MASS-SPECTROMETRIC STUDY OF CARBOHYDRATES

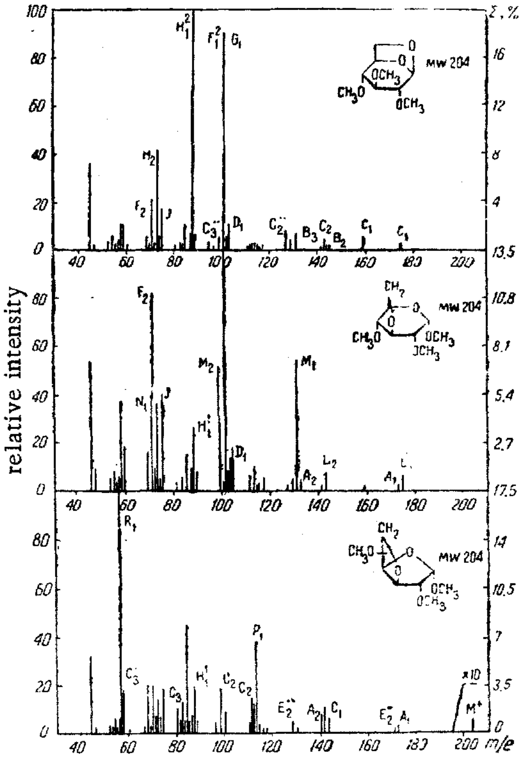
Methyl Ethers of Some Anhydrosugars

N. K. Kochetkov, O. S. Chizhov, and B. M. Zolotarev

Khimiya Prirodnykh Soedinenii, Vol. 2, No. 3, pp. 152–158, 1966

The mass-spectrometric investigations of carbohydrates that we have carried out previously [1, 2] have permitted us to study the mass spectra of the methyl ethers of some anhydrosugars. The use of the mass-spectrometric method makes it possible to establish the structure of some natural compounds. Data on the mass spectrometry of anhydrosugars are limited to a single paper by Reed et al., [3], who obtained the mass spectra of methyl 3, 6-anhydro-β-D-glucopyranoside and methyl 3, 6-anhydro-α-D-gluco-, D-galacto-, and -mannopyranosides. As the subject of our investigation we chose the methyl ethers of anhydrosugars, which are more suitable for mass spectrometry in view of their volatility. These ethers are of interest as possible degradation products in the study of polysaccharides (for example, agar and other related polysaccharides of red algae). Moreover, by working with methyl ethers it might be possible to make a direct comparison of the modes of fragmentation of anhydrosugars with the fragmentation of ordinary monosaccharides [1, 2, 4].

We have recorded the mass spectra of 2, 3, 4-tri-O-methyl-1, 6-anhydro-D-glucose (I), methyl 2, 4-di-O-methyl-3, 6-anhydro-α-D-glucopyranoside (II), and methyl 2, 5-di-O-methyl-α-D-glucofuranoside (III). Compound (I) was obtained by methylating the triacetate of levoglucosan by Haworth's method; the constants agreed with published data [5]. The starting material for the synthesis of (II) and (III) was methyl 2, 3-anhydro-α-D-allopyranoside, which was converted into methyl 3, 6-anhydro-α-D-glucopyranoside and methyl 3, 6-anhydro-α-D-glucofuranoside by heating with a 1 N solution of caustic soda [6]. Methylation of these substances by Purdie's method gave the methyl ethers (II) and (III) with constants identical with those given in the literature [7].



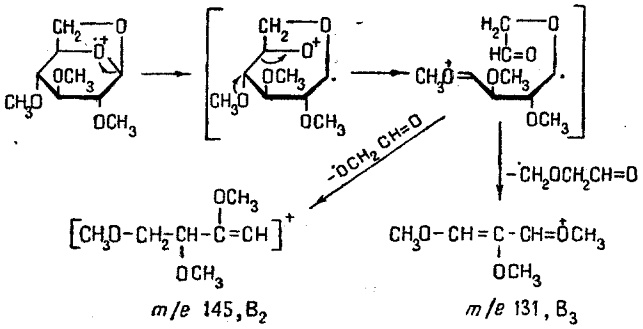
Mass spectra of 1, 2, 3-tri-O-methyl-1, 6-anhydro-D-glucose; methyl 2, 4-di-O-methyl-3, 6-anhydro-α-D-glucopyranoside; and methyl 2, 5-di-O-methyl 3, 6-anhydro-α-D-glucofuranoside.

The mass spectra were taken on a MKh-1303 mass spectrometer with an ionizing voltage of 70 eV and an inlet system temperature of 175° C. The intensities of the peaks were calculated with respect to the intensity of the main peak of the spectrum and to the total intensities of all the peaks of the spectrum from M^+ to m/e 45 for the purpose of conveniently comparing the spectra. The mass spectra of compounds (I)–(III) are given in the figure.

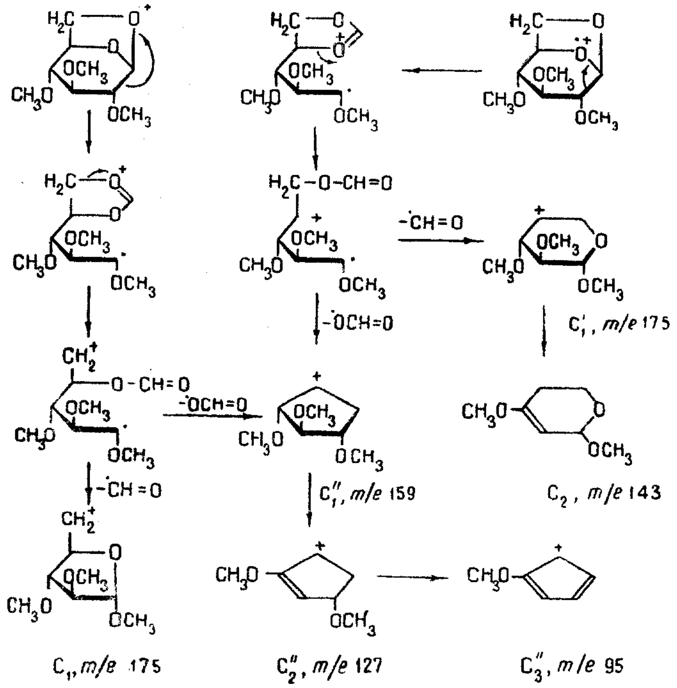
The mass spectra of the anhydrosugars can be interpreted only partially by starting from the rules established for the decomposition of the methyl ethers of ordinary pentoses and hexoses [1, 2, 4]. The closest analogy was found between the mass spectra of (I) and of methyl 2, 3, 4, 6-tetra-O-methyl-α-D-glucoside [1], although the presence in substance (I) of an additional ring leads to the appearance of several peculiarities in the decomposition* of this compound. Thus, in the mass spectrum of (I), as was to be expected, the peaks corresponding to the ions of series A and E disappear (the latter arise as a result of primary ruptures of the C_1–glycosidic oxygen and C_5–C_6 bonds respectively). Peak B_1 is also absent, in spite of the formation of ions B_2 and B_3.

---

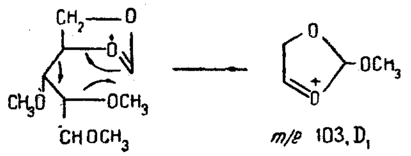
* In the subsequent discussion of the mass spectra, we shall make use of our previously introduced system of symbols for ions and decomposition routes [2].



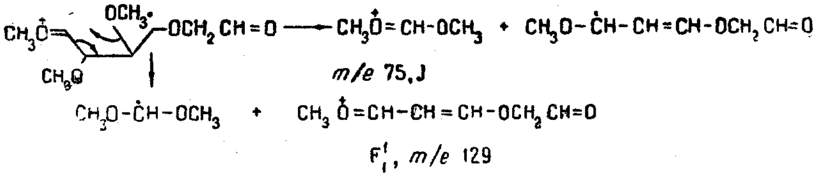
The initial rupture of the C_1-C_2 bond leads to several series of ions of similar structures with m/e 175, 159, 143, 127, and 95, partially recalling the ions of series C for methyl 2, 3, 4, 6-tetra-O-methyl-β-D-galactoside [2]:



