1130. *Electron Impact and Molecular Dissociation. Part X.*[1] *Some Studies of Glycosides.*

By P. A. FINAN, R. I. REED, W. SNEDDEN, and J. M. WILSON.

The electron-induced fragmentations of some glycosides and anhydro-sugars are reported. Correlations between the mass fragment ions and probable structures have been made. A bond-dissociation energy has been measured for the anomeric methyl D-glucopyranosides.

FOR the useful application of the mass spectrometer to problems in carbohydrate chemistry an understanding of the behaviour of these compounds on electron impact is necessary. The results obtained for certain monosaccharide derivatives are included in the Table. This study has been confined to glycosides, since they are sufficiently volatile for investigation in the usual way. A qualitative examination of the cracking patterns has been made.

The spectra obtained from carbohydrates are complex, as many rearrangements occur and fragmentation is often accompanied by the facile loss of one or more hydrogen atoms. Also, while it is customary to formulate a fragment ion which has a simple structural relationship to its precursor, such assumptions do not always have a good theoretical justification. However, the method of empirical correlations, which has proved so useful in many other series, is employed here also.

Mass spectra of methyl glycopyranosides.*

A, Methyl α-D-glucopyranoside. B, Methyl β-D-glucopyranoside. C, Methyl α-D-galactopyranoside. D, Methyl α-L-fucopyranoside. E, Methyl β-L-arabinopyranoside. F, Methyl 3,6-anhydro-α-D-glucopyranoside. G, Methy- 3,6-anhydro-β-D-glucopyranoside. H, Methyl 3,6-anhydro-α-D-galactopyranoside. J, Methyl 3,6-anhydro-α-D-mannopyranoside. K, Glucal.

