MASS-SPECTROMETRIC STUDY OF CARBOHYDRATES.

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Figure 1: Structural formulas of compounds I-III

Abstract

Full Text

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MASS-SPECTROMETRIC STUDY OF CARBOHYDRATES.

METHYL ETHERS OF SOME METHYLDEOXYHEXOSIDES

Continuing our studies on the mass spectrometry of carbohydrates ($^{1-3}$), we have investigated the mass spectra of deoxy sugar derivatives, information on which was practically absent (^{2,4}).

We recorded the mass spectra of 2-deoxy-3,4,6-tri-O-methyl-α,β-methyl-D-arabohexoside (I), 3-deoxy-2,4,6-tri-O-methyl-α-methyl-D-ribohexoside (II), and 4-deoxy-2,3,6-tri-O-methyl-α-methyl-D-xylohexoside (III). Compound I was obtained from 2-deoxy-D-glucose by methylation according to the method of R. Kuhn (^{5}) in the modification proposed by Uokers et al. (^{6}). The starting material for the synthesis of II was α-methyl-3-deoxy-4,6-O-benzylidene-D-ribohexoside (IV), described by P. Karrer (^{7}). Partial hydrolysis of this compound with 0.03 N hydrochloric acid in 60% aqueous acetone gave α-methyl-3-deoxy-D-ribohexoside (V), which, without additional purification, was converted into II by methylation according to Kuhn. Compound III was prepared by methylation of α-methyl-4-deoxy-2,3-di-O-methyl-D-xylohexoside (^{8}) by Purdie' s method. Compounds I-III were homogeneous according to thin-layer chromatography on silica gel and gave satisfactory elemental analyses.

Mass spectra were recorded on an MX-1303 mass spectrometer at an ionizing voltage of 70 eV and an inlet-system temperature of 175°. Peak intensities were calculated as percentages of the total intensity of all peaks of the spectrum from M^+ to m/e 45.

Mass spectra of compounds I-III

m/e	220	189	188	175	157	156	149	143	129	128	125	115	111	102	101	97	88	75	73	71	59	58	45
Code	M^+	A_1	A'_1	E_1	A_2	A'_2	D_1	E_2	C_2	C'_2	A_3	B_2	E_3	K_1	F_1	G_1C_3	H_1	J_1	H_2	F_2	—	—	—
I	0.05	0.05	0.2	4.6	1.3	2.7	—	4.2	—	—	0.5	3.5	0.7	3.5	9	0.9	22	7	4	9.5	3.3	1.1	5.5
II	0.02	0.15	0.15	0.6	2.3	0.4	—	1.0	0.6	1.0	0.6	1.4	0.8	20	6.8	2.0	7.2	5.4	2.6	16	3.0	2.0	6
III	0.01	0.25	0.02	0.4	2.0	0.1	0.7	1.4	0.8	5.0	1.0	1.9	0.3	2.4	2.4	2.8	24	12	9.4	6.0	2.8	0.7	6.0

For the mass spectra of deoxyhexosides I-III, the presence of a clearly expressed peak of the M^+-ion is characteristic; this peak usually cannot be observed in the mass spectra of carbohydrates ($^{1-4}$). The formation of the M^+-ion peak reflects an increase in its stability: cleavage of the bonds adjacent to the deoxy unit is hindered, since it should lead to the formation of ions and radicals of the type $R—CH_2^+$ and $R—\dot{C}H_2$, which are less stable than particles of the type $R—CH{=}OCH_3^+$ or $R—\dot{C}H—OCH_3$, formed from the M^+-ion of ordinary pentoses or hexoses. The peak of the M^+-ion has the greatest intensity in the mass spectrum of 2-deoxy-

hexoside I, and the least—in the case of the 4-deoxy derivative III, which is readily explained if one recalls that, in the fragmentation of monosaccharide derivatives, most ions are formed as a result of cleavage of the $C_1—C_2$ bond ($^{1-4}$).

