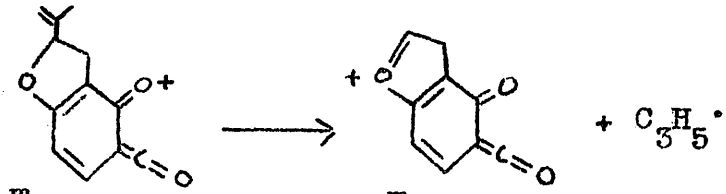
in I and II are lost in this manner.

In the mass range covered there are two other fairly intense ions, at $\frac{m}{e}$ = 161 and 185. The latter involves the loss of neutral fragments of mass 35 from the molecular ion. From an ion containing carbon, hydrogen and oxygen, these can only be H_2O and $^{\cdot}OH$. It is probable that the oxygen atoms are from the two hydroxyl groups (phenolic and carboxylic).

Benzoic acid loses a hydroxyl radical very readily[27]. Phenol loses its oxygen atom as CO or CHO, but alkyl phenols do eliminate H_2O to some extent[43]. A fission of the following type can be proposed for the formation of the ion of $\frac{m}{e}$ = 185.



The ion of $\frac{m}{e}$ = 161 can be more readily explained by a process involving removal of the isopropenyl group.



$\frac{m}{e}$ = 202 $\frac{m}{e}$ = 161

Isotubaic acid shows distinct differences in its spectrum (Table II) from that of tubaic acid. The loss of a methyl group from the molecular ion occurs to an extremely small extent, but the $(P - H_2O)^+$ ion is very abundant. The ion of $\frac{m}{e}$ = 187 is again the most intense in the spectrum; therefore there must be a very ready loss of a methyl group from the $(P - H_2O)^+$ ion. The most striking features of this spectrum are the low intensity of all ions of mass less than $\frac{m}{e}$ = 187 and the increased abundance of doubly charged ions. The ion $(P - 33)^{2+}$ has an intensity of 2.9% of the corresponding

singly charged ion compared to 0.7% for the same ion in the spectrum of tubaic acid. These two features of the spectrum reflect the increase in stability of the benzfuran ring system over the dihydrobenzfuran system of tubaic acid.

It is noticeable that these ions of lower intensity in the spectrum of isotubaic acid appear at the same $\frac{m}{e}$ ratios as the significant ions in the spectrum of tubaic acid. The same metastable ions appear at $\frac{m}{e}$ = 185.5 and 173.1. The ion of $\frac{m}{e}$ = 161 is also present. For tubaic acid it was suggested that this ion is produced by the removal of an isopropenyl radical. It is therefore possible that a rearrangement may take place involving a double bond shift.

In tubaic acid the successive loss of two molecules of carbon monoxide from the ion $(P - 33)^+$ produced a series of ions of high intensity:

$$187^+ \longrightarrow 159^+ \longrightarrow 131^+$$

In isotubaic acid these ions have lower intensity but the series is extended as follows:

$$C_{11}H_7O_3^+ \longrightarrow C_{10}H_7O_2^+ \longrightarrow C_9H_7O^+ \longrightarrow C_8H_7^+ \longrightarrow C_6H_5^+$$

$$\frac{m}{e} = 187 \qquad \frac{m}{e} = 159 \qquad \frac{m}{e} = 131 \qquad \frac{m}{e} = 103 \qquad \frac{m}{e} = 77$$

The removal of a third molecule of carbon monoxide will produce the ion $C_8H_7^+$ which may have the styryl structure. This further loses acetylene.

In dihydro-β-tubaic acid methyl ether (Table III) the $(P - H_2O)^+$ ion cannot be formed by the process involving a

six-membered ring intermediate. This ion is, however, still present though of reduced intensity. It may be possible that the extra hydrogen atom migrates either from the methoxyl group or the saturated ring of the chroman system. The latter appears most probable because the $(P - H_2O)^+$ ion is not formed so readily from β-tubaic acid which contains the unsaturated chromene system. The other intense ions in the upper mass range of the spectrum are $(P - CH_3)^+$ and $(P - 33)^+$. The three fragment ions so far mentioned are related in the same way as the corresponding ions in the tubaic and isotubaic acid spectra. Metastable ions confirm the following transitions:

$$236^+(P) \longrightarrow 221^+ + 15 \qquad \frac{m}{e} = 206.9$$

$$236^+ \longrightarrow 218^+ + 18 \qquad \frac{m}{e} = 201.4$$

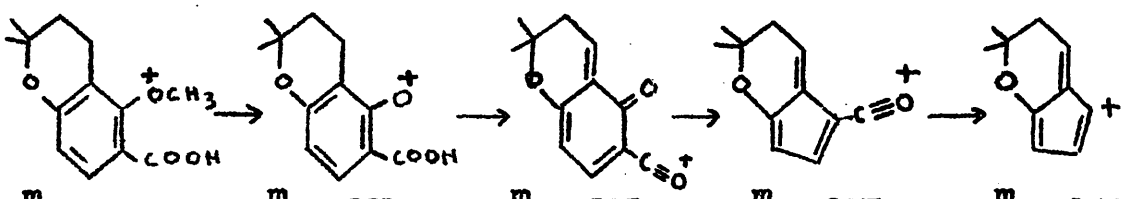
$$221^+ \longrightarrow 203^+ + 18 \qquad \frac{m}{e} = 186.5$$

There are a few ions which appear to be derived from the most intense ion $(P - 33)^+$, by successive elimination of 28 mass units. This appears similar to the behaviour

$$203^+ \longrightarrow 175^+ + 28$$

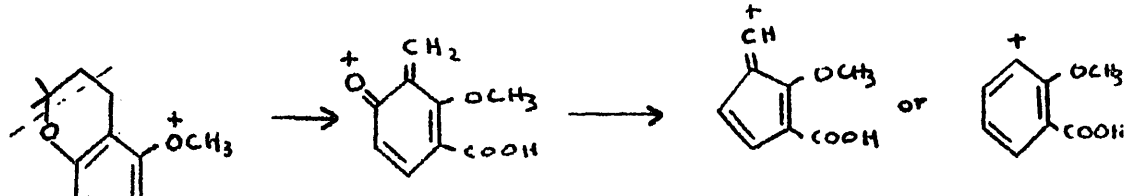
$$175^+ \longrightarrow 147^+ + 28$$

of tubaic and isotubaic acids, but the removal of two molecules of carbon monoxide is only possible if the methoxyl methyl group is first eliminated.



$\frac{m}{e}$ = 236 $\frac{m}{e}$ = 221 $\frac{m}{e}$ = 203 $\frac{m}{e}$ = 175 $\frac{m}{e}$ = 147

The other major fragment ions appear to be derived by fission of the chroman ring.



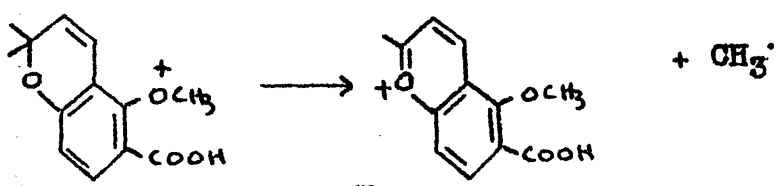
$\frac{m}{e}$ = 180 $\frac{m}{e}$ = 151

The ion of $\frac{m}{e}$ = 181 is very intense and can be obtained by the above process with a concomitant hydrogen migration. This would be a specific rearrangement of type C [15]. The ion of $\frac{m}{e}$ = 134 can be obtained by removal of a hydroxyl radical from the carboxyl group in the ion of $\frac{m}{e}$ = 151.

In this spectrum a large number of intense fragment ions is found as in tubaic acid. The presence of the non-aromatic ring renders the molecular ion less stable. The ease of removal of a C_4 fragment from the 2:2-dimethylchroman ring system distinguishes this compound from the other two acids studied. Examination of other compounds containing this system should confirm whether or not this is a general rule.

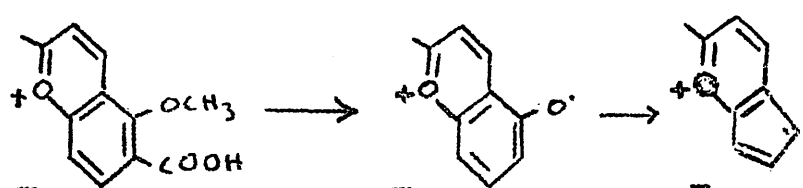
β-tubaic acid methyl ether has a mass spectrum (Table IV) most strikingly different to any of the three already discussed. The most intense ion in the spectrum is the

$(P - CH_3)^+$ ion at $\frac{m}{e} = 219$. This ion is so much more intense than the molecular ion that there must be a driving force for its formation which does not exist for the other three acids. Besides being at a quaternary centre and at a position β to an ether oxygen atom the two labile methyl groups in β-tubaic acid are allylic. A further driving force is the possibility of formation of the completely aromatic benzpyrylium ion.



$\frac{m}{e} = 234$ $\frac{m}{e} = 219$

This transition is confirmed by a metastable ion at $\frac{m}{e} = 205.0$. The only other very intense ion in the spectrum is at $\frac{m}{e} = 160$. This involves the removal of fragments of mass 59 from the $(P - 15)^+$ ion, probably $C_2H_3O_2$ from the methoxy and carboxyl groups. An ion such as the one shown can be formed by loss



$\frac{m}{e} = 219$ $\frac{m}{e} = 160$ $\frac{m}{e} = 132$

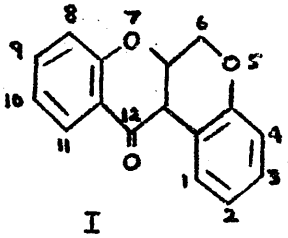
of $(CH_3 + CO_2)$ and can further eliminate carbon monoxide to form the ion of $\frac{m}{e} = 132$. All other ions in the spectrum are of low intensity.

As with isotubaic acid, the presence of a bicyclic aromatic system results in a spectrum with few intense fragment ions. The difference in this case is that this system is not present in the molecular ion but only in the $(P - 15)^+$ ion. The intensity of this ion, expressed as a percentage of total ion intensity is shown below with the values for the intensities of the $(P - 15)^+$ ions of the other acids.

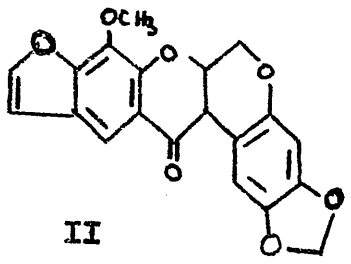
Tubaic acid	0.98
Isotubaic acid	0.18
Dihydro-β-tubaic acid methyl ether	1.58
β-Tubaic acid methyl ether	27.1

In the various cyclic forms of the isoprenoid group as it occurs in natural phenolic compounds the 2:2-dimethyl chromene group appears to lose its methyl group much more readily and can be distinguished from the others by this ready loss of a methyl group.

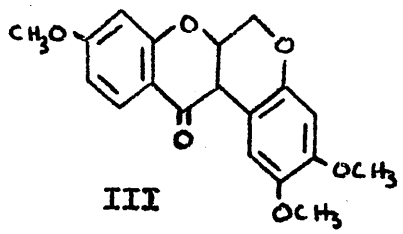
The spectra of ten rotenoids have been obtained (II - XI, Fig.I). It will be noticed that all these compounds contain the chromanochromanone ring system (I, Fig.I) and that all except Pachyrrhizone (II, Fig.I) have methoxyl groups at C_2 and C_3. This is reflected in the similarity in the spectra of these compounds (Tables V, VI and VII) at mass numbers less than $\frac{m}{e} = 193$. The similarity can be seen more readily in the reproduction of the mass spectra of munduserone and elliptone (Fig.II).