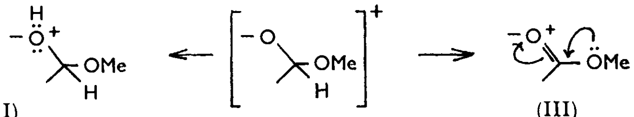
m/e	A	B	C	D	E	F	G	H	J	K
195	0·4	0·35	0·15							
193	0·4	0·3	0·05							
179				0·02						
177				0·03						
165					2·0					
164	0·1	1·0	0·6							
163	6·75	8·1	4·7							
162	0·5		0·2							
148				0·15						
147		0·45	0·55	0·15						1·60
146	3·75	0·6	0·95							11·96
145	1·25	4·7	5·75			11·7	1·1	0·75	3·3	
144	2·5	6·95	4·2							
135				0·15						
133	2·5	1·85	2·6	0·15	3·3					
132	3·75	1·1	0·35							
131	5·0	12·0	3·65	0·1						
129	0·2	0·5m	0·5m	0·1						
127	0·95	0·8	1·3							
121	1·7	2·95	2·25							
120	0·6	0·65	1·05	0·3						
119	0·75			0·1						
118				0·3						
117		1·2	1·45	0·1						
116	5·6	7·35	5·6	0·3	3·3					
115		0·65	0·95			1·8	1·65	2·5	10·0	
110								6·25		
105			0·55							
104	1·1	3·8	3·2		6·0					
103	2·5	4·5	6·8	0·5	10·6					
102	•	4·5				74·0	17·6	43·75	5·76	
101	0·85	1·1	1·85	0·2						
100			0·5	0·5						
99	1·15	2·6	2·25							1·24
98	5·0	8·9	6·8	0·2	10·5	4·5				1·24
97	11·8	6·6	6·3	0·3		4·5			23·75	8·34
96	0·8		0·7		9·5					
95	2·4		0·2							
92			0·35							
91	2·5	1·05	8·25							
90		0·3								
89	2·25	1·55	2·15	1·0	2·6					
88	3·25	1·0	1·3	0·25	0·5	2·25				
87	11·8	7·0	9·1	3·0		3·60	13·2	37·5		0·85
86	3·15	3·1	3·4	1·5		2·25	11·0	26·5		7·49
85	10·0	6·25	8·4	2·25	6·6	2·25	13·2	45·0	5·75	3·94
83					4·6					2·24
81					14·6					3·59
79					5·3					
77					2·6					
75		12·25	10·05	9·0		7·2				2·38
74	31·25	44·3	54·1	48·0	2·5	51·0	3·3	62·5	19·0	25·77
73	28·75	46·8	43·65	22·5	5·3	57·0	47·0	95·0	20·0	*100·0*
72	2·5	2·9	3·6	2·25	1·4	7·2	36·0	37·5		1·85
71	15·0	22·0	29·7	36·0	18·6	20·0	43·5	57·5		15·23
70	4·6	6·6	6·4	1·5	9·3	14·4	25·5	40·0		2·09
69	11·6	7·25	7·4	3·75	20·0	56·0	84·0	45·0	40·0	22·15
68		0·8			4·6					
62		1·5	2·5							
61	20·0	32·5	31·4	31·5	6·0	38·0		65·0	20·0	1·95
60	84·2	*100·0*	*100·0*	*100·0*	24·4	56·0	41·0	85·0	34·0	4·08
59	6·25	6·1	9·7	13·5	1·3	10·8	39·5	75·0		0·67
58	5·0	2·45	4·6	26·75	8·1	7·2	16·5	52·5		3·73
57	*100·0*	34·35	41·45	33·0	32·0	87·0	88·0	*100·0*	60·0	19·13
56	9·4	10·9	10·7	6·0	21·0	7·2	19·8	40·0	20·0	34·40
55	21·8	6·15	7·2	12·75	34·0	39·5	53·0	57·5	46·0	32·09
54		1·1	0·8		5·3			7·5		0·99
53		0·75	1·0		9·6			15·0		4·79
51					1·0					1·60
47			1·3			0·9				4·22
46		1·1								1·46
45	6·2	10·75	16·9	24·75	3·3	32·0	51·0	55·0	35·0	15·44
44	8·7	5·9	6·6	24·0	10·0	18·0	37·0	62·5	69·0	7·67
43	18·7	11·1	18·15	36·0	*100·0*	38·0	75·0	65·0	84·0	28·05
42	5·3	5·9	8·4	12·0	20·0	24·0	55·0	53·75	46·0	7·56
41	8·75	4·4	6·4	15·0	67·0	28·0	66·0	60·0	55·0	15·87
40	1·8		1·0		3·3	2·7	13·2	22·5	17·0	2·17
39	4·4		4·1	6·75	26·5	11·4	44·0	47·5	34·0	11·64
36									18·5	
33	1·25	4·8	7·1	7·5		18·0	29·0	36·25	10·0	
32	10·6	2·4	2·0	1·5	26·5	2·7	16·5	47·5	34·0	
31	14·3	10·8	22·6	30·0	10·0	76·0	79·0	50·0	51·0	
30	2·5	1·15	1·8	3·75		3·6	33·0	32·5	15·0	
29	13·4	10·8	19·6	36·0	56·0	100·0	100·0	55·0	62·0	
28	25·0	13·0	17·8	45·0	74·0	29·0	55·0	65·0	100·0	
27	6·5	3·0	7·3	12·0	33·0	28·0	61·5	55·0	51·0	

* The relative intensities of peaks are expressed as a percentage of the base-peak of the spectrum. Scanning below *m/e* = 27 was not attempted.

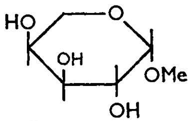
---

[1] Part IX, Reed and Reid, preceding paper.

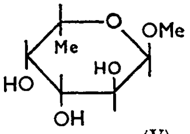
*Methyl Glucopyranosides.**—The spectra of five simple glycopyranosides show many similar features. First, none of these compounds gives a parent molecular ion, but each shows an ion at $(P + 1)^+$, the product of an ion–molecule interaction. As mentioned in Part IX,[1] these ions depend upon the second power of the sample pressure and are, therefore, easily recognised. Their presence in this series, which might result from the protonation of an oxygen to give an oxonium ion of type (II), complicates the interpretation of the spectra.