The mass spectra obtained can, on the whole, be interpreted from the standpoint of the ideas developed earlier ($^{1-3}$) concerning the decomposition of methyl ethers of aldoses under electron impact. At the same time, possessing a number of characteristic differences, these mass spectra make it possible to determine with confidence the position of the deoxy unit in the molecule. These differences are most conveniently followed in discussing the decomposition pathways of compounds I—III, in the course of which we shall use the system of designations proposed by us previously (^{2}).

Series A and A′ (see scheme). To series A belongs a group of peaks of small or medium intensity. The greatest mass among the ions of this series is possessed by fragment A_1 with m/e 189, formed from the M^+-ion by elimination of the glycosidic methoxyl group. Ions A_2 and A_3 arise as a result of the loss by this ion of one or two molecules of methanol, respectively. It is interesting to note that in the case of compound I a somewhat different, although closely related, decomposition path A' strongly predominates: the first ion of this series, A'_1, with m/e 188, arises from the M^+-ion as a result of elimination of a molecule of methanol; the ion A'_2 formed from it has m/e 156. In the mass spectrum of II, ions A_1 and A'_1 have approximately equal intensity, while peak A_2 is much larger than A'_2. For compound III, decomposition by path A' practically does not occur.

reaction scheme: formation of ion C_2, m/e 129

Figure 2: reaction scheme: formation of ion C_2, m/e 129

reaction scheme: formation of ion D_1, m/e 149

Figure 3: reaction scheme: formation of ion D_1, m/e 149

(scheme)

$$A_1,\ m/e\ 189 \xrightarrow{-CH_3OH} A_2,\ m/e\ 157 \xrightarrow{-CH_3OH} A_3,\ m/e\ 125$$

$$A_1',\ m/e\ 188 \xrightarrow{-CH_3OH} A_2',\ m/e\ 156$$

Series B (see scheme). An ion of type B_1 (^{1,2}) is not observed in the spectra of compounds I—III; however, in all spectra there is a peak corresponding to an ion with m/e 115 (B_2), which probably arises from ion B_1 by elimination of one of the methoxyls.

(scheme)

$$B_2,\ m/e\ 115$$

Series C and C′ (see scheme). To series C belong fragments C_2 and C_3 with m/e 129 and 97, respectively. The first is formed by simultaneous elimination from the M^+-ion of a molecule of methyl formate and the radical $CH_3O\cdot$; the second, by elimination of a molecule of methanol from the first.

The ion-radical C_2', close in structure to ion C_2, differs from it only in that it is formed as a result of the elimination of two neutral molecules with an even number of electrons—methyl formate and methanol—and not of the radical $CH_3O\cdot$. In the case of the 3-deoxy and 4-deoxy compounds II and III, both types of transformations occur, although the C' pathway predominates, especially for III. The intensities of the peaks of these series decrease in the order III > II > I. For the last compound the intensities of the peaks C_2 and C_2' are extremely small, as was to be expected, since replacement of the methoxyl by a hydrogen atom in the 2-position should lead to a sharp destabilization of the ion-radical C_1 (cf. (4)).

Ion D_1. Ion D_1 with m/e 149 is formed by the following route:

The corresponding peak is present only in spectrum III, since for I cleavage of the C_1—C_2 bond is energetically unfavorable, while in II there is no methoxyl group at C_3.

Series E. The parent ion of this series, E_1, is formed from the molecular ion by elimination of the side chain; ions E_2 and E_3 are formed by elimination from ion E_1 of one or two methanol molecules, respectively:

reaction scheme: E_1, m/e 175; E_2, m/e 143; E_3, m/e 111

Figure 4: reaction scheme: E_1, m/e 175; E_2, m/e 143; E_3, m/e 111

In the case of the 2-deoxy derivative I, the peaks E_1 and E_2 have a fairly appreciable intensity; in the case of II and III they are small. This phenomenon may apparently be explained by the fact that, in the formation of ion E_1, the distance between the substituents located at C_1—C_2 and C_3—C_4 and in the *cis* position decreases. In the case of II and III this leads to increased repulsion between the methoxyls at C_1 and C_2, whereas in the case of I such an unfavorable steric effect is absent.