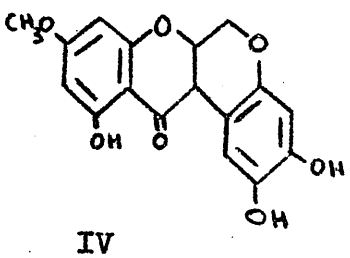
I



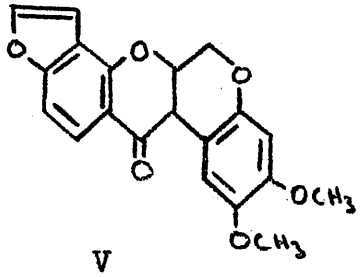
II



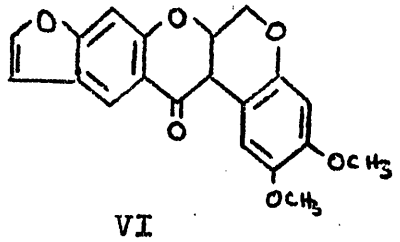
III



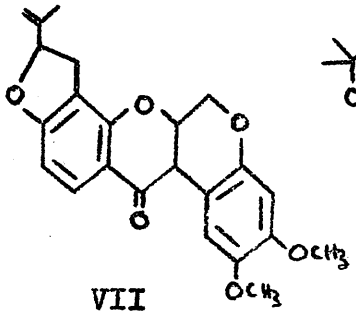
IV



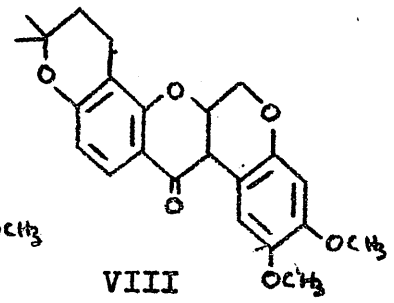
V



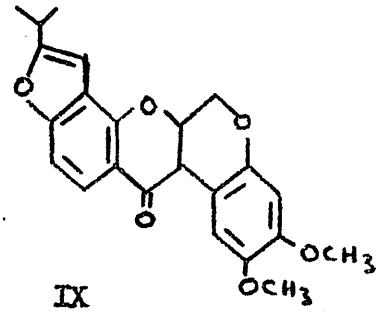
VI



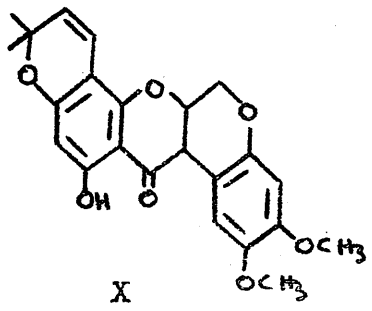
VII



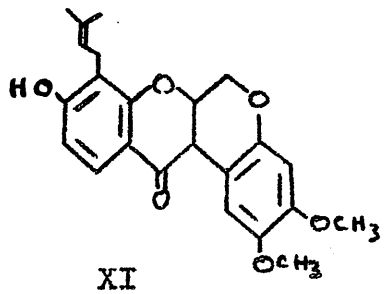
VIII



IX

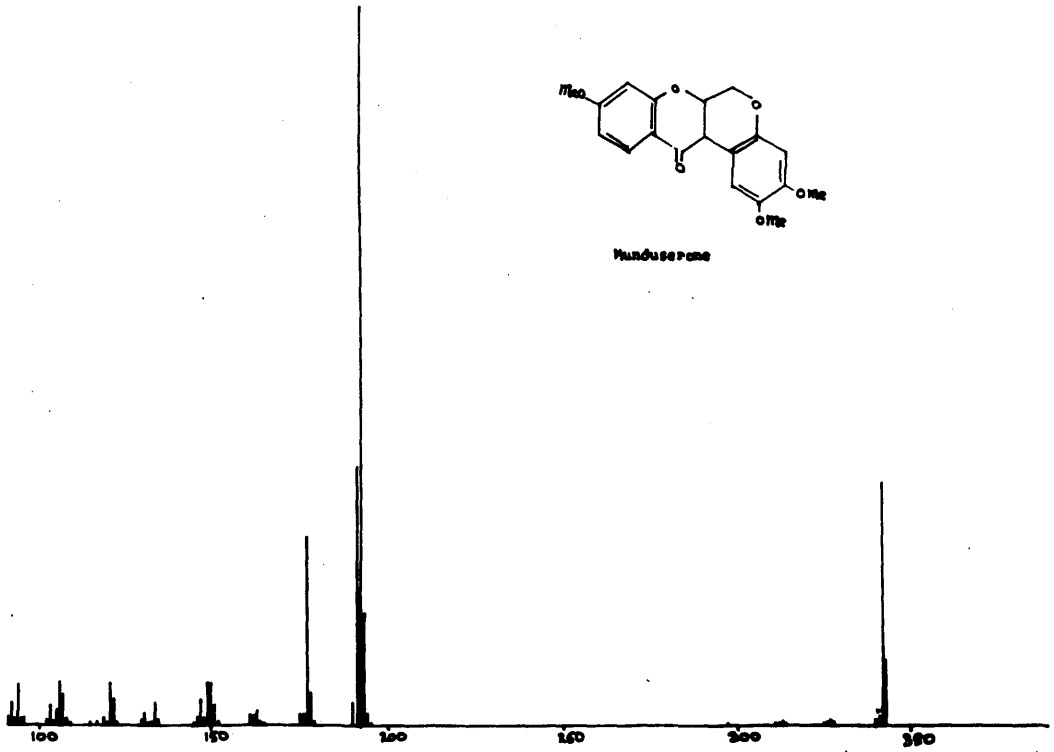


X

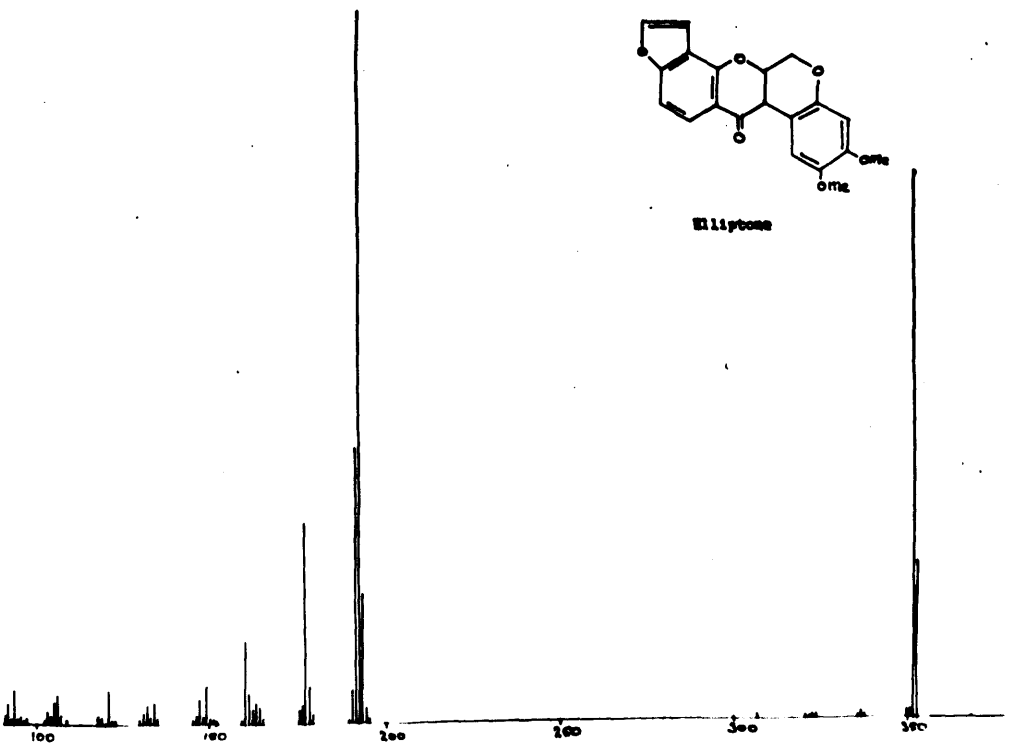


XI

FIG. I



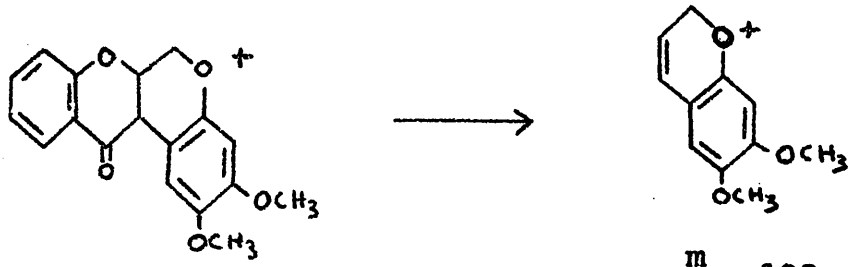
Pseudosesamone



Ellipsone

FIG. II.

The ions common to both spectra are at $\frac{m}{e}$ = 192, 191, 177, 163.2 (metastable), 161, 149, 134, 121 and 106. These must arise from the part of the molecule common to both compounds, i.e. the dimethoxychroman grouping. The most intense ion in the spectra of compounds III - XI (Fig.I) is at $\frac{m}{e}$ = 192. This must arise from the following fission:



$\frac{m}{e}$ = 192

The bonds broken are both labile. One is benzylic and α to a carbonyl group. The other is α to an ether oxygen atom. In the fragment ion a double bond is formed which is in conjugation with a benzene ring.

The other ions mentioned above can be shown to be derived from this 6:7-dimethoxychromene ion. The scheme shown for their formation is shown in Fig.III. The loss of a hydrogen atom to form the ion of $\frac{m}{e}$ = 191 is confirmed by the presence of a metastable ion at $\frac{m}{e}$ = 190.0. This makes a small contribution to a fragment ion of $\frac{m}{e}$ = 190, which is not noted in the tables as being a metastable ion. The ion of $\frac{m}{e}$ = 191 will be stabilised by the formation of the benzpyrylium ring system. The ion of $\frac{m}{e}$ = 177 results from the loss of one

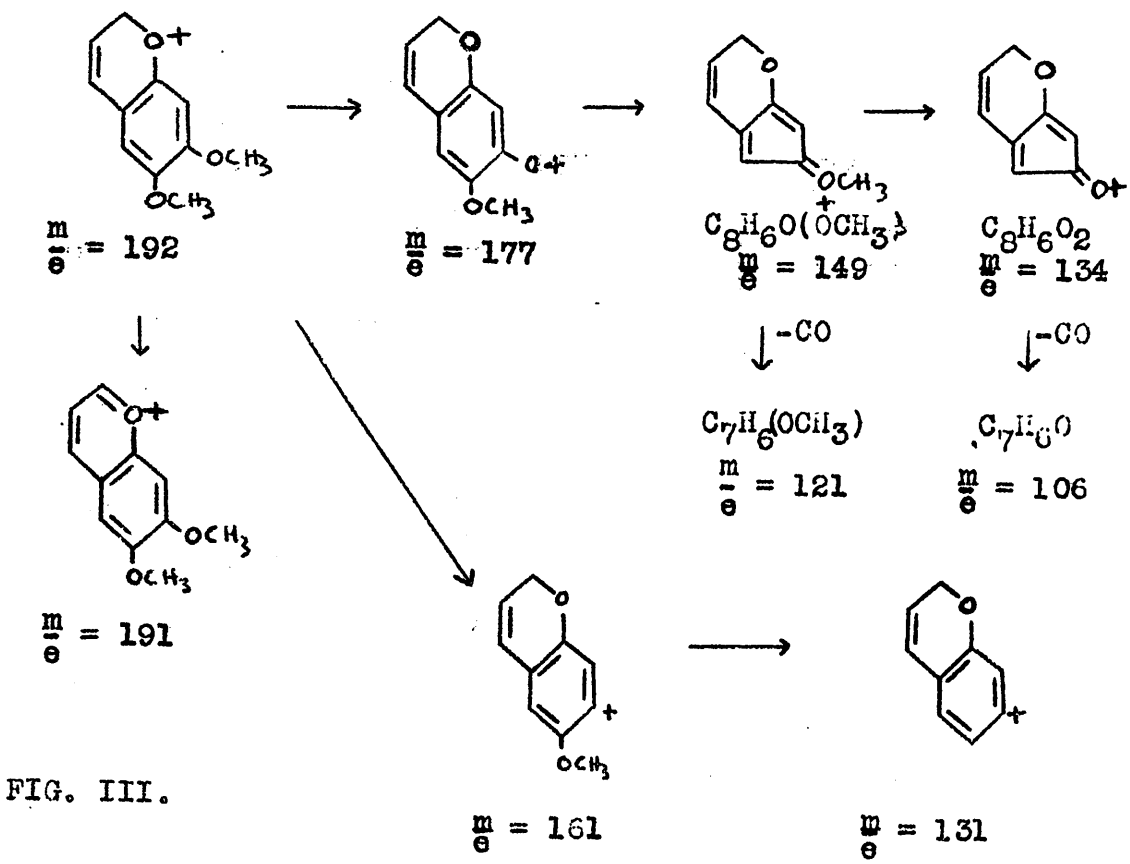


FIG. III.

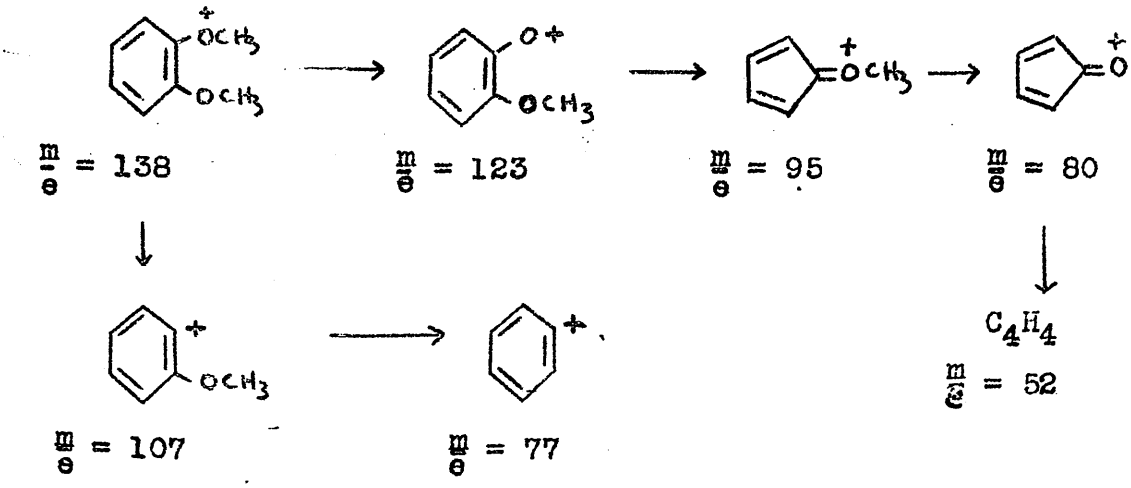
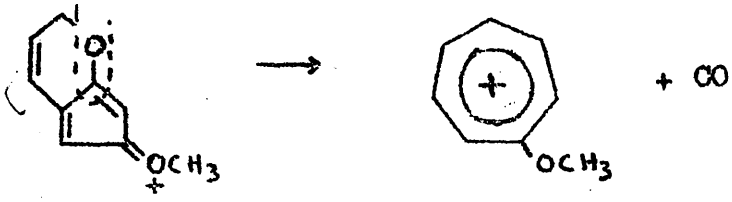


FIG. IV.

of the methoxyl methyl groups. Loss of methyl in a similar fashion from the chromene fragment ion of pachyrrhizone, which has no methoxyl groups, is almost negligible. The origin of this ion is confirmed by the presence of a metastable ion at $\frac{m}{e}$ = 163.2 which corresponds to the transition:

$$192^{+} \longrightarrow 177^{+} + 15.$$

Most of the other ions are typical of the degradation of an aromatic dimethoxy compound, e.g. veratrole[57] which decomposes as in Fig.IV. The one ion which does not fit into this scheme is at $\frac{m}{e}$ = 121. It will result from the loss of carbon monoxide from the ion of $\frac{m}{e}$ = 149. This process involves the fission of three bonds but the stable methoxytropylium ion will be formed.



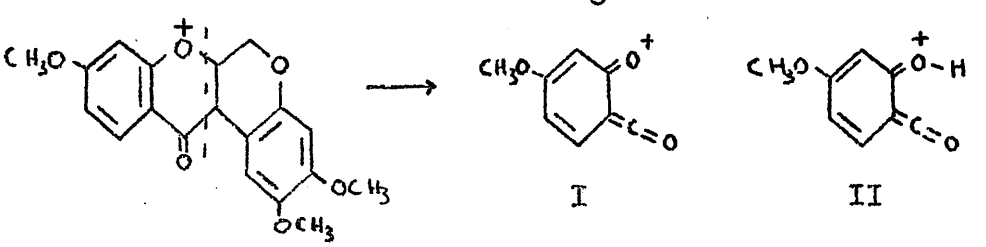
The other important ions in these spectra are those containing the intact tetracyclic system and those containing ring A. They will be discussed separately for each compound.

Munduserone (III, Fig.I).