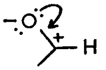
(II) (I) (III)



(IV)

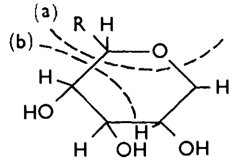


(V)

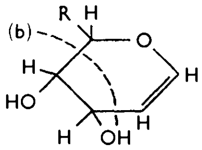


(VI)

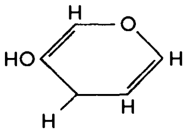
With the exception of β-L-arabinopyranoside, each glycoside spectrum has an ion corresponding to the loss of a single hydrogen atom. This is a rather uncommon process in the fragmentation of organic ions but has previously been reported for acetals, toluene, and some heterocycles.[2] In the present instance it arises by the loss of molecular hydrogen from the $(P + 1)^+$ ion. For all the methyl glucopyranosides, as well as for the 3,6-anhydro-compounds subsequently discussed, there is an ion of fairly high abundance $(P - 31)^+$, which can arise either by the loss of a methoxyl or a hydroxymethyl group. The latter grouping cannot easily be lost from either methyl β-L-arabinopyranoside (IV) or methyl α-L-fucopyranoside (V), and in these cases at least it must arise by the elision of the glycosidic methoxyl group. The $(P - OMe)^+$ ion can be represented as (VII; R = CH$_2$·OH for galacto- and gluco-pyranosides, R = H for arabinopyranosides, and R = Me for fucopyranosides).



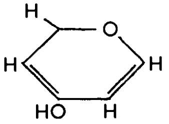
(VII)



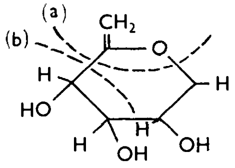
(VIII)



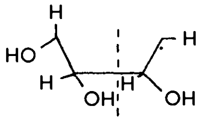
(IX)



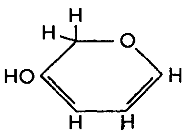
(X)



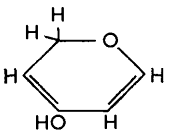
(XVII)



(XVIII)



(XI)



(XII)

Most of the remaining ions in the spectra can be interpreted as arising from the further dissociation of (VII) by one or more of the following steps: (i) progressive loss of hydroxyl groups and of water from the cyclic triol system; (ii) elimination of any side-chain that may be attached at C-5; (iii) fragmentation of the pyran or

---

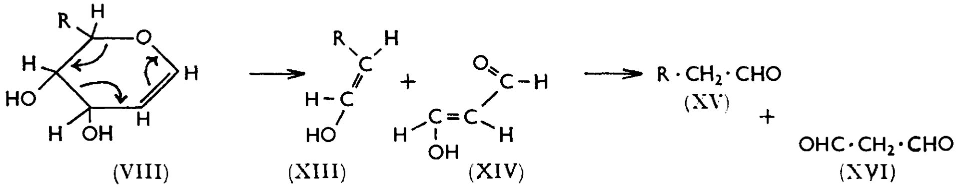
* Throughout this paper, the molecular ion produced by the removal of an electron from the parent molecule is denoted by P^+.

[2] Beynon, " Mass Spectrometry and its Application to Organic Chemistry," Elsevier, London, 1960, p. 362 *et seq.*

modified pyran ring system which may result from processes (i) and (ii). For clarity the stereochemistry of the asymmetric carbon atoms is ignored in the formulæ.

In each spectrum, with the exception of fucopyranoside in which there are ions at $(P - 47)^+$ and $(P - 49)^+$, there is an ion $(P - 48)^+$. This ion might arise from the loss of a hydroxyl from (VII), or by the elimination of water from a protonated form of (VII), giving (VIII), to which a glycal type structure is now assigned. There is close similarity between the spectrum of D-glucal (VIII; $R = CH_2{\cdot}OH$) and those of the glycopyranosides. In the spectrum of D-glucal there is a moderately abundant ion $m/e = 97$ $(P - 49)^+$ which most probably arises from the successive loss from the parent molecular ion of molecular water, and a hydroxymethyl group. This ion $(P - 49)^+$ probably has structure (IX) or (X), depending on whether the hydroxyl on C-3 or C-4, respectively, is removed in the elimination of water. Similar explanations can be made for the ion, $m/e = 97$, in the spectra of the galacto- and gluco-pyranosides. This ion is absent from the cracking pattern of arabinopyranoside which does not have a side-chain on C-5. The ion $m/e = 98$ may have a different constitution, a hypothesis which it is hoped to test in a later study. The spectra of the other glucopyranosides, as well as of D-glucal, have an ion, $m/e = 98$, the formula of which is almost certainly $C_5H_6O_2$. Any formulation other than (XI) or (XII) is exceedingly difficult to accommodate, having regard to its origins.

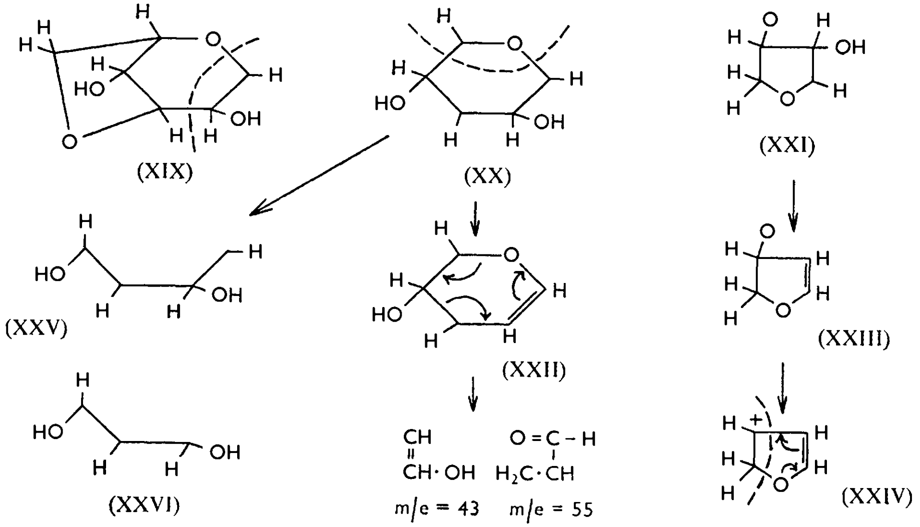
Other fragmentation routes may operate in the further dissociation of the $(P - 49)^+$ ions of the glucal type, as represented by (VIII). Thus, a reverse Diels–Alder reaction



may be expected to give (XIII) and (XIV), and then (XV) and (XVI). Further dissociation of (XV) and (XVI) would account for many of the other fragment ions of lower mass.

The glucopyranosides, however, dissociate by routes other than those discussed. In the spectra of the galacto- and gluco-pyranosides there is a fragment ion, $m/e = 145$, $(P - OMe - H_2O)^+$. This assignment is confirmed by the presence in the fragmentation pattern of methyl α-D-galactopyranoside and methyl β-D-glucopyranoside of a metastable ion, $m/e = 129{\cdot}0$, which corresponds to the transition $163^+ \longrightarrow 145^+ + 18$. This proves the loss of molecular water. There is no corresponding ion in the spectrum from arabinopyranoside so it appears that the $(P - OMe)^+$ ion in the hexapyranosides (VII; $R = CH_2{\cdot}OH$) loses water by a breakdown of the side-chain, giving (XVII) which undergoes further fragmentation giving $m/e = 103$ (XVIII), an ion which is common to all the spectra although only weakly present in fucopyranoside and one which, moreover, could also arise directly from ion (VII) by cleavage at (a). The primary alcohol side-chain also seems to undergo degradation accompanied by the migration of a hydrogen atom to C-5, as in the reaction, (VII; $R = CH_2{\cdot}OH$) $\longrightarrow$ (VII; $R = H$). This is the breaking of a bond β to an ether linkage, the pyranose oxygen, with a concomitant hydrogen shift, a common fragmentation process.[1] Dissociations of this kind have also been observed in some anhydrohexitols, which have a primary alcohol group as the side-chain on a pyranoid ring. Loss of molecular water from the ion (XVIII) would yield the ion, $m/e = 85$, which is present in all the spectra, while a further breakdown of (XVIII) would give the ions $m/e = 60$ and 43, both of which are abundant in the spectra. The ion $m/e = 60$ which is, moreover, the base peak in the β-gluco-, α-galacto-, and α-fuco-pyranoside could also be produced by the further cleavage of (VII), (VIII), or (XVII) at (b).

