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O. S. CHIZHOV, L. A. POLYAKOVA,

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Abstract

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CHEMISTRY

O. S. CHIZHOV, L. A. POLYAKOVA,
Corresponding Member of the Academy of Sciences of the USSR N. K. KOCHETKOV

MASS-SPECTROMETRIC STUDY OF CARBOHYDRATES

METHYL ETHERS OF DISACCHARIDES

Mass spectrometry is finding ever broader application in carbohydrate chemistry and is used to determine the ring size in acetates ([1]) or methyl ethers ([2]) of monosaccharides, to establish the configuration of the glycosidic linkage in methyl glycosides ([3]), to determine the position of a free hydroxyl in partially methylated monosaccharides ([4]-[6]), and to prove the structure of isopropylidene derivatives of monosaccharides ([7]). Mass spectra also make it possible to judge the molecular weight of monosaccharide derivatives ([1], [2], [4]). However, until now no attempts have been made to apply mass spectra to the study of the structures of disaccharides. A substantial obstacle to the mass-spectrometric study of disaccharides is the very low volatility both of the disaccharides themselves and of most of their derivatives. The methyl ethers of disaccharides that we selected as the object of investigation are, in this respect, one of the few exceptions.

We studied the mass spectra of disaccharides with different types of linkages: α-methyl hepta-O-methylgentiobioside (I), α,β-methyl hepta-O-methylmelibioside (II) (linkage 1 → 6); α,β-methyl hepta-O-methylcellobioside (III), α,β-methyl hepta-O-methylmaltoside (IV), α,β-methyl hepta-O-methyllactoside (V) (linkage 1 → 4), and α-methyl hepta-O-methylsophoroside (VI) (linkage 1 → 2). Compounds II, III, IV, and V were prepared by methylation of the corresponding disaccharides according to P. Kuhn ([8], [9]). Compound VI was obtained by methylation of α-methylsophoroside, which had been synthesized by the method of B. Coxon and H. Fletcher ([10]). Compound I was prepared by the reaction of acetobromoglucose with 2,3,4-tri-O-methyl-α-methyl-D-glucoside ([11]), followed by saponification of the resulting gentiobiose derivative and further complete methylation according to Purdie. Paper chromatography of the products of acid hydrolysis of compounds I—VI in all cases revealed only the corresponding schematic structure of a disaccharide with rings A and B and OCH_3 group

Figure 1: schematic structure of a disaccharide with rings A and B and OCH_3 group

tetra- and tri-O-methylhexoses, confirming the structure of the methyl ethers of disaccharides that we obtained.

The mass spectra were recorded on an MX-1303 mass spectrometer equipped with a glass inlet system, at an ionizing voltage of 30 eV and an inlet-system temperature of 175°*. Peak intensities were expressed as percentages of the total intensity of the spectrum, which makes comparison of the spectra of different substances more legitimate than when calculating relative peak intensities with respect to the main peak of the spectrum.

Schematically, the structure of a disaccharide may be represented as follows:

Since, as a first approximation, it may be assumed that the decomposition of both monosaccharide components of the disaccharide molecule proceeds independently, it can be predicted in advance that all ions formed in the mass spectrometer from disaccharide derivatives will fall into two categories: ions formed as a result of the cleavage of ring A (series A) and ions formed as a result of the cleavage of ring B (series B). Peaks corresponding to ions of series A should be common to the spectra of all six methylated disaccharides, whereas the positions of the peaks of series B should be different for disaccharides with different types of linkage (1\$→6, 1→4, *or*1→\$2). The nature of the monosaccharides and the configuration of the glycosidic linkage can be reflected only in some change in the intensity of individual peaks, but not in their complete disappearance or in the appearance of new peaks, as follows from our previous data (4).

Indeed, consideration of the mass spectra of the disaccharide derivatives studied by us (Fig. 1) shows that, along with a large number of peaks common to the spectra of all the substances, there are peaks characteristic only of disaccharides with a given type of linkage. Thus, in mass spectra I and II (1\$→\$6 linkage) there is a peak corresponding to the fragment with m/e 353, which is absent from the spectra of the other compounds; and the peaks of fragments with m/e 380 and 305, characteristic of spectra III, IV, V, and VI, are not observed in spectra I and II. Spectra III, IV, and V differ from spectrum VI by the presence of a peak of medium intensity ($\sim 1\%$), corresponding to an ion with m/e 161, which is practically absent in spectrum VI (intensity $\sim 0.2\%$). In spectra I and II this peak is also absent. Thus, as we assumed earlier (4), mass spectra make it possible to determine reliably the type of linkage in disaccharides.*

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* The mass spectra were recorded by N. F. Madudina, to whom the authors express their gratitude.