This is the simplest known rotenoid. In its mass spectrum (Table V) the molecular ion, at $\frac{m}{e}$ = 342 is the only intense ion above $\frac{m}{e}$ = 192. It will be seen from Fig.II that

there are a few ions of mass less than 192 which do not appear in the elliptone spectrum, or appear with greater intensity than in the elliptone spectrum. These are at $\frac{m}{e}$ = 151, 150 and 122.

The ion of $\frac{m}{e}$ = 150 will be the other fragment ion which can be produced by the same fission which gives the dihydroxychromene ion. It will have structure I which is similar to that of the ions produced from esters of salicylic acid[53]. The ion of $\frac{m}{e}$ = 151 will have structure II



I II

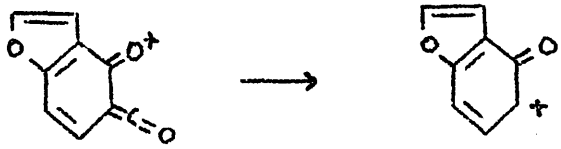
and be produced by the same process as for I, but with a concomitant hydrogen migration. In some of the rotenoids it is found that ions of the type II are more abundant than those of type I. In a few cases a hydrogen atom migrates in the opposite direction and the ion obtained appears at a mass number one unit lower than would be expected for the ion of type I.

The ion of $\frac{m}{e}$ = 122 is obtained by loss of carbon monoxide from I. This is analogous to the formation of the ion of $\frac{m}{e}$ = 174 in tubaic acid.

Elliptone. (V, Fig. I)

As with munduserone, the spectrum of this compound

(Table V) has only a few ions which distinguish it from the other rotenoids. There is an intense molecular ion at $\frac{m}{e}$ = 352 and the dimethoxychromene spectrum similar to that in munduserone. As in all the 2:3-dimethoxyrotenoids the most intense ion in the spectrum is at $\frac{m}{e}$ = 192. The only other ions which can be used to identify the molecule are at $\frac{m}{e}$ = 160 and 132. The former ion has the structure shown below and is analogous to I from munduserone. The ion of $\frac{m}{e}$ = 132 is derived from it by loss of carbon monoxide.



$\frac{m}{e}$ = 160 $\frac{m}{e}$ = 132

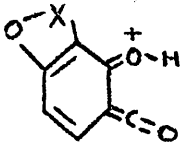
Rotenone (VII, Fig.I) and Isorotenone (IX, Fig.I).

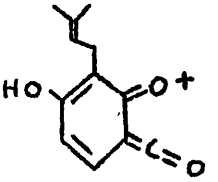
These compounds differ only in the position of the double bond in the isoprenoid group. The spectra of these two compounds (Table VI) are so similar that they can be considered together. The molecular ion appears at $\frac{m}{e}$ = 394: its intensity is greater in the case of rotenone than in isorotenone.

With the introduction of an isoprenoid group there is an increase in the intensity of the $(P - 15)^+$ ion. This ion is present to an extent of 4.4% of the molecular ion in rotenone and 2.6% in isorotenone; i.e. the methyl

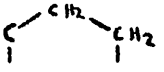
group is lost more readily from the isopropenyl group of rotenone than from the isopropyl group of isorotenone. This is the same order as is found with the loss of a methyl group from tubaic and isotubaic acids.

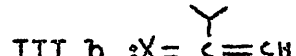
The first significant ion to appear at a lower mass number is at $\frac{m}{e}$ = 203. This is the ion analogous to II from munduserone and has the structure

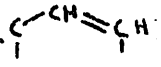




III a :X = 

III c : X =  IV

III b :X = 

III d :X = 

IIIa for rotenone and IIIb for isorotenone. In both cases the ion of $\frac{m}{e}$ = 202, which would be the unrearranged ion analogous to I, is of very low intensity. In both cases there is, however an ion at $\frac{m}{e}$ = 187 which is derived from $\frac{m}{e}$ = 202 by loss of a methyl group. These should be the same ions which are present in high abundance in the spectrum of tubaic and isotubaic acids. The expected transition

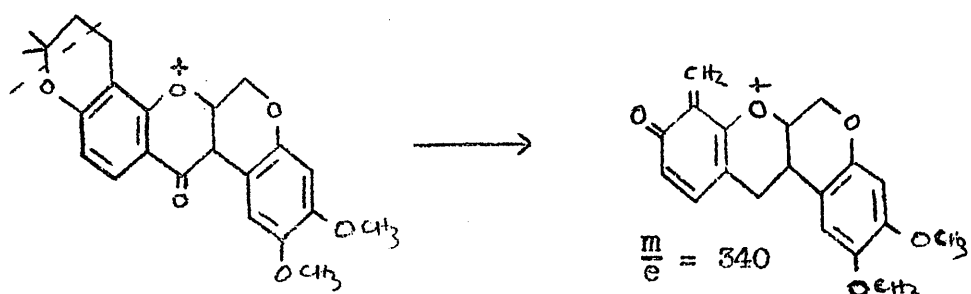
$$202^{+} \longrightarrow 174^{+} + CO$$

may occur but ions derived from this source are of very low intensity and sometimes cannot be detected among the abundant ions of the dimethoxychromene spectrum.

β-Dihydrorotenone(VIII, Fig.I) and Rotenonic Acid(IX, Fig I).

These compounds have the same molecular weight and their spectra (Table VI) are very similar. Both spectra have an intense molecular ion at $\frac{m}{e}$ = 396 and have the most intense ion at $\frac{m}{e}$ = 192. The ions at mass numbers between these two are of low intensity but a few of these are significant. The $(P - 15)^+$ ions are present to an extent of 2.7% and 2.6% of the intensity of the molecular ion for *β*-dihydrorotenone and rotenonic acid respectively.

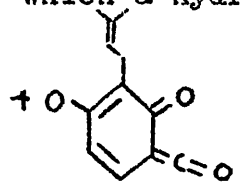
There are also ions present which correspond to the loss of C_4 fragments from the molecular ion. Similar behaviour was found with dihydro-*β*-tubaic acid which contains the 2:2-dimethylchroman group as does *β*-dihydrorotenone. The formation of an ion of $\frac{m}{e}$ = 340 involves the loss of C_4H_8. This can be formulated as follows:



The fragment eliminated in the case of dihydro-*β*-tubaic acid was C_4H_7. The above ion is present only to an extent of 2.1% of the intensity of the molecular ion. This is, however, sufficient to make it distinguishable among other fragment ions of low intensity.

Rotenonic acid contains the $\gamma:\gamma$-dimethyl-allyl group which degrades by benzylic fission. The products are an ion of $\frac{m}{e}$ = 341 and the radical C_4H_7.

In the β-dihydrorotenone spectrum there is an ion of $\frac{m}{e}$ = 205 which will have structure IIIc. The corresponding ion, IV, from rotenonic acid has very low intensity. There is a more intense ion at $\frac{m}{e}$ = 203. This may have the structure V, in which a hydrogen atom has migrated from



V

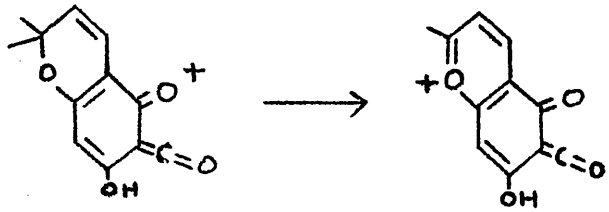
the hydroxyl group to the neutral fragment. The ions of $\frac{m}{e}$ = 205, 204 and 203 are of low intensity and fragment ions derived from these cannot be detected among the abundant ions derived from the hydroxychromene ion.

Toxicarol.(X, Fig.I).

This is an 11-hydroxyrotenone with the isoprene unit present as the 2:2-dimethylchromene grouping. As would be expected by analogy with β-tubaic acid there is a facile loss of a methyl group (Table VII). The $(P - 15)^+$ ion has in this case an intensity of 70% of the molecular ion. Comparative figures for some other rotenoids are as follows:

Rotenone	4.3%
β-dihydrorotenone	2.7%
Isorotenone	2.7%
Rotenonic acid	2.6%

The ion of $\frac{m}{e}$ = 203 is more intense than that at $\frac{m}{e}$ = 218. This is further evidence of the ready loss of a methyl group from 2:2-dimethylchromene ions.



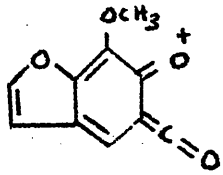
$\frac{m}{e}$ = 218 $\frac{m}{e}$ = 203

The ion of $\frac{m}{e}$ = 218 is accompanied by a more intense ion of $\frac{m}{e}$ = 217. This is analogous to the behaviour of rotenonic acid in which the ion at $\frac{m}{e}$ = 203 is more intense than that at $\frac{m}{e}$ = 204. This can again be explained by a migration of the hydrogen atom from the hydroxyl group.

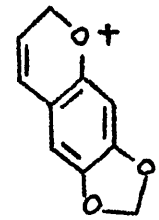
Pachyrrhizone. (II, Fig.I)

In this molecule there is a 2:3-methylenedioxy group instead of the usual 2:3-dihydroxy group. The spectrum (Table VIII) is therefore different from those of all the other rotenoids. The predominant fission occurs, however, by the same process and the most intense ion in the spectrum is the 6:7-methylenedioxychromene ion (VII) of $\frac{m}{e}$ = 176.

By a similar fission the ion VI of $\frac{m}{e}$ = 190 is formed. This is analogous to the ion I from munduserone.



VI



VII

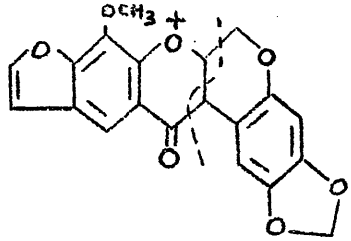
The ions at lower mass numbers are of lower intensity. They appear at $\frac{m}{e}$ = 175, 174, 163, 162, 161, 147, 138 and 133. Since this is the only compound available with the 2:3-methylene dioxy group, it is not possible to determine whether these ions are derived from VI or VII. As an example, there are four possible methods of formation of the ion of $\frac{m}{e}$ = 163.

(1) from VI by loss of C_2H_3. This seems improbable.

(2) from VII by loss of CH. This is also improbable because of the high energy of the CH· radical (ΔH_f = 142 k.cal.[58]).

(3) by loss of carbon monoxide from the rearrangement product at $\frac{m}{e}$ = 191.

(4) from the molecular ion by the following type of fission:

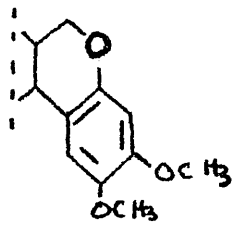


If the latter proposal is correct, the ions of $\frac{m}{e}$ = 179 in the spectra of isorotenone and toxicarol may be formed by the same process.

Sermundone.(IV, Fig.I).

The following is an example of the determination of a partial structure by mass spectrometry. The sample was isolated from the bark of Mundulea Sericea. Its ultraviolet absorption spectrum suggested that it was a rotenoid or flavonoid type of compound.

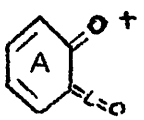
A preliminary examination of the mass spectrum is sufficient to demonstrate that this compound is a rotenoid. There is a substantial molecular ion at $\frac{m}{e}$ = 358 and the most intense ion is at $\frac{m}{e}$ = 192. At lower mass numbers there are ions at $\frac{m}{e}$ = 191, 177, 163.2 (metastable), 161, 149, 147, 134 and 121. The intensities of these ions are characteristic of the spectrum of a 2:3-dihydroxy-rotenoid. This confirms the presence of the following feature in the molecule, with one reservation. The same group with a



difference in the orientation of the methoxyl groups may give a spectrum similar to the above.

The other fragment of the molecule must have mass 166 and there are ions present at $\frac{m}{e}$ = 167, 166 and 165 which must be obtained by ionization of this fragment with and without concomitant hydrogen migrations. The presence of the ion at $\frac{m}{e}$ = 165 suggests that there may be a hydroxyl

group on ring A (c.f. $\frac{m}{e}$ = 203 from rotenonic acid and $\frac{m}{e}$ = 217 from toxicarol). The ion of $\frac{m}{e}$ = 166 will be of the following type:

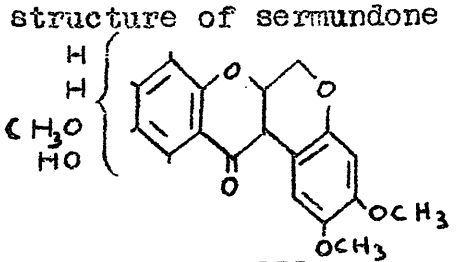


This unsubstituted ion would have $\frac{m}{e}$ = 120, which is 46 mass units less than the ion obtained. The only combination of carbon, hydrogen and oxygen which can satisfy normal valence requirements and have a total mass of 46 units is CH_2O_2.

Ring A must therefore be $C_6H_2(OCH_3)OH$, $C_6H_2(CH_2OH)OH$ or $C_6H(OH)_2CH_3$. There are several ions in the spectrum which appear to be derived from the ion of $\frac{m}{e}$ = 166. These are at $\frac{m}{e}$ = 151, 138 and 123. They can be related in the following manner. There must therefore be a labile methyl

$$\begin{array}{ccc} 166^+ & \xrightarrow{-CH_3} & 151^+ \\ \downarrow -CO & & \downarrow -CO \\ 138^+ & \xrightarrow{-CH_3} & 123^+ \end{array}$$

group on ring A. A nuclear methyl group would not be labile so there must be a methoxyl group present. The formula $C_6H_2(OCH_3)OH$ can now be written for ring A and the partial structure of sermundone will be VIII.



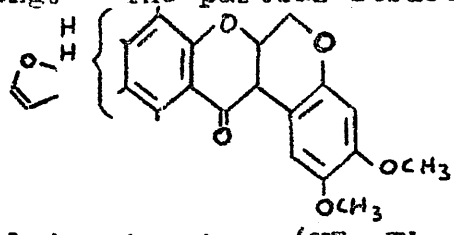
VIII

The structure IV (Fig.I) has been proposed independently[59] and has since been proved to be correct by an unambiguous synthesis from toxicarol[59].