Series F and G. These series include three-carbon fragments having the following structures:

$$\mathrm{CH_3O{-}CH{=}CH{-}CH{=}\overset{+}{O}CH_3} \quad (F_1,\ m/e\ 101), \qquad \mathrm{CH_3O{-}CH{-}CH{-}OCH_3}$$

$$\backslash \overset{+}{CH} /$$

$$(G_1,\ m/e\ 101), \qquad \mathrm{CH_2{=}CH{-}CH{=}\overset{+}{O}CH_3} \quad (F_2,\ m/e\ 71)$$

In the case of compound I the peak m/e 101 may correspond to ions F_1^1 (including C_1, C_2, and C_3), F_1^3 (C_4, C_5, and C_6) and G_1^3 (C_2, C_3, and C_4); for compound II–

ions F_1^2 (C_2, C_3, and C_4), F_1^3 (C_4, C_5, and C_6) and G_1^1 (C_1, C_2, and C_3); for compound III–F_1^1 (C_1, C_2, and C_3), G_1^1 (C_1, C_2, and C_3) and G_1^2 (C_2, C_3, and C_4). Which of these ions makes the greatest contribution in each case is as yet difficult to say. The intensity of the peak m/e 101 decreases in the order I > II > III.

Series H. This series includes the two-carbon fragments H_1 with m/e 88 and H_2 with m/e 73, the latter arising from H_1 by elimination of a methyl group in the form of a CH_3 radical (metastable peak m/e 60.6):

$$\mathrm{(CH_3O{-}CH{=}CH{-}OCH_3)^{\cdot +}} \rightarrow \mathrm{CH_3^{\cdot}} + \mathrm{CH_3O^{+}{=}CH{-}CH{=}O}$$

$$H_1\ m/e\ 88 \qquad\qquad H_2\ m/e\ 73$$

For compounds I and III the peak at m/e 88 is the principal peak of the spectrum, whereas for compound II it has medium intensity. The only possible source of formation of the H_1 ion in the latter case is C_1 and C_2 with their methoxyl groups. Evidently, such a route of molecular decomposition is unfavorable.

Ion K_1. The principal peak in the mass spectrum of compound II is located at m/e 102 and is structurally close to ion F_1^3:

$$(\mathrm{CH_3O{-}CH_2{-}CH{=}CH{-}OCH_3})^{\cdot+}$$

$$K_1,\ m/e\ 102$$

It contains the fourth, fifth, and sixth carbon atoms. In the case of compounds I and III this ion is formed in a relatively small amount, and the corresponding peak has low intensity.

Ion J. This ion with m/e 75, formed as a result of migration of one of the methoxyls (most often the methoxyl from C_3 to C_1) (^{2,3}), has the structure $\mathrm{CH_3O{-}CH{=}\overset{+}{O}CH_3}$. The corresponding peak has the highest intensity in the mass spectrum of III.

Thus, the mass spectrum of compound I is characterized by a high intensity of the peaks of series A' and E and by the absence of fragments of series C and D; the mass spectrum of II—by high intensity of the peaks K_1 and F_2, reduced intensity of the peaks H_1, H_2, J, C_2, and C_2', and absence of the peak D_1; for the mass spectrum of III—by relatively high intensity of the peaks C_2' and J, the appearance of peak D_1, reduced intensity of the peaks K_1 and F_1, and the almost complete absence of peaks of series A', which, as is evident from the foregoing, can to a considerable extent be explained on the basis of the regularities derived earlier for the decomposition of methylated methylhexosides and methylpentopyranosides ($^{1-3}$). The indicated features of the mass spectra are quite sufficient to distinguish confidently and unambiguously 2-, 3-, and 4-deoxyhexoses by their mass spectra; at the same time, these spectra differ from the mass spectra of 6-deoxyhexoses (^{2}). Taken together, all this makes it possible to use mass spectra for analytical purposes in determining the structure of deoxy sugars.

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Note: Figure translations are in progress. See original paper for figures.