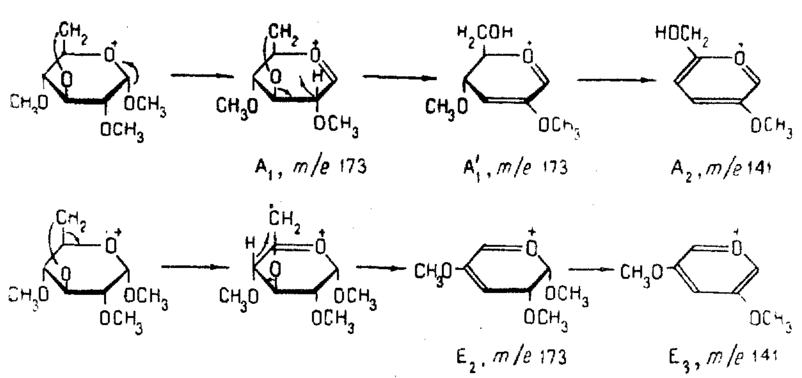
In other respects, also, the mass spectrum of substance (I) recalls the mass spectra of the completely methylated methyl hexosides; it has peaks of the ions F_1^2 and G_1^2 (m/e 101), H_1^2 and H_1^3 (m/e 88), H_2 (m/e 73), F_2(m/e 71), and others characteristic of the permethylhexosides. The peak of the ion D_1 is found at m/e 103:



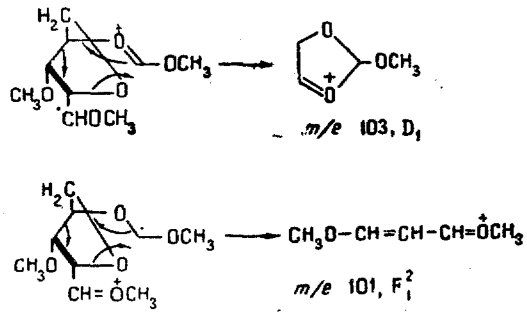
The ion J(m/e 75) has a lower intensity and apparently arises mainly by the following process:



The mass spectrum of substance (II) differs considerably from that of (I), and the fragmentation of (II) is characterized by processes which are not encountered in the decomposition of the completely methylated methyl hexosides, although some features of similarity are still retained. Thus, the peaks at m/e 173 and 141 evidently owe their origin to the isomeric ions A_1 and A_2 (m/e 173) and A_2 and A_3 (m/e 141):

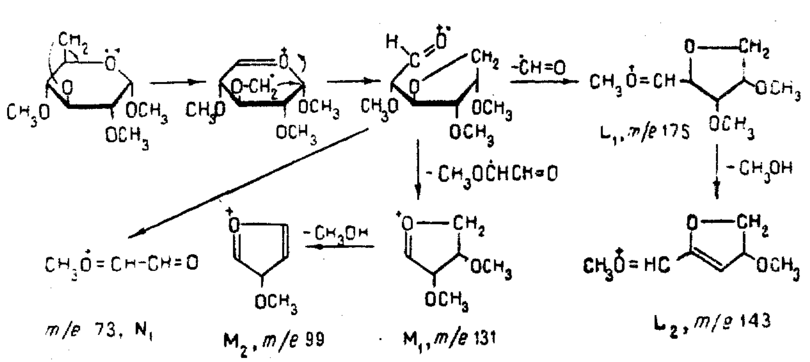


The mass spectrum of (II) exhibits a fairly intense peak of the fragment D_1 (m/e) 103), while the main peak of the spectrum is that for m/e 101, which possibly corresponds mainly to the ion F_1^2. The formation of these two fragments in the case of (II) probably takes place in a similar manner to that proposed for the completely methylated methyl hexosides [2]:



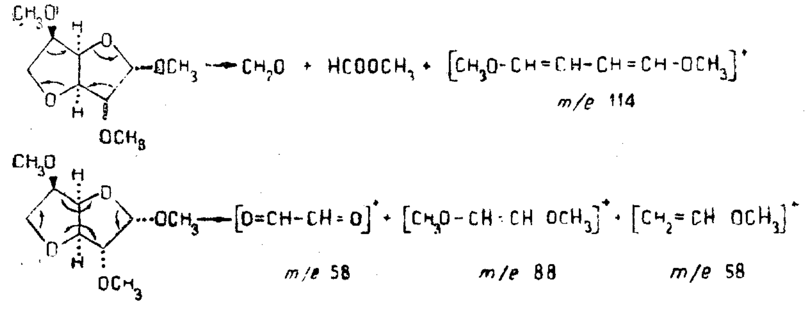
The peak with m/e 88, as was to be expected, has a comparatively low intensity and probably corresponds to the ion H_1^1 including C_1 and C_2 with their methoxyl groups.

The mass spectrum of (II) is characterized by a relatively high intensity of the peaks with m/e 175, 143, 131, 99, and 73, whose presence is difficult to explain unless the following rearrangement is assumed:

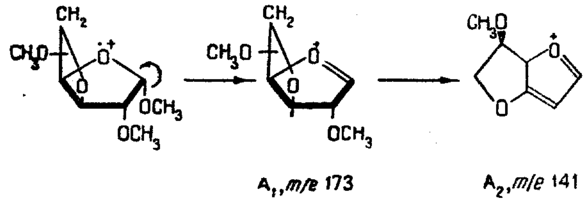


In order to confirm this hypothesis, selectively labeled compounds whose synthesis entails considerable difficulties must be used.

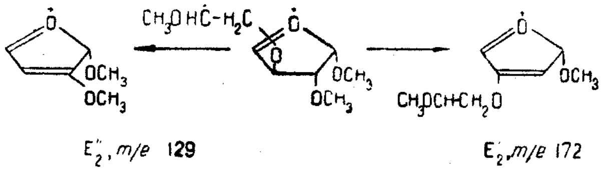
The mass spectrum of the anhydrofuranoside (III) differs considerably from the spectra of the two isomers considered above. The first difference consists in the presence of the peak of the M^+ ion, which reflects the generally greater stability of the molecule as compared with substance (II) (cf. [7, 6]). The appearance of the strongest peaks of the mass spectrum of (III), with m/e 114 and 58, can be explained by the following two processes of conjugated electron transfer, recalling to some extent the route of formation of fragments H_1^2 and K_1 in the case of the completely methylated glycosides [2, 3]:



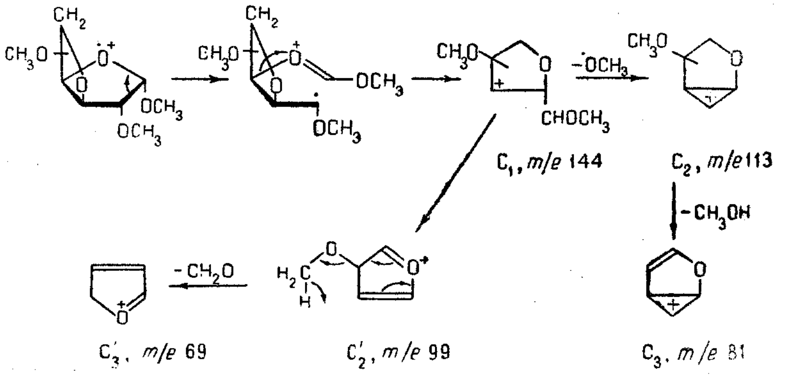
A series of other ions arises in an analogous manner to the corresponding fragments in the mass spectrum of methyl 2,3,5-tri-O-methyl-α,β-L-arabofuranoside [2]. Thus, the ions A_1 (m/e 173) and A_2 (m/e 141) are formed by the successive elimination of a CH_3O radical and a molecule of methanol:



The ions E'_2 and E''_2 are formed in the same way as the ions E_2^1 and E_2^2 :



The origin of the ion C_1 (m/e 144) and its further fragmentation are clear from the following scheme:



It is not yet possible to explain the origin of some other peaks, including one of the strongest peaks in the spectrum at m/e 85. Further investigations of the mass spectra of corresponding labeled compounds are necessary for this purpose.

The results given show that the presence of the additional ring in the anhydrosugars, as well as its size and position, introduce specific features into the mass-spectrometric behavior of these compounds. These features of the mass spectra permit the use of the mass-spectrometric method for determining the structure of the anhydrosugars even with the incomplete treatment of mass spectra which is possible at the present time.

Summary

The mass spectra have been recorded of three anhydrosugars: 2, 3, 4-tri-O-methyl-1, 6-anhydro-D-glucose, methyl 2, 4-di-O-methyl-α-D-glucopyranoside, and methyl 2, 5-di-O-methyl-3, 6-anhydro-α-D-glucofuranoside. An interpretation of the spectra obtained has been given.

REFERENCES

1. N. K. Kochetkov, et. al., Tetrah., 19, 2209, 1963.
2. N. K. Kochetkov and O. S. Chizhov, Tetrah., 21, 2029, 1965.
3. P. A. Finan, et al., J. Chem. Soc., 5945, 1963.
4. K. Heyns, and D. Müller, Tetrah., 21, 55, 1965.
5. J. C. Irvine and J. W. H. Oldham, J. Chem. Soc., 119, 1744, 1921.
6. A. B. Foster, M. Stacey, and S. V. Vardheim, Acta Chem. Scand., 12, 1819, 1958.
7. W. N. Haworth, L. N. Owen, and F. Smith, J. Chem. Soc., 88, 1941.

6 May 1965

Institute of the Chemistry of Natural Compounds, AS USSR