Isoelliptone.(VI, Fig.I)

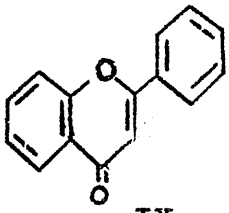
This is another example of a partial structure determination by mass spectrometry. The presence of the dimethoxychromene and derived fragment ions indicates the presence of the dimethoxychroman group. The other important ions in the spectrum are at $\frac{m}{e}$ = 352 (molecular ion), 160 and 132. There is a great similarity to the spectrum of elliptone. The significant ions appear at the same mass numbers in both spectra. The only differences are in intensity, and are small enough to suggest that the two compounds are isomeric.

Since both compounds contain the 2:3-dihydroxychroman system the difference must be in the other fragment. The only possible difference is in the position of fusion of the furan ring. The partial structure is as follows:

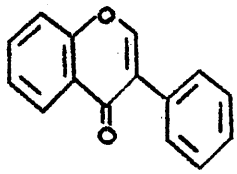


The complete structure (VI, Fig.I) has been proposed[59] from comparisons of the ultra-violet and infra-red spectra of elliptone and isoelliptone.

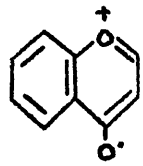
Flavones and Isoflavones.



IX

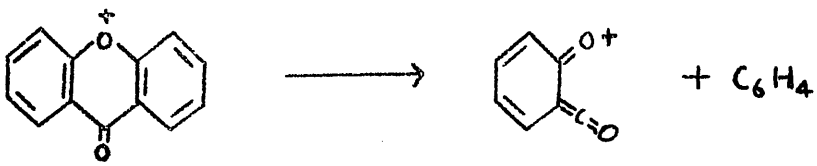


X

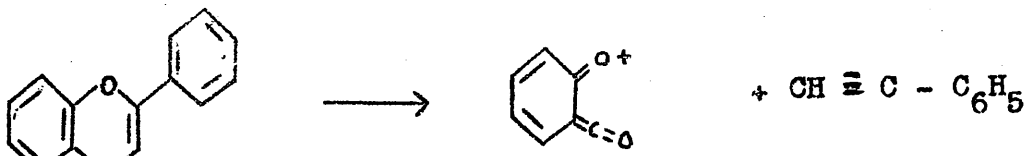


XI

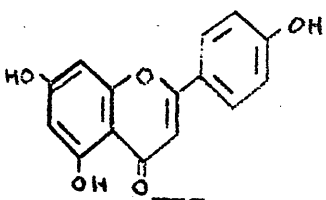
The flavones (IX) and isoflavones (X) both have the chromenone ring system. This may take the completely aromatic form XI when ionized. Fission across the heterocyclic ring, as was found in the rotenoids, will be more difficult in these cases. The same type of fission is found in the mass spectrum of xanthone [4] to a small extent.



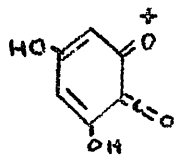
The neutral product formed will not be a stable molecule as is possible with the same type of fission in the flavones.



Apigenin (XII).

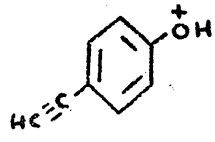


XII



$\frac{m}{e}$ = 152

XIII

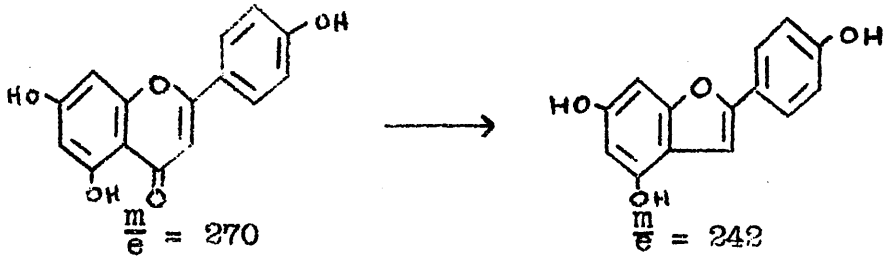


$\frac{m}{e}$ = 118

XIV

This is a simple flavone. The most intense ion in the spectrum (Table I X) is the molecular ion. The only intense

fragment ion in the higher mass range is at $\frac{m}{e}$ = 242. It is probably produced by elimination of carbon monoxide from the molecular ion. The same process occurs in the spectrum of xanthone. In the case of apigenin the product should be

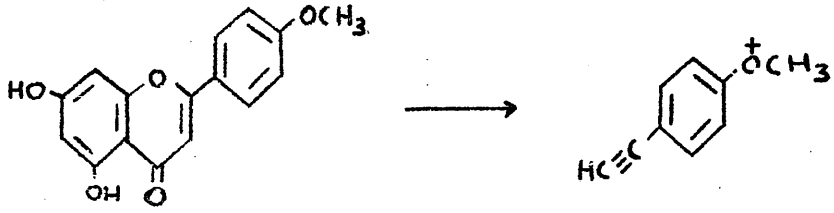


a benzfuran. There is a further loss of CHO to give an ion of $\frac{m}{e}$ = 213. The oxygen atom involved may be either from the ether or from one of the phenolic groups.

The ions of $\frac{m}{e}$ = 152 and 118 (XIII and XIV) are produced by fission of the heterocyclic ring. A similar type of fission produced the most intense ion in the rotenoid spectra. In the flavones the fragment ions are of much lower intensity. The ion of $\frac{m}{e}$ = 124 is derived from XIII by loss of carbon monoxide.

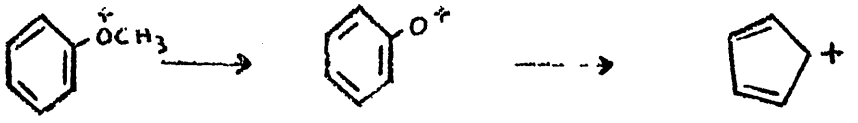
Acacetin.(XV)

The spectrum of this compound (Table IX) confirms the process of fission of the chromenone ring proposed for apigenin. The relevant ions appear at $\frac{m}{e}$ = 152 (XIII) and 132 (XVI).



XV. XVI

The most intense ion is the molecular ion ($\frac{m}{e}$ = 284). The upper mass range of the spectrum gives evidence of degradation of the methoxyl group besides the loss of carbon monoxide as in apigenin. The ions involved are at $\frac{m}{e}$ = 269 (P - CH_3), $\frac{m}{e}$ = 256 (P - CO) and $\frac{m}{e}$ = 241 (P - CH_3,CO). The latter ion is the most intense of the group as is generally found with aromatic methoxyl compounds[57]. The usual process of formation is as follows:



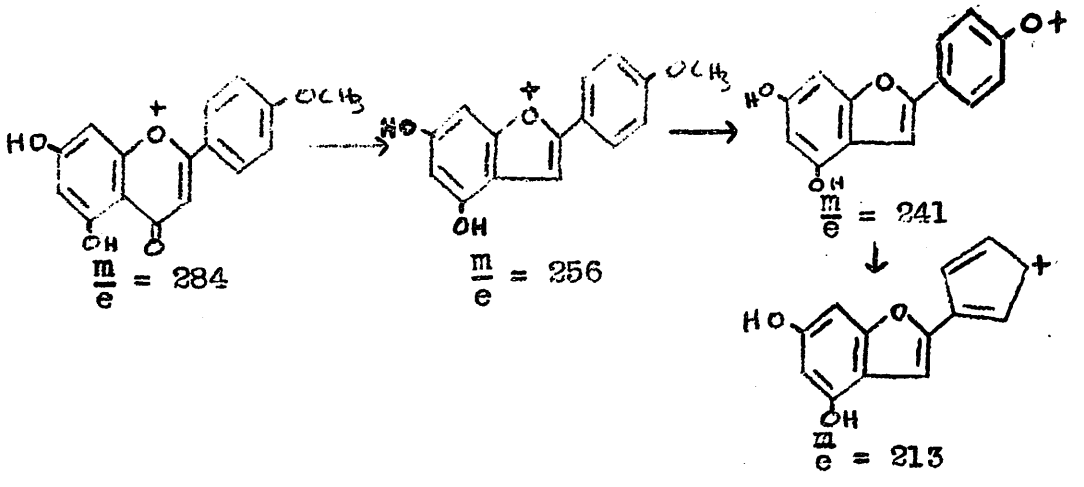
$(P)^+$ $(P - CH_3)^+$ $(P - CH_3CO)^+$

In this case, however, there is evidence of another process leading to the formation of the ion of $\frac{m}{e}$ = 241. There are metastable ions present which correspond to the following transitions:

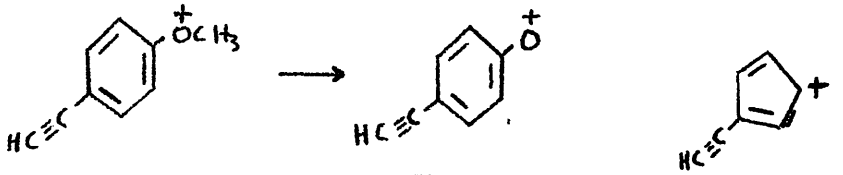
$284^+ \longrightarrow 256^+ + 28$ $\frac{m}{e}$ = 230.8

$256^+ \longrightarrow 241^+ + 15$ $\frac{m}{e}$ = 226.9

The presence of an ion of $\frac{m}{e}$ = 213 suggests that the ion of $\frac{m}{e}$ = 241 may be further degraded. The complete process may be as follows:



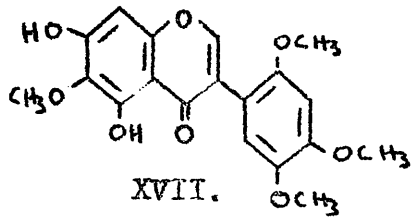
The ion XIII can lose two molecules of carbon monoxide consecutively to form the ions of $\frac{m}{e}$ = 124 and 96. XVI decomposes in a manner typical of aromatic methoxyl compounds.



$\frac{m}{e}$ = 132 $\frac{m}{e}$ = 117 $\frac{m}{e}$ = 89

Caviunin. (XVII)

This is an isoflavone with a rather complicated substitution pattern. The presence of four methoxyl groups



XVII.

increases the probability of the loss of a methyl group from the molecular ion. The $(P - CH_3)^+$ ion has an intensity 34.5% of the molecular ion, which is the most intense in the spectrum (Table X). The other ions expected from the degradation of an aromatic methoxyl group are also intense. These appear at $\frac{m}{e}$ = 343 $(P - OCH_3)$ and 331 $(P - CH_3CO)$. The mechanism of formation of the latter is confirmed by the presence of a metastable ion at $\frac{m}{e}$ = 305.2. This corresponds to the transition:

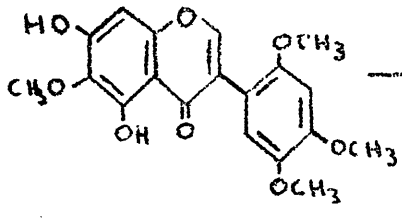
$$359^+ \longrightarrow 331^+ + 28.$$

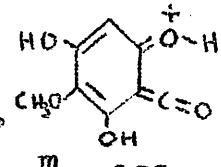
The ion of $\frac{m}{e}$ = 356 must be formed by the elimination of water from the molecular ion. This is confirmed by another metastable transition:

$$374^{+} \longrightarrow 356^{+} + 18 \qquad \frac{m}{e} = 338.8$$

One would expect this to involve one of the phenolic hydroxyl groups and possibly a hydrogen atom from the adjacent methoxyl group. Similar types of fragmentation do not occur in the cracking pattern of guaiacol (o - methoxy phenol)[57] but the loss of a phenolic hydroxyl group and of water does take place from the molecular ions of polyhydroxyanthraquinones[30] and o-cresol[42].

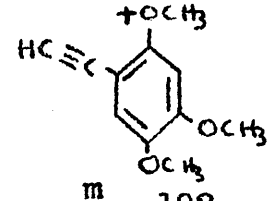
Various ions are observed in the mass range immediately below $\frac{m}{e}$ = 331, which are derived by degradation of the ring substituents. These ions and the number of possible methods of formation of each are so numerous that no purpose can be served by trying to derive mechanisms for their formation. At the lower mass range it is, however, possible to detect the ions formed by fission of the heterocyclic ring. These ions are XVIII and XIX.





$\frac{m}{e}$ = 183

XVIII

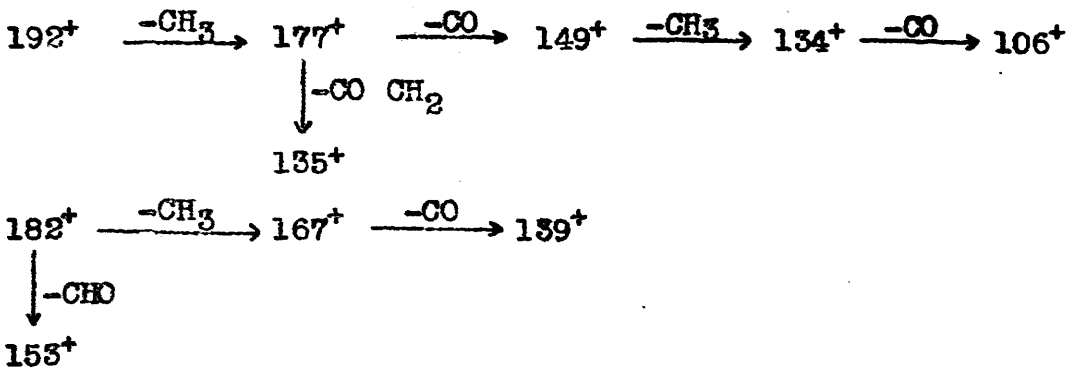


$\frac{m}{e}$ = 192

XIX

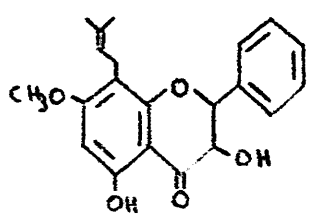
Other prominent fragment ions at lower mass numbers appear to be derived from XIX and from the ion of $\frac{m}{e}$ = 182, which is the simple fission product of structure similar to XVIII. These fragment ions appear to be related in

the following manner:



The spectrum in this region is complicated by the presence of intense doubly charged ions. The fragment ions XVIII and XIX are, however, sufficiently abundant to be recognised.