Scheme 1: Decomposition of methyl ethers of disaccharides with a 1$→$4 linkage, showing fragment ions with m/e 380, m/e 161, and m/e 305.

Figure 2: Scheme 1: Decomposition of methyl ethers of disaccharides with a 1$→$4 linkage, showing fragment ions with m/e 380, m/e 161, and m/e 305.

Let us briefly consider the probable structures and pathways of formation of the ions corresponding to the most important peaks in mass spectra I–VI. The fragmentation of disaccharides with a 1$→$4 linkage (III, IV, and V) may be represented by Scheme 1.

Scheme 1

Decomposition of methyl ethers of disaccharides with a 1$→$4 linkage

The ion with m/e 380, characteristic of III, IV, and V and differing from the molecular ion by 74 mass units, is evidently formed, analogously to the ion with m/e 176 in the spectrum of 2,3,4,6-tetra-*O*-methyl-α-methyl-*D*-glucoside (^{4}), by cleavage of the fifth and sixth carbon atoms of ring B in the form of methoxyacetaldehyde. It is interesting to note that a similar process does not occur in ring A, since in spectra I and II the peak of the fragment with m/e 380 is absent. The ion with m/e 380 then decomposes in two directions: one of them is cleavage of the monosaccharide residue A in the form of a radical, leading to the formation of an ion with m/e 161; such a process in the case of VI is evidently impossible; the other direction is cleavage of 75 mass units, apparently in the form of the radical $(CH_3O)_2CH\cdot$, giving an ion with m/e 305. The formation of the ion with m/e 305 from the ion with m/e 380 is confirmed by the presence of a metastable peak m/e 245 (calculated 244.8). Cleavage of the methoxyl group specifically from the third, and not from the second, carbon atom is consistent with the fact that in spectrum VI there is a peak of a fragment with m/e 305. If our ideas about the formation of ions with m/e 380, 305, and 161 are correct, then in the mass spectra of disaccharides with a $1 \to 3$ linkage one should expect the appearance only of the peak of the fragment with m/e 380, and not of 305 and 161.

The formation of the ion with m/e 353 in spectra I and II is associated with the loss of 101 mass units; by analogy with the fragment m/e 149 in the spectrum of 2,3,4,6-tetra-*O*-methyl-α-methyl-*D*-glucoside, in light of our new data it may be represented as follows:

Although one can easily imagine an analogous process occurring in ring A, in fact it does not take place, since the peak of the fragment with m/e 353 is not observed in the spectra of disaccharides with $1 \to 4$ and $1 \to 2$ linkages.

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* There is every reason to suppose that the mass spectra of methyl ethers of disaccharides with a 1$→$3 linkage, which we are currently studying, will also differ in a characteristic way from the mass spectra of disaccharides with other types of linkage.

reaction scheme showing formation of fragment m/e 353

Figure 3: reaction scheme showing formation of fragment m/e 353

mass spectra of compounds III, VI, and I

Figure 4: mass spectra of compounds III, VI, and I

Fig. 1. Mass spectra of α,β-methyl-heptamethylcellobioside (III), α-methylheptamethylsophoroside (VI), and α-methylheptamethylgentiobioside (I)

The fragment with m/e 279 is formed from all the substances studied. Therefore, its formation is apparently connected with cleavage of ring A and is analogous to the process of formation of the ion with m/e 75 in the case of methylated methyl glycosides. Further decomposition of the ion with m/e 279 leads to formation of a fragment with m/e 219, with loss of 60 mass units in the form of a neutral molecule of methyl formate. The existence of such a pathway for formation of the fragment with m/e 219 is confirm-

is accounted for by the existence of a metastable peak at m/e 172 (calculated 171.9). Evidently, the fragment with m/e 219 also arises as a result of cleavage of the disaccharide bond; below is a scheme for the formation of fragments with m/e 279 and 219 (Scheme 2).

Scheme 2

Cleavage of ring A in methyl ethers of disaccharides

The origin and structure of the remaining fragments are, apparently, analogous to the corresponding fragments in the mass spectrum of 2,3,4,6-tetra-*O*-methyl-α-methyl-*D*-glucoside (4).

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Scheme 2: Cleavage of ring A in methyl ethers of disaccharides. The scheme shows fragmentation pathways leading to ions with m/e 219 and m/e 279.

Figure 5: Scheme 2: Cleavage of ring A in methyl ethers of disaccharides. The scheme shