

CHEMICAL IONIZATION MASS SPECTRA OF SUGARS

A.M. Hogg* and T.L. Nagabhushan

Department of Chemistry

University of Alberta

Edmonton, Alberta, Canada

(Received in USA 15 August 1972; received in UK for publication 23 October 1972)

A number of sugars have been studied by electron impact and field ionization mass spectrometry (1), yet for the average carbohydrate chemist this analytical method has been of little practical utility mainly due to the fact that the spectra are characterized by the absence of molecular ions, the low intensity of high mass ions and multiplicity of fragmentation pathways. Therefore, in spite of the availability of high resolution instruments, the spectra are not amenable to computation of elemental composition of unknown sugars. In the hope of producing spectra which can be readily interpreted, we have studied chemical ionization mass spectra (C.I.) (2) of a number of sugars and their derivatives using a modified AEI MS12 mass spectrometer (3) and the results are presented in this communication.

In Fig. 1, the C.I. spectra of D-glucose, methyl α -D-glucopyranoside, β -D-glucose pentaacetate and α,α -trehalose octaacetate using ammonia as the reagent gas (4) are shown. In all cases the major peak corresponds to the $(M+\overset{+}{\text{NH}}_4)$ ion. D-Glucose and methyl α -D-glucopyranoside show, in addition to the $(M+\overset{+}{\text{NH}}_4)$ ion, a smaller peak corresponding to $(M+\overset{+}{\text{NH}}_4-\text{H}_2\text{O})$ and $(M+\overset{+}{\text{NH}}_4-\text{CH}_3\text{OH})$, respectively. Both β -D-glucose pentaacetate and α,α -trehalose octaacetate show virtually a single peak at $(M+\overset{+}{\text{NH}}_4)$. To date, this technique has permitted ready determination of molecular weights of pentoses, hexoses, simple glycosides of monosaccharides, O-acetyl derivatives of monosaccharides and three disaccharides (maltose, trehalose and sucrose).

The methane C.I. spectra of hexoses exhibit prominent peaks at $(\overset{+}{\text{MH}}-\text{H}_2\text{O})$,

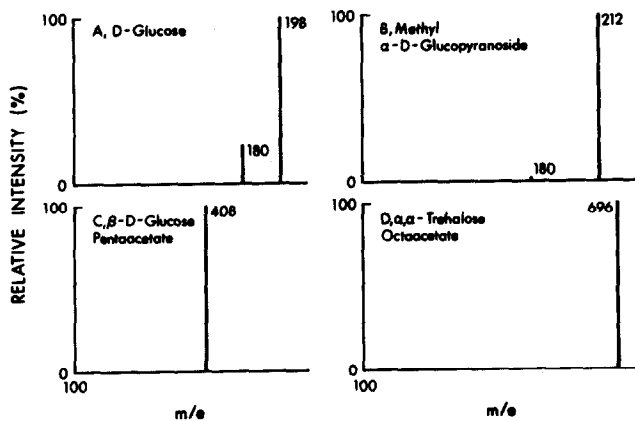
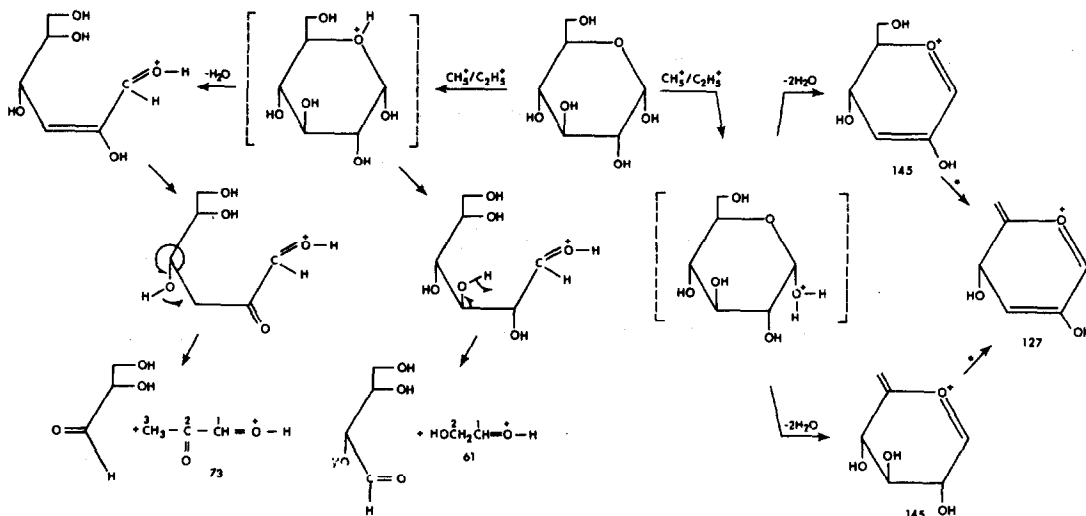
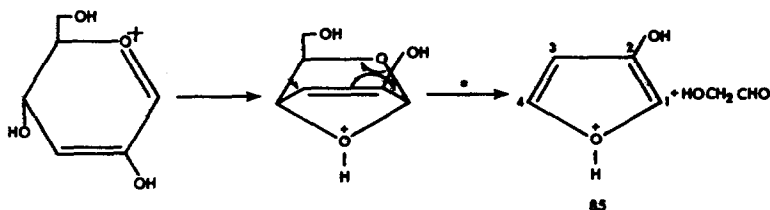


Fig. 1 The Ammonia C.I. Spectra

$(MH-2H_2O)^+$ and $(MH-3H_2O)^+$ and m/e 61, 73 and 85. In contrast to this, the spectrum of methyl α -D-glucopyranoside shows, as should be expected, peaks at $(MH-CH_3OH)^+$, $(MH-CH_3OH-H_2O)^+$ and $(MH-CH_3OH-2H_2O)^+$, but there are no prominent peaks at 61 and 73. On the other hand, 3-O-methyl-D-glucose exhibits intense peaks at $(MH-H_2O)^+$, $(MH-H_2O-CH_3OH)^+$, $(MH-2H_2O)^+$ and $(MH-CH_3OH-2H_2O)^+$ and low intensity peaks at 61 and 73. The peak at 73 is 25% more intense than the one at 61. 6-Deoxy-D-glucose shows prominent peaks at $(MH-H_2O)^+$, $(MH-2H_2O)^+$, m/e 61 and 73, the ratio of the latter two being the same as that found in the spectra of D-glucose (2:1). It is apparent from these studies that the methane C.I. spectra of hexoses are characterized by two fragmentation pathways as illustrated below.



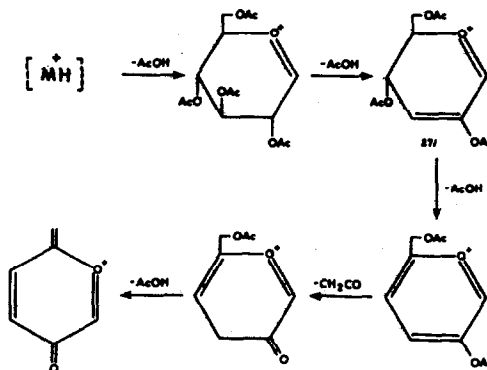
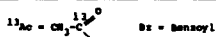
The ion m/e 85 in the fragmentation of D -glucose arises from $(MH-2H_2O)^+$ presumably as shown below.



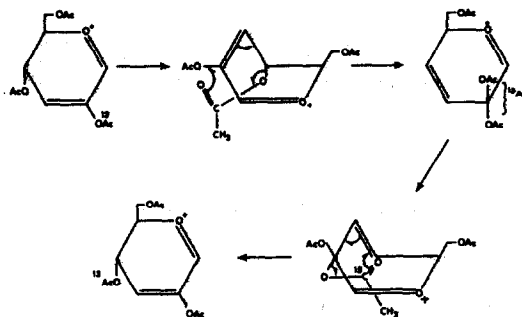
The methane C.I. spectrum of D -glucose pentaacetate is very simple involving losses of four molecules of acetic acid and one of ketene; these peaks accounting for 87% of the total ionization above m/e 50. Using the compounds listed in Table 1, the mechanism was confirmed for the fragmentation of hexose pentaacetates and is illustrated below.

Table 1
Characteristic Ions in the Methane C.I. Spectra of Derivatives of D -Glucose

Compound	1st loss from C1 m/e 331	2nd loss from C1 m/e 271	3rd loss from C6 (C2) m/e 211	4th loss from C2 (C4) m/e 189	5th loss m/e 109
	AcOH	AcOH	AcOH	CH_2CO	AcOH
	MeOH (80%) AcOH (20%)	AcOH	AcOH	CH_2CO	$^{13}AcOH$
	AcOH	AcOH	AcOH (64%) $^{13}AcOH$ (36%)	$^{13}CH_2CO$ (64%) CH_2CO (36%)	AcOH
	AcOH	AcOH	AcOH	CH_2CO	
	BzOH (90%) AcOH (10%)	AcOH	AcOH	CH_2CO	AcOH



The ion at m/e 271 appears to rearrange in such a way that the O-acetyl groups on C4 and C2 become partially scrambled most probably as shown below.



Peracetylated disaccharides give spectra which are readily interpreted on the basis of the mechanism discussed for the monosaccharide acetates. Preliminary experiments using this technique has permitted recognition of the position of linkage in the disaccharide molecule.

In conclusion, while the use of ammonia reagent gas provides a powerful method for the determination of molecular weights of sugars and substituted sugars on a micro scale, the use of methane with O-acetylated sugars allows determinations of substitution on a sugar ring.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. R.U. Lemieux of this department for the samples.

REFERENCES

- 1) N.K. Kochetkov and O.S. Chizhov, *Advances in Carbohydrate Chemistry*, 21, 39 (1966); *Methods in Carbohydrate Chemistry*, Vol. VI, Ed. R.L. Whistler and J.N. Be Miller, Academic Press, New York, 1972, p. 54.
- 2) B. Munson, *Anal. Chem.*, 43, 28A (1971).
- 3) A.M. Hogg, *Anal. Chem.*, 44, 227 (1972).
- 4) A.M. Hogg and P. Kebarle, *J. Chem. Phys.*, 43, 449 (1965).