Leaserone.(XX)



XX

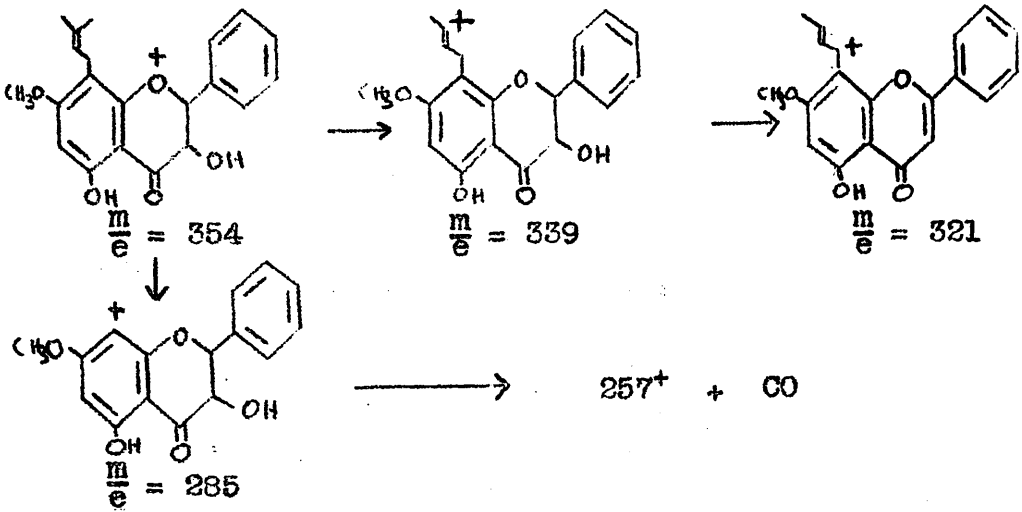
This compound is a hydroxyflavanone and it is noticeable that the heterocyclic ring is similar to that in the rotenoids. The spectrum (Table XI) shows more extensive fragmentation than is found with the flavones and isoflavones, but the most intense ion is still the molecular ion. In this respect fragmentation appears to be less extensive than in the rotenoids.

The spectrum in the mass range immediately below the

molecular ion shows the sort of fragmentation typical of the substituents present in the ring system. The ion derived by loss of a methyl group is of considerable intensity, but not sufficiently intense to be confused with a 2:2-dimethyl chromanoid spectrum. The elimination of water to give the ion of $\frac{m}{e}$ = 336 is as expected from a cyclic alcohol. The ion of $\frac{m}{e}$ = 325 is formed by loss of CHO from the molecular ion. The ɣ:ɣ -dimethylallyl group loses C_4H_7, as did rotenonic acid, but appears to fragment more readily at the phenylallylic bond as follows:

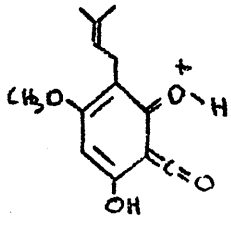
$$354^+ \longrightarrow 285^+ + C_5H_9$$

Other major fragment ions can be formed by the following processes:

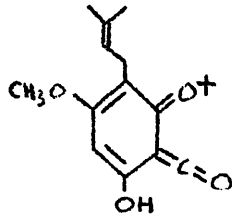


As with the rotenoids, flavones and isoflavones, the fragment ions become less intense at lower mass numbers, until the fragment ions appear which are derived from the molecular ion by fission of the heterocyclic ring. Three

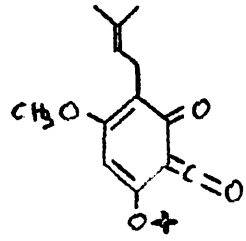
intense ions appear at $\frac{m}{e}$ = 235, 234 and 233, which are derived by this type of fission.



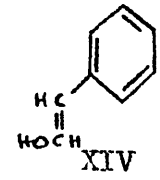
XXI $\frac{m}{e}$ = 235



XXII $\frac{m}{e}$ = 234



XXIII $\frac{m}{e}$ = 233



XIV

XXI and XXII are similar to fragment ions obtained from the rotenoids and flavones. XXIII is analogous to certain ions in the spectra of the hydroxyrotenoids, e.g. V from rotenonic acid.

The other fragment from the fission which produces XXII may be ionized, and appears at $\frac{m}{e}$ = 120 (XIV). The other ions in this region of the spectrum are decomposition products of XXII. They are produced by the following processes:

$$234^+ \longrightarrow 219^+ + CH_3$$

$$234^+ \longrightarrow 206^+ + CO$$

$$234^+ \longrightarrow 179^+ + C_4H_7$$

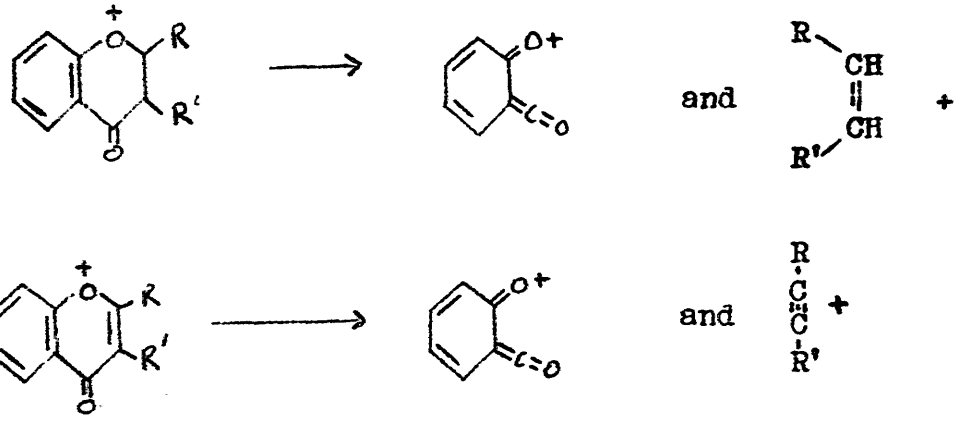
$$206^+ \longrightarrow 191^+ + CH_3$$

General Observations.

From the study of the mass spectra of these compounds it can be seen that such evidence can be useful in the

determination of structures of flavones and related compounds. All compounds which contain the chromenone ring system produce fragment ions of low to moderate intensity in the lower mass ranges. Those with the chromanone system fragment much more readily. It is, however, impossible to distinguish between flavones and isoflavones from the evidence so far accumulated.

In all the compounds studied the ions produced by the following fissions could be detected:



From the mass/charge ratios of these ions, it is possible to obtain some information about the distribution of substituents between the two benzene rings. Some knowledge of the nature of the substituents can be gained by an examination of the ions produced by the removal of small fragments from the molecular ion.

A limited amount of information may be obtained concerning the nature of any isoprenoid group present.

The 2:2-dimethylchroman group is easily recognised.
It may be possible to detect the presence of a $\gamma:\gamma$ -dimethyl-allyl or 2:2-dimethyl-chroman group but it is not easy to distinguish between the two.

PART III.

The Mass Spectra of some Carbohydrate Derivatives.

INTRODUCTION:

The carbohydrates form another group of naturally occurring compounds which have not been examined by the mass spectrometric method until recently. The reason for this neglect is the difficulty in obtaining a sufficient pressure of the compound in the vapour phase without extensive decomposition, which would be unavoidable in the normal heated inlet system. There is, however, some useful information to be obtained from the behaviour under electron impact of simpler saturated oxygen compounds.

Some authors have commented on the facile elimination of water from alcohol molecular ions.[60,61] For higher normal chain alcohols the majority of ions appear to be derived from the $(P - H_2O)^+$ ion.[60] Secondary and tertiary alcohols have a tendency to cleave at a carbon-carbon bond adjacent to a hydroxyl group. This tendency has been explained by assuming that the fragment ion is stabilised by oxonium ion formation.

$$R - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \overset{+}{O}H \longrightarrow CH_3 - CH = \overset{+}{O}H + R^{\cdot}$$

The largest chain branch is usually lost from the ion.

Aliphatic ethers[56] are similar in behaviour to the alcohols. Cleavage α and β to the oxygen atom can take place. α - Cleavage sometimes takes place with rearrangement of one hydrogen atom, i.e.

$$R - CH_2 - CH_2 - \overset{+}{O}R \longrightarrow R - CH = \overset{+}{C}H_2 \quad + \quad ROH.$$

β-Cleavage will allow the formation of a stable oxonium ion as with the alcohols. The most intense

$$CH_3 - \overset{+}{O} - CH_2R \longrightarrow CH_3 - \overset{+}{O} = CH_2 \quad + R^{\cdot}$$

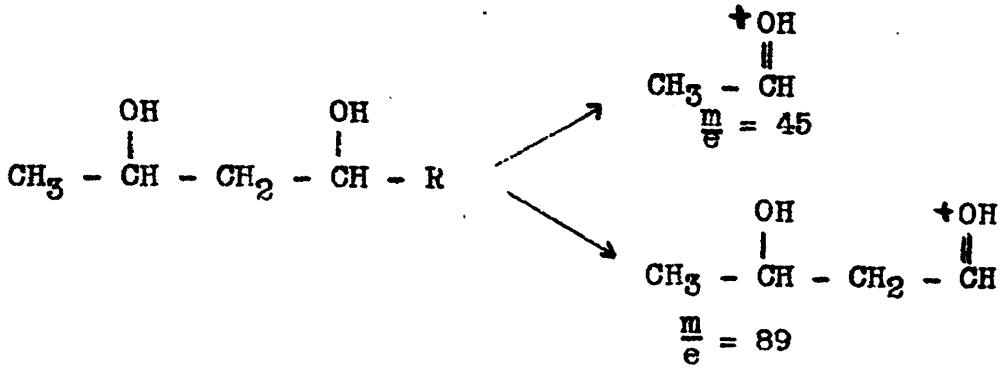
$$\frac{m}{e} = 45$$

ion in many methyl ether spectra is at $\frac{m}{e} = 45$. There are also present in some ether spectra prominent ions produced by α and β cleavage with concomitant hydrogen migration: e.g.

$$CH_3\text{-}CH_2 - \overset{+}{O} - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3 \longrightarrow C_2H_4 \quad + \quad H\overset{+}{O} = \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} \quad + \quad CH_3^{\cdot}$$

$$\frac{m}{e} = 59$$

In studies on the structure of phthiocerol[62], Ryhage discussed the spectra of some 1:3-diols. In phthiocerol and similar diols the most intense ions in the spectra are produced by fission processes similar to those of monohydric secondary alcohols.



The acetals differ from these compounds in that there is present a saturated carbon atom bonded to two oxygen atoms. It has already been noted by Beynon[8] that this is an unstable system. Friedel and Sharkey[63] find for a series of acetals that there is a very small molecular ion in some cases and it is absent in others. In methyl acetals there is loss of a hydrogen atom and of a methoxyl group; i.e. fission takes place at bonds α and β to the oxygen atom.

Determination of the molecular weight of such compounds is difficult because of the absence of the molecular ion in many cases. There is, however, a suitable method which can be employed if there is sufficient sample pressure in the ionization chamber. Under this condition ion-molecule reactions can take place and the most common of such reactions which occurs in conventional mass spectrometers is the formation of the $(P + H)^+$ ion. This reaction in methanol[64] is as follows:

$$CH_3OH + e \longrightarrow CH_3\overset{+}{O}H + 2e$$

$$CH_3\overset{+}{O}H + CH_3OH \longrightarrow CH_3\overset{+}{O}H_2 + CH_3O$$

The same type of ion has been found in the spectra of ethers[56] and of other basic compounds. The relative intensity of such an ion is proportional to the square of the sample pressure. It is also sensitive to changes of the repeller voltage. These effects can be used to identify the ion.

There have been a few examples of electron impact studies on carbohydrates by Reed and his collaborators. They measured appearance potentials of the ion $C_6H_{11}O_5$ from the methyl glucosides and other glycosides[65]. These values were correlated with the glycoside bond energies. In a preliminary report on the mass spectrum of a sample of methylated laminarin[66], attention was confined to a series of low intensity ions which were derived by fission at the glycosidic links of this polysaccharide. These were ions containing up to three glycoside units.

Further work by this group[67] included a study of the principal ions in the mass spectra of the inositols. It was suggested that some of these ions were derived from a furanoid intermediate. In this section of the thesis the complete spectra will be discussed. These have been obtained for the eight possible isomers. The spectra of some other carbohydrate derivatives are discussed and an attempt will be made to distinguish between types of polyhydroxy compounds by their mass spectra.

EXPERIMENTAL:

The inositols were provided by Professor S.J.Angyal of the University of New South Wales, Sydney. The other samples were provided by Dr. P.A.Finan of the University of Sheffield.

Spectra were obtained by the same procedure and under the same conditions (3 kV, 50 eV) as in Part II. The nature of the $(P + 1)^+$ and $(P - 17)^+$ ions of the inositols were confirmed by noting the change in relative intensity of these ions on reduction of the voltage on the Nier Repeller Plate.

TABLE I.

Mannitol.

m/e	Relative Intensity	m/e	Relative Intensity
183	0.8	81	2.8
165	0.4	80	0.6
151	0.5	79	1.0
147	0.7	78	0.3
146	3.9	77	0.8
137	0.7	76	0.5
136	0.4	75	4.1
135	0.9	74	45.3
134	2.8	73	100.0
133	23.9	72	2.9
129	0.8	71	10.5
128	0.5	70	2.3
123	1.0	69	8.2
122	0.5	68	1.8
121	1.6	67	2.3
116	1.6	66	0.6
115	3.3	65	0.6
111	1.4	64	1.2
109	1.3	63	0.7
105	1.6	62	3.4
104	8.1	61	68.9
103	66.4	60	19.9
102	0.9	59	5.0
99	0.8	58	3.2
98	1.1	57	24.6
97	3.3	56	24.4
96	1.2	55	15.0
95	2.3	54	1.9
94	0.8	53	1.8
93	0.7	52	0.4
92	0.7	51	0.7
91	8.2	47	3.6
89	1.7	46	3.2
87	2.1	45	46.0
86	2.9	44	51.9
85	12.1	43	68.4
84	1.3	42	1.4
83	2.7	41	1.7
82	1.5	40	0.4
		39	0.7

TABLE II.