Methyl 3,6-*Anhydrohexapyranosides.*—The fragmentation patterns of four methyl 3,6-anhydro-D-hexapyranosides are also given in the Table. Again none of the spectra gives a detectable parent ion, nor, in this instance, is there a $(P + 1)^+$ or $(P - 1)^+$ ion. The failure to detect any of these ions may indicate that thermal degradation is occurring, at least in part, and the interpretation of the observed ions becomes more difficult. However, the ion of highest mass value, *m*/*e* = 145 in each case, $(P - 31)^+$ is formed by the elimination of the glycosidic methoxyl. The fragment ion can be represented by (XIX), the stereochemistry being ignored. The further ions at *m*/*e* = 115, 102, 85, 74, 73, 69, 60, 57, 56, and 55 are common to all the cracking patterns and these can be derived as shown. It will be seen that two degradative routes are given, and this seems the minimum possible without assuming extensive and sometimes uncommon rearrangements. The still smaller fragment ions may have many origins and some of the more likely of these have been included.



Appearance Potential Measurements.—These have been carried out upon the anomeric methyl D-glucopyranosides. The glycosyl residue, $C_6H_{11}O_5$, is represented by G and a subscript α or β is attached to indicate an α- or a β-glucopyranoside, respectively. The thermo-chemical relationship

$$A(G_\alpha^+) = I(G_\alpha) + D(G_\alpha - OMe) + \sum E_\alpha$$

may be employed where $A(G_\alpha^+)$ represents the appearance potential of the appropriate ion, $I(G_\alpha)$ its ionisation potential, $D(G_\alpha - OMe)$ is the bond-dissociation energy of the relevant bond, and $\sum E_\alpha$ represents the total contribution of all the energy terms, kinetic, vibrational, rotational, and electronic. The measured values are $A(G_\alpha^+) = 12{\cdot}9 \pm 0{\cdot}16$ ev and $A(G_\beta^+) = 13{\cdot}5 \pm 0{\cdot}16$ ev, respectively.

Now, the carbon atom C-1 in the glycosyl radical has trigonal symmetry, and therefore $I(G_\alpha) = I(G_\beta)$. If, further, one makes the plausible assumption that $\sum(E_\alpha) = \sum(E_\beta)$ it follows that $A(G_\beta^+) - A(G_\alpha^+) = D(G_\beta - OMe) - D(G_\alpha - OMe) = 0{\cdot}6 \pm 0{\cdot}32$ ev.

Thus, these figures suggest that the C-1–OMe bond-dissociation energy in methyl β-D-glucopyranoside is about 6 kcal./g. mole greater than the corresponding bond in methyl α-D-glucopyranoside. These measurements are consistent with the view that the methyl glucopyranosides adopt the C-1 conformation where the methoxyl group in the β-glucopyranoside is present as an equatorial substituent on the pyranose ring. It is present as an axial substituent in the α-glucopyranoside. Attention must be drawn to the fact that the measurements were carried out on the vapour, and this result is not necessarily opposed to the relative reactivity of the anomers in solution.

EXPERIMENTAL

The cracking patterns were obtained on a Metropolitan Vickers M.S.2 mass spectrometer with an N.E.P. 1050 ultra-violet recorder. The samples were introduced into the ion chamber by our usual technique.[1]

The appearance potentials were measured in the conventional manner which has been adequately described previously.[3] In the present series the ion abundances were necessarily small by reason of the low vapour pressures of the compounds, and this is reflected in the rather large experimental errors. Nevertheless, the difference between them is real, since a mixture of the two compounds shows a discontinuity in the ion-abundance–electron-voltage curve some 0·3 ev above the onset of the graph.

We acknowledge with thanks an Imperial Chemical Industries Limited Fellowship at the University, Edinburgh (P. A. F.), a D.S.I.R. Studentship (W. S.), and a grant from the Mass Spectrometry Panel of the Institute of Petroleum (J. M. W.), during the tenure of which this work was carried out. We wish also to express our indebtedness to Professor E. L. Hirst, F.R.S., Edinburgh University, and to Professor R. A. Raphael, F.R.S., Glasgow University, for their interest in this study.

THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW W.2.
[Present addresses: (P. A. F.) CHEMISTRY DEPARTMENT, THE UNIVERSITY, SHEFFIELD 10.
(W. S.) SHELL LTD., THORNTON RESEARCH CENTRE, P.O. BOX 1, CHESTER.
(J. M. W.) THE CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY,
STANFORD, CALIFORNIA, U.S.A.]
[*Received, January* 29*th*, 1963.]

[3] Reed, *Trans. Faraday Soc.*, 1956, **52**, 1195.