1:4-anhydro-Mannitol.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
165	0.9	109	0.7	84	2.0
147	1.0	106	0.2	75	3.9
146	2.4	105	2.0	74	9.9
134	0.8	104	3.4	73	75.0
133	5.1	103	44.5	72	2.2
131	0.4	102	1.0	71	14.5
129	0.6	101	0.4	70	6.2
128	1.2	100	0.8	69	30.0
119	1.5	99	4.5	68	2.2
118	0.3	98	1.2	62	1.2
117	4.0	97	2.0	61	39.8
116	0.9	96	0.5	60	29.6
115	6.6	91	2.3	59	7.8
113	0.3	89	0.8	58	3.7
112	0.4	88	3.1	57	55.8
111	1.6	87	11.1	56	21.5
110	0.5	86	100.0	55	20.1
		85	18.1	54	2.5

2-deoxy-1:5-anhydrosorbitol.

m/e	Relative Intensity	m/e	Relative Intensity	m/e	Relative Intensity
149	0.5	98	1.0	68	1.3
148	0.2	97	0.5	62	2.5
131	0.1	91	2.1	61	56.8
130	2.5	89	1.2	60	79.2
129	0.5	88	14.7	59	13.4
120	0.9	87	38.0	58	69.7
119	1.1	86	3.6	57	96.1
118	4.6	85	1.5	56	34.1
117	60.7	84	1.4	55	25.3
116	1.6	76	0.7	54.	2.2
113	3.9	75	9.9	47	6.1
112	0.9	74	38.7	46	2.4
102	1.6	73	31.7	45	53.3
101	2.6	72	6.4	44	39.0
100	7.4	71	61.8	43	100.0
99	37.6	70	38.6	42	25.5
		69	17.0		

TABLE III.

I.= Methyl-β-D-Glucopyranoside.
II.= Methyl-α-D-Galactopyranoside.

m/e	Relative Intensity I.	II.	m/e	Relative Intensity I.	II.
195	0.34	0.15	85	6.2	8.4
193	0.29	0.03	75	12.3	10.1
164	1.0	0.6	74	44.3	54.1
163	8.1	4.7	75	46.8	43.6
147	0.4	0.5	72	2.9	3.6
146	0.6	1.0	71	22.0	29.7
145	4.7	5.7	70	6.6	6.4
144	6.9	4.2	69	7.3	7.4
133	1.9	2.6	62	1.6	2.5
132	1.1	0.3	61	32.5	35.4
131	12.0	3.7	60	100.0	100.0
129(m)	0.5	0.5	59	6.1	9.7
127	0.8	1.3	58	2.5	4.6
121	3.0	2.2	57	34.3	41.5
120	0.7	1.1	56	10.9	10.7
117	1.2	1.4	55	6.2	7.2
116	7.3	5.6	54	1.1	0.8
115	0.6	0.9	47	1.1	1.3
104	3.8	3.2	45	10.8	16.9
103	4.5	6.8	44	5.9	6.6
102		0.4	43	11.1	18.1
101	1.1	1.8	42	5.9	8.4
100		0.5	41	4.4	6.4
99	2.6	2.2	33	4.8	7.1
98	8.9	6.8	32	2.4	2.0
97	6.6	6.3	31	10.8	22.6
91	1.1	8.2	30	1.2	1.8
90		0.3	29	10.8	19.6
89	1.5	2.1	28	13.8	17.8
88	1.0	1.3	27	3.0	7.3
87	7.0	9.1			
86	3.1	3.4			

TABLE IV.

Inositols.

m/e	Cis	L	Neo	Allo
181	0.94	0.08	0.18	0.26
163	0.08	0.04	0.35	0.25
145	0.4	0.3	0.6	0.4
144	4.2	2.5	2.2	1.4
127	0.1	0.2	0.4	0.3
126	0.4	0.5	0.9	0.4
115	0.7	1.6	1.0	0.7
109	0.3	0.3	1.4	0.8
103	0.2	1.0	0.7	0.7
102	3.4	14.6	10.3	10.9
101	0.3	0.4	0.4	0.3
98	0.6	0.8	1.1	0.7
97	0.9	1.2	2.0	1.5
91	2.9	2.4	3.3	2.5
90	0.5	0.7	0.7	0.5
89	1.6	3.4	2.7	2.6
85	0.7	1.3	2.1	1.8
84	0.5	0.6	0.9	0.8
83	0.7	0.6	1.6	1.4
81	0.6	0.5	1.9	1.4
75	0.6	0.6	0.7	0.6
74	4.2	4.7	4.8	4.4
73	100.0	100.0	100.0	100.0
72	3.9	5.5	5.7	4.8
71	7.7	8.9	8.8	9.5
70	0.6	0.7	1.2	0.9
69	1.6	1.6	2.9	2.7
61	2.5	3.9	3.2	3.7
60	11.2	17.6	17.1	20.0
57	2.9	3.7	4.8	5.8
56	2.6	1.5	2.2	2.4
55	2.6	3.2	4.3	4.9
54	0.9	1.2	1.1	1.2
53	0.4	0.5	0.7	0.8
47	0.6	1.2	0.7	1.0
45	3.9	4.9	4.1	4.8
44	2.0	2.9	3.8	2.3
43	6.6	9.8	8.3	10.4
42	4.4	6.7	2.6	5.4
41	1.9	2.4	3.2	4.0
39	1.2	1.4	1.5	1.7

- Cont'd -

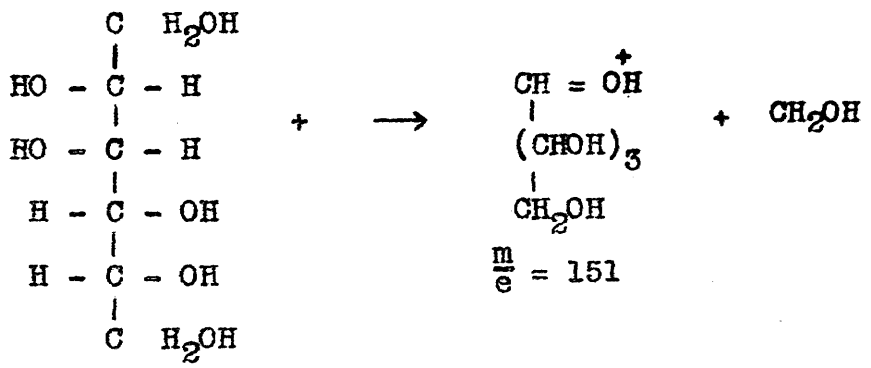
TABLE IV. (Cont'd)

Inositols.

m/e	Scyllo	Muco	Epi	Myo
181	0.08	0.18	0.96	0.26
163	0.15	0.12	0.08	0.10
145	0.1	0.3	0.4	0.3
144	0.8	2.8	3.5	2.1
127	0.1	0.3	0.1	0.2
126	0.2	0.2	0.3	0.3
115	0.4	0.5	0.6	0.6
109	0.3	0.5	0.3	0.7
103	0.4	0.5	0.4	0.9
102	8.3	8.6	5.6	11.8
101	0.6	0.5	0.5	0.5
98	0.7	0.4	0.5	0.6
97	1.1	0.8	0.8	0.9
91	2.9	2.5	2.8	3.0
90	0.6	0.5	0.5	0.6
89	3.7	2.3	1.9	3.2
85	1.7	1.3	1.1	1.5
84		0.4	0.5	0.5
83	0.9	0.5	0.6	0.6
81	0.7	0.5	0.4	0.5
75	0.7	0.7	0.6	0.9
74	6.1	5.0	5.4	5.8
73	100.0	100.0	100.0	100.0
72	6.5	5.2	4.6	6.8
71	10.3	8.8	7.5	13.8
70	0.8	0.6	0.5	0.9
69	2.2	1.4	1.4	2.6
61	4.6	3.4	2.6	5.8
60	21.1	15.3	19.6	20.3
57	4.1	3.1	2.6	3.7
56	2.1	1.5	2.1	1.9
55	3.6	2.6	2.2	3.3
54	1.3	1.2	0.9	1.3
53	0.5	0.5	0.4	0.5
47	1.3	0.7	0.6	1.2
45	4.9	3.5	3.0	
44	2.6	1.8	1.7	
43	9.4	6.5	4.9	
42	5.6	4.7	2.7	
41	2.6	1.6	1.4	
39	1.4	1.1	0.8	

DISCUSSION:

The simplest carbohydrate derivatives are the sugar alcohols. One typical sample has been used in this case, mannitol (I). This compound has molecular weight 182 but no molecular ion is observed (Table I). The molecular weight can, however, be found from the $(P + 1)^+$ ion at $\frac{m}{e} = 183$. The $(P - H_2O)^+$ ion is also absent. It should appear at $\frac{m}{e} = 164$, but there is an ion at $\frac{m}{e} = 165$ which can be derived by loss of $\cdot OH$ from the molecular ion or of H_2O from the $(P + 1)^+$ ion. The $(P - 2H_2O)^+$ ion at $\frac{m}{e} = 146$ is more intense. The ion of $\frac{m}{e} = 151$ is probably formed as follows:-



I

All the other intense ions in the spectrum can be obtained by simple carbon-carbon bond fission, elimination of water or by combinations of these processes, as in Fig. I.

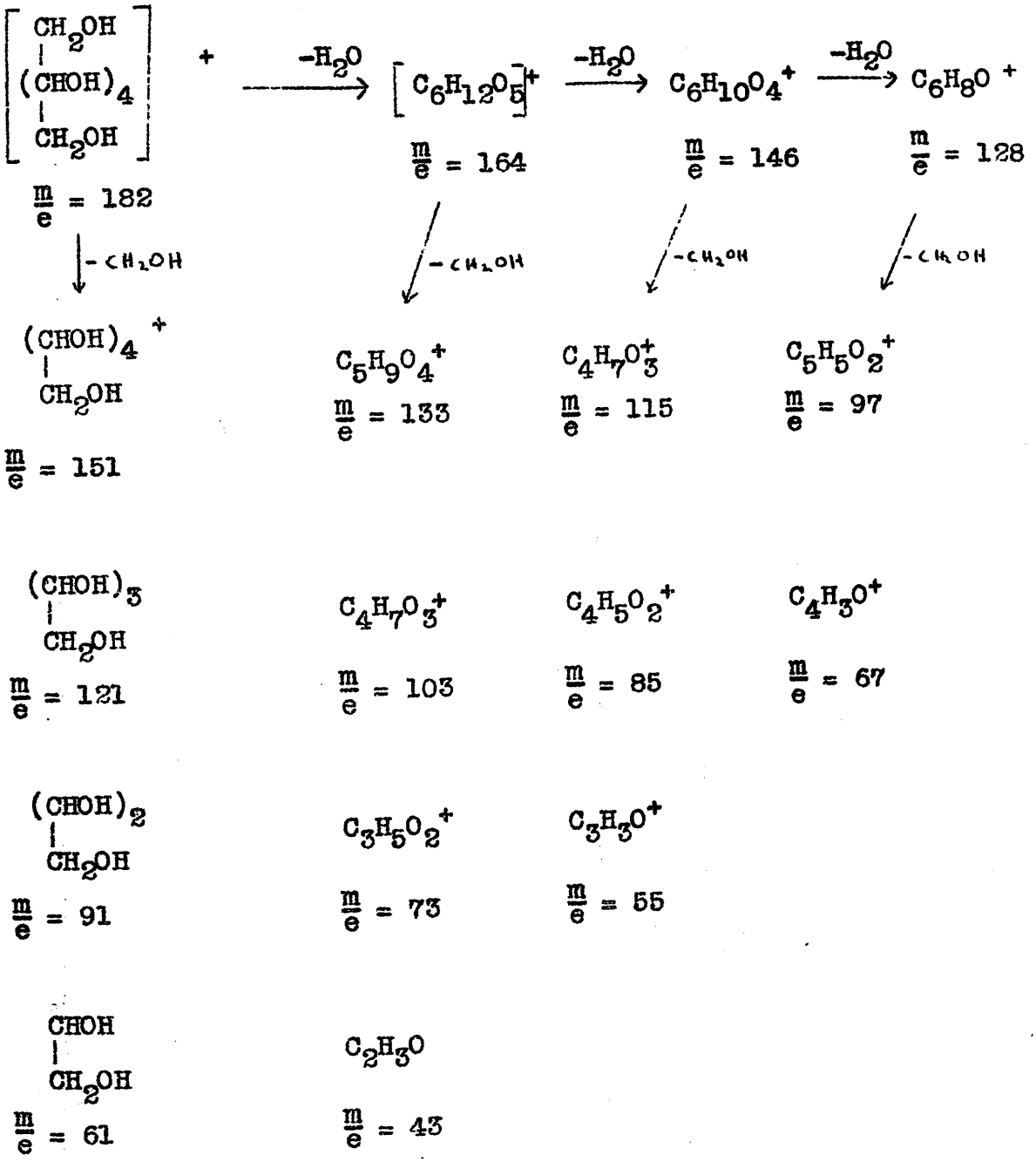
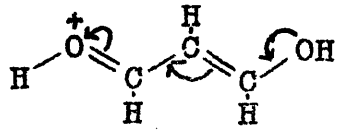
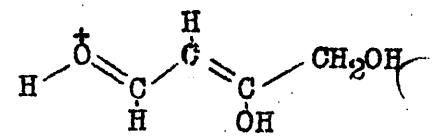

CH2OH
(CHOH)4
CH2OH
-H2O
C6H12O5+
-H2O
C6H10O4+
-H2O
C6H8O+
m/e = 182
m/e = 164
m/e = 146
m/e = 128
-CH2OH
-CH2OH
-CH2OH
-CH2OH
(CHOH)4
CH2OH
m/e = 151
C5H9O4+
m/e = 133
C4H7O3+
m/e = 115
C5H5O2+
m/e = 97
(CHOH)3
CH2OH
m/e = 121
C4H7O3+
m/e = 103
C4H5O2+
m/e = 85
C4H3O+
m/e = 67
(CHOH)2
CH2OH
m/e = 91
C3H5O2+
m/e = 73
C3H3O+
m/e = 55
CHOH
CH2OH
m/e = 61
C2H3O
m/e = 43

FIG. I.

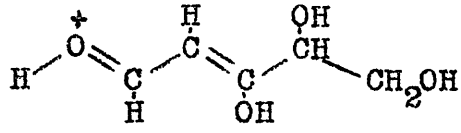
The most intense ion in the spectrum, at $\frac{m}{e}$ = 73 is probably the resonance stabilised ion II. The sharing of the positive charge between the two oxygen atoms occurs by the conjugative mechanism shown. For this reason the



II.



III.



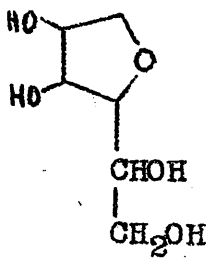
IV.

ions II, III ($\frac{m}{e}$ = 103) and IV ($\frac{m}{e}$ = 133) are, respectively, more intense than the ions of $\frac{m}{e}$ = 91, 121 and 151 which are obtained by the corresponding carbon-carbon bond fissions. The appropriate pair of ions containing two carbon atoms, however, have almost equal intensities ($\frac{m}{e}$ = 61 and 43). This is owing to the fact that the ion of $\frac{m}{e}$ = 43 has only one oxygen atom and cannot therefore be stabilised by delocalisation of charge.

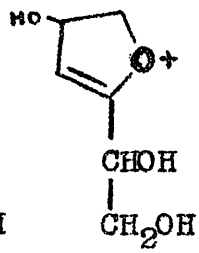
The exact nature of the fission and rearrangement processes which take place still remains unknown. There are five possible ways in which a 1:2 elimination of water can take place in the molecular ion. As can be seen in

Fig I most of the intense ions at lower mass numbers can be obtained by combinations of several possible fissions.

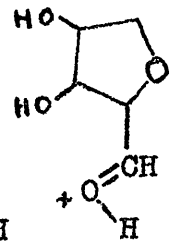
The anhydro sugar alcohols present an easier problem. The spectrum of 1:4-anhydromannitol (V) is shown in Table II. Again the molecular ion is absent, and the molecular weight can be obtained from the $(P + 1)^+$ ion. Stable ions are obtained by loss of H_2O and CH_3O. The loss of H_2O can take place in several ways; the most probable structure for the resultant ion will be one with the double bond $\alpha:\beta$ to the oxygen atom which bears the positive charge, e.g. VI or X. The CH_3O fragment which is lost on the



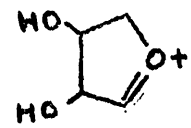
V.



VI.



VII.



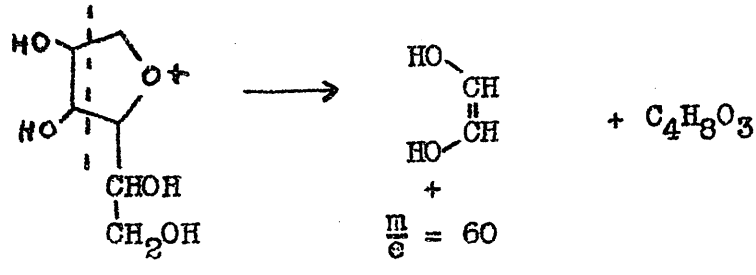
VIII

IX

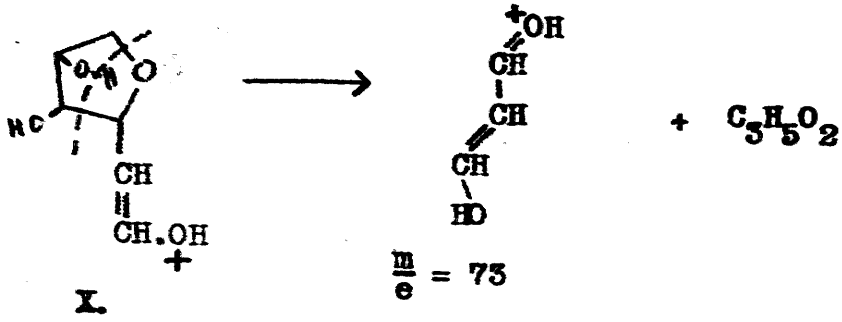
formation of the ion of $\frac{m}{e}$ = 133 is probably the terminal hydroxymethyl group. This ion is stabilised by oxonium ion formation (VII). Elimination of water from VII gives the ion of $\frac{m}{e}$ = 115 which is only of moderate intensity. It is noticeable that the 1:2:3-trihydroxy grouping which makes possible the formation, without rearrangement of ions of the type III, IV or V is not present in this molecule.

The most intense ion in the upper mass range is at $\frac{m}{e}$ = 103; it is produced by the loss of $C_2H_5O_2$ from the molecular ion, i.e. by the loss of the side chain from the ring. Such a degradation is common in cyclic compounds and in this case involves fission of a bond which is β to two oxygen functions. The ion is probably an oxonium structure (VIII). It further degrades with loss of OH to form the most abundant ion, at $\frac{m}{e}$ = 86; probably a hydroxydihydrofuran ion which loses OH rather than H_2O. The ion formed ($\frac{m}{e}$ = 69) may be a protonated furan (IX).

The mass/charge ratios of the other intense ions in this spectrum, at $\frac{m}{e}$ = 73, 61 and 60 cannot be reconciled with structures containing the intact furan ring. Ionization of the side chain will give an ion of $\frac{m}{e}$ = 61. This may also be the source of the ion of $\frac{m}{e}$ = 60, though it may also be obtained by a fission as follows:



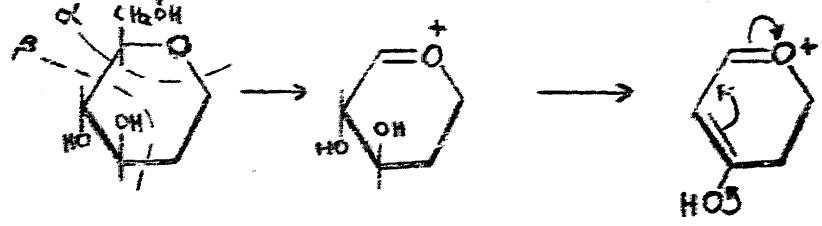
The ion of $\frac{m}{e}$ = 73 can be derived by fission of the dehydrated molecular ion X, with concomitant hydrogen migration.



X.

This seems most probable because it is the only method by which the stable 1:3-dihydroxyallyl ion can be formed without extensive rearrangements.

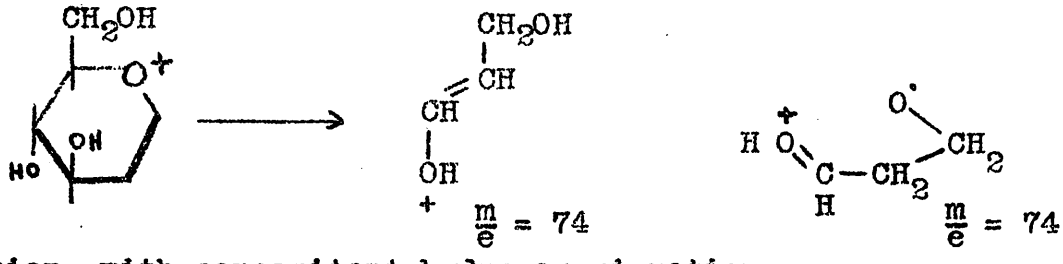
In the spectrum (Table II) of 2-deoxy-1:5-anhydro-sorbitol (XI) it will be noted that the molecular ion ($\frac{m}{e}$ = 148) is present though of low intensity. Since there are only three hydroxyl groups in this ion it should be more stable than the molecular ions of the compounds previously discussed. The $(P - H_2O)^+$ ion is of moderate intensity and as in 1:4-anhydromannitol the most intense ion in the upper mass range is produced by loss of the largest side chain, the hydroxymethyl group. Further, this ion loses water and the proposed mechanism is shown below. The intense ions at $\frac{m}{e}$ = 71 and 70 are probably



XI $\frac{m}{e}$ = 148 $\frac{m}{e}$ = 117 XII $\frac{m}{e}$ = 99

obtained by loss of CO and CHO from XII. The ions of $\frac{m}{e}$ = 60 and 61 could be obtained by fissions of the type α or β from XI with and without concomitant hydrogen migration. The neutral fragments from these degradations can also be ionized and appear at $\frac{m}{e}$ = 88 and 87. As with 1:4-anhydro-mannitol, ions in the lower mass range of the spectrum are products of ring fission and are less useful for diagnostic purposes than the ions of higher mass.

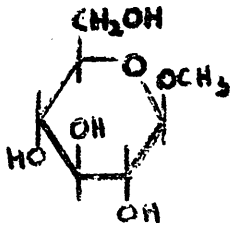
The ion of $\frac{m}{e}$ = 74 can be obtained by the following type of fission: the ion of $\frac{m}{e}$ = 73 can be obtained by the same



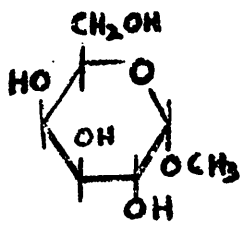
fission, with concomitant hydrogen migration.

The methyl glycosides all contain the unstable acetal grouping. The effect on the spectra of these compounds appears to be that neither the molecular ion nor the $(P - H_2O)^+$ ion is present. From the spectrum (Table III) of methyl β-D-glucopyranoside (XIII) and methyl-α-D-glactopyranoside (XIV) it will be seen that the $(P + 1)^+$ and $(P - 1)^+$ ions are present. The $(P - 1)^+$ ion is present in many methyl acetal spectra[63]. The first fragment ion to appear below these is the $(P - CH_3O)^+$ ion, which is also common in methyl acetal spectra. The stability of such ions has been ascribed to the formation

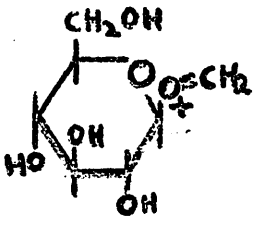
of oxonium ions and these are best represented as XV and XVI (as derived from methyl-β-D-glucopyranoside).



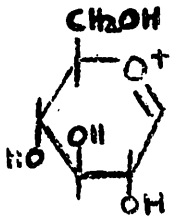
XIII.



XIV.

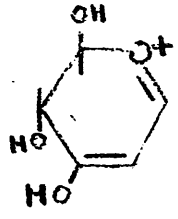


XV.

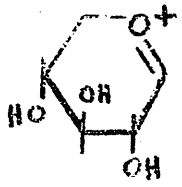


XVI.

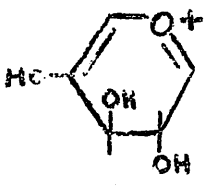
The ion of $\frac{m}{e}$ = 145 is produced by elimination of water from the $(P - CH_3O)^+$ ion. This transition is confirmed by the presence of a metastable ion at $\frac{m}{e}$ = 129.0. The ion produced will be XVII which gains stability by the same method as III and XII. There is also evidence of degradation of the hydroxymethyl group of XVI. This is lost as CH_2O to give XVIII and as CH_4O to give XIX. The ion of $\frac{m}{e}$ = 116 is probably XX, derived from XVIII.



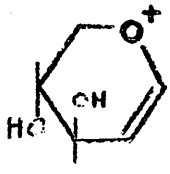
XVII



XVIII ($\frac{m}{e}$ = 133)



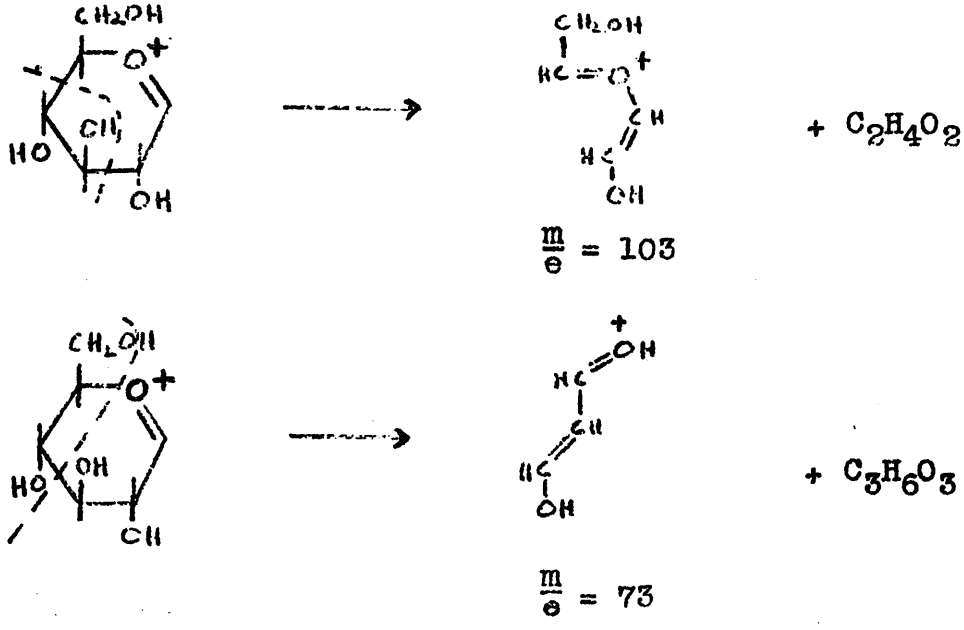
XIX ($\frac{m}{e}$ = 131)



XX

Another ion at $\frac{m}{e}$ = 98 may be derived from XX by loss of water.

The other ions at lower mass numbers can be more readily explained by fission of the pyranose ring of the molecular ion or of the $(P - OCH_3)^+$ ion, as in the following scheme:



$\frac{m}{e}$ = 103

$+ C_2H_4O_2$

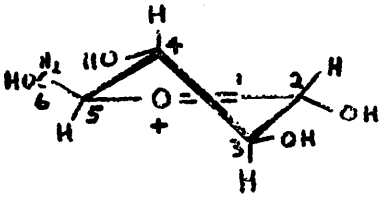
$\frac{m}{e}$ = 73

$+ C_3H_6O_3$

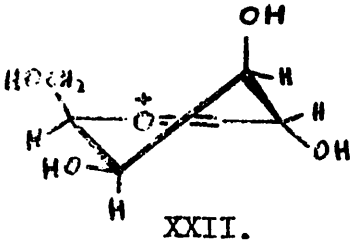
The most intense ion in the spectrum is at $\frac{m}{e}$ = 60, for which the probable formula is $C_2H_4O_2^+$. This can be readily obtained from the molecular ion by four different mechanisms involving fission of C_2 or carbon-oxygen fragments from the pyranose ring.

The mechanisms proposed for the degradation of XVI provide an explanation of the differences in intensity between the two spectra. A six-membered ring with one double bond usually takes up a half-chair conformation[68].

In the $(P - OCH_3)^+$ ion from methyl β-D-glucopyranoside it is possible for both hydroxyl groups on C 3 and C 4 to take up equatorial conformations (XXI). In the corresponding ion from methyl α-D-galactoside one must be axial (XXII).



XXI.

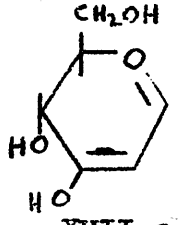


XXII.

Biemann and Seibl have shown[14] that an axial hydroxyl group is more readily eliminated as water than an equatorial hydroxyl group. The behaviour of the above ions is consistent with this: the intensity ratio $\frac{m}{e} = 163 : \frac{m}{e} = 145$ is 0.83 for methyl α-D-galactoside and 1.72 for methyl β-D-glucoside.

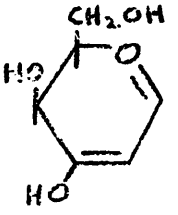
The ion of $\frac{m}{e} = 145$ (XVII) loses a further molecule of water to give an ion of low intensity at $\frac{m}{e} = 127$.

XVII is planar and the stereochemistry is as follows:



XVII a.

from methyl β-D-glucopyranoside



XVII b.

from methyl α-D-galacto-pyranoside.

XVII b. is more crowded than its epimer and should therefore lose a molecule of water more readily. The

intensity ratio $\frac{m}{e} = 127 : \frac{m}{e} = 145$ is 0.23 for methyl α-D-galactopyranoside and 0.17 for methyl β-D-glucopyranoside. These are the only ions for which the intensity can be readily related to a known stereochemical feature of the molecule.

Spectra have been obtained for all eight inositols (Fig.II) and are shown in Table IV. As with mannitol the $(P + 1)^+$ and $(P - 17)^+$ ions are present but the molecular ion and $(P - 18)^+$ ion are absent. The intensity of the $(P - 17)^+$ ion at $\frac{m}{e} = 163$ is pressure sensitive and may result from the fission process:-

$$181^+ \longrightarrow 163^+ + H_2O.$$

There are also ions present at $\frac{m}{e} = 144$ and $\frac{m}{e} = 126$ which are produced by the loss of two and three molecules of water from the molecular ion.

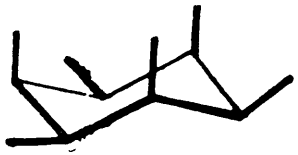
The intensity of the ion of $\frac{m}{e} = 163$, relative to the intensity of the $(P + 1)^+$ ion, is greatest where there is the largest number of 1:4-trans hydroxyl groups. Such groupings are present in the inositols in the following decreasing order:

Neo, scyllo > myo, allo > epi, L > muco, cis.

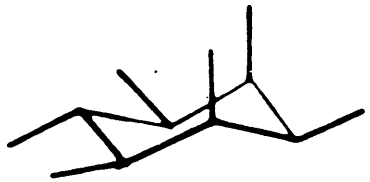
The relative intensities of the ions of $\frac{m}{e} = 163$ (expressed as a percentage of the intensity of the $(P + 1)^+$ ion) are in the order:

Neo, scyllo > allo > muco > L > myo > epi, cis.

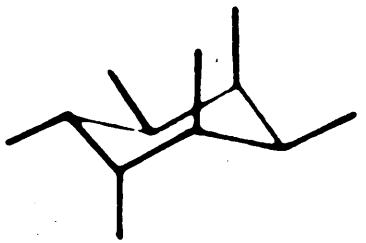
FIG. II.



cis

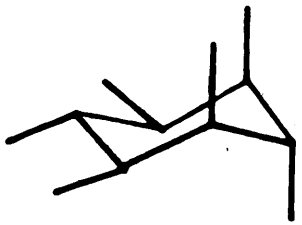


epi

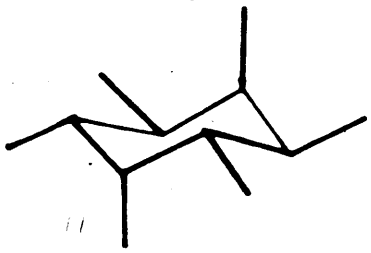


allo

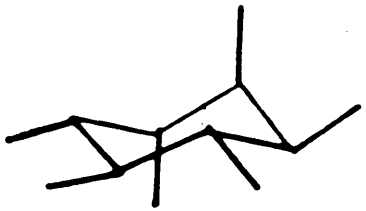
myo



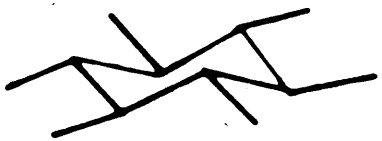
muco



neo



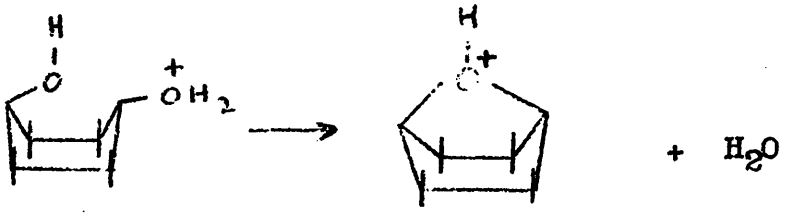
L



scyllo

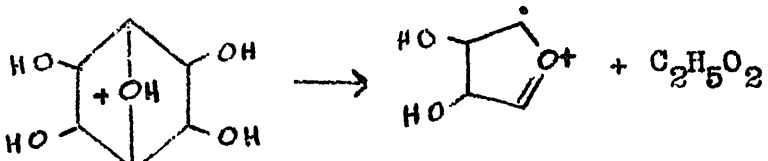
—— represent hydroxyls, hydrogens not shown.

This similarity suggests that the following type of reaction may occur, and the formation of the ion of



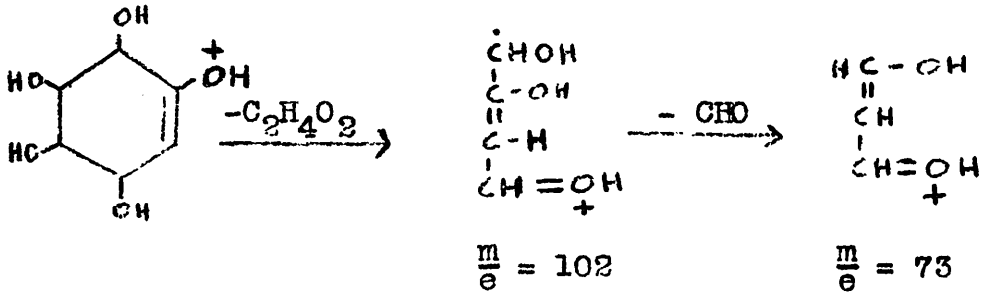
$\frac{m}{e}$ = 163

$\frac{m}{e}$ = 102 will take place by a fission similar to that of bicyclo-2:2:1-heptane[54].



$\frac{m}{e}$ = 102

The most intense ion in these spectra is at $\frac{m}{e}$ = 73. It can be obtained from the ion of $\frac{m}{e}$ = 102 by loss of a formyl radical. The stability of the ion of $\frac{m}{e}$ = 73 in most of these spectra has been attributed to the structure of type III for the ion obtained from mannitol. This cannot be readily obtained by a simple degradation of the furanoid ion shown above. This is one argument in favour of an alternative process as follows:



$\frac{m}{e}$ = 102 $\frac{m}{e}$ = 73

It is not yet possible to determine whether either or both of these mechanisms are valid.

The other fragment ions at lower mass numbers can be obtained by a variety of routes. As an instance, the ion of $\frac{m}{e}$ = 60 can be obtained in six ways by removal of $C_2H_4O_2$ fragments from the molecular ion.

It can thus be seen, from the evidence afforded by the few examples quoted here that some information about the structure of small polyhydroxy compounds can be derived from their mass spectra at higher mass numbers. At lower mass numbers there is a greater possibility that several processes will give rise to ions of the same mass. The use of the continuous volatilisation method appears to be quite adequate to deal with such involatile compounds. Ion-molecule reactions provide a method for accurate molecular weight determination.

REFERENCES

1. Magat, M. and Viallard, R.: Compt.Rend. Acad.Sci., 228, 1118 (1949).

2. Beynon,J.H., Saunders,R.A., Topham,A. and Williams,A.E.: J.Phys.Chem., 65, 114 (1961).

3. Beynon,J.H. : "Mass Spectrometry and its applications to Organic Chemistry", Elsevier, Amsterdam, 1960.

4. McLafferty,F.W.: Mass Spectrometry in "Determination of Organic Structures by Physical Methods", to be published.

5. Bleakney,W. and Delfosse,J.: Phys.Rev.,56,956 (1939).

6. Bloom,E.G., Lengel,J.H., Mohler,F.L. and Wise,C.E.: J.Res.Nat.Bur.Stan., 41, 129 (1948).

7. Reed,R.I.: J.Chem.Soc., 1958, 3432.

8. Beynon,J.H.: Mikrochim, Acta., 1956, 446.

9. A.P.I. Reports. Project No.44. Mass Spectral Data. Serial Nos. 184, 185.

10. Eyring,H., Rosenstock,H.B., Wahrhaftig,A.L. and Wallenstein,M.B.: Proc.Nat.Acad.Sci., 38, 667 (1952).

11. Friedland,S.S., Lane,G.H., Longman,R.T., O'Neal,M.J.,Jr.: Anal. Chem., 31, 169 (1959).

12. Beynon,J.H. : "Advances in Mass Spectrometry", ed. Waldron,J.D., Pergamon, London, 1959.

13. Friedel,R.A., Langer,S.H. and Sharkey,A.G.,Jr.: Anal. Chem., 29, 770 (1957).

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

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

16. Gilpin, J.A. and McLafferty,F.W. : Anal.Chem., 29, 990 (1957).

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

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

19. Happ,G.P. and Stewart,D.W.: J.Amer.Chem.Soc., 74, 4404 (1952).

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

21. Friedel,R.A., Hickam,W.M. and Sharkey,A.G.,Jr. : A.S.T.M. Committee E-14 on Mass Spectrometry, 5th Annual Meeting, New York, 1957.

22. Dibeler,V.H. and Wacks,M.E. : J.Chem.Phys., 31, 1557 (1959).

23. Reed,R.I. : Fuel, XXXIX, 341 (1960).

24. Lester,G.R. : "Advances in Mass Spectrometry", ed. Waldron,J.D., Pergamon, London, 1959.

25. Meyerson,S., Rylander,P.N. and Grubb,H.M.: J.Amer.Chem.Soc., 79, 842 (1957).

26. Lossing,F.P. and Pottie,R.F.:J.Amer.Chem.Soc.,83, (1961

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

28. McLafferty,F.W.: Anal.Chem.,31, 2072 (1959).

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

30. Beynon,J.H., and Williams,A.E.: App.Spectroscopy, 14, 156 (1960).

31. Beynon,J.H. and Williams,A.E.: App.Spectroscopy, 13, 101 (1959).

32. de Mayo,P., and Reed,R.I.: Chem.and Ind.,1956,1481.

33. Sponagel,P. and Ullmann,F. : Ann., 350, 90 (1906).

34. Berger, M.E.: C.R.Acad.Sci., Paris, 141, 1027 (1905).

35. Huang,R.L. : J.Chem.Soc., 1955, 3295.

36. Findlay,A. and Japp,F.R.: J.Chem.Soc.,71, 1115 (1897).

37. Beringer,F.M., Brierley,A., Drexler,M., Gindler,E.M. and Lumpkin,C.C.: J.Amer.Chem.Soc., 75, 2708 (1953).

38. Beringer,F.M., Drexler,M., Gindler,E.M. and Lumpkin,C.C.: J.Amer.Chem.Soc., 75, 2705 (1953).

39. Shearer,G. : B.Sc. Thesis, Glasgow, 1960.

40. A.P.I. Research Project 44, Mass Spectral Data. Serial No.893.

41. Ref.40. Serial No.1296.

42. Aczel,T. and Lumpkin,H.E.: Anal.Chem., 32, 1819 (1960).

43. Field,F.H. and Franklin,J.L.: "Electron Impact Phenomena and the Properties of Gaseous Ions". Academic Press, New York, 1957.

44. Nilsson,M., Ryhage,R. and von Sydow,E.: Acta.Chim.Scand., 11, 634 (1957).

45. Ryhage,R., Ställberg-Stenhagen,S. and Stenhagen,E.: Arkiv for Kemi, 14, 259 (1959).

46. Ryhage,R. and Stenhagen,E.: Arkiv för Kemi, 13, 523 (1959); idem, ibid, 15, 291 (1960); idem, ibid, 15, 333 (1960).

47. Gilchrist,T. and Reed,R.I.: Experientia, XVI,134 (1960).

47 a. Bruun,H.H., Ryhage,R. and Stenhagen,E.: Acta.Chem.Scand., 12, 789 (1958). Bruun,H.H., Ryhage,R. and Stenhagen,E.: Acta.Chem.Scand., 12, 1355 (1958).

48. Biemann,K., Gapp,F. and Seibl,J.: Biochem. and Biophys. Res.Comm., 1, 307.

49. Biemann,K., Gapp,F. and Seibl,J. : J.Amer.Chem.Soc., 81, 2274 (1959); Biemann,K.: Chimia, 14, 393(1961)

50. Biemann,K.: Tetrahedron Letters, 9, 1960. Biemann,K. and Friedman-Spiteller,M.: Tetrahedron Letters, 68, 1961. Biemann,K., Djerassi,C., Gilbert,B., Johnson,L.F. and Shoolery,J.N.: Experientia, XVII, 162 (1961).

51. Ref.40. Serial Nos. 178, 179, 180.

52. Crable,G.F., Kearns,G.L. and Norris,M.S.: Anal.Chem., 32, 13 (1960).

53. Emery,E.M.: Anal.Chem., 32, 1495.

54. Reed,R.I.: "The Production of Ions by Electron Impact", Academic Press, London, 1961.

55. Aczel,T. and Lumpkin,H.E.: Anal.Chem., 33, 386.

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

57. A.S.T.M. File of Uncertificated Spectra: anisole, guaiacol and veratrole spectra contributed by Philip Morris Inc., Richmond, Virginia.

58. A.P.I. Research Project 44: Chemical Thermodynamic Properties. Series I, Table 23 - 3.

59. Personal Communication from Dr. W.D.Ollis.

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

61. Brown,R.A., Nicolaides,N. and Young,W.S.: Anal.Chem., 26, 1653 (1954).

62. Ryhage,R.: Arkiv för Kemi, 14, 211 (1959).

63. Friedel,R.A. and Sharkey,A.G.,Jr.: Anal.Chem., 28, 940 (1956).

64. Schissler,D.O. and Stevenson,D.P.: J.Chem.Phys., 24, 926 (1956).

65. Finan,P.A., Reed,R.I. and Snedden,W,: Chem. and Ind., 1958, 1172.

66. FinanP.A. and Reed,R.I.: Nature, 184, 1866 (1959).

67. Reed,R.I. and Shannon,J.S.: I.U.P.A.C. Conference, Sydney, Australia (1960).

68. Barton,D.H.R. and Cookson,R.C.: Q.Rev.,X, 44 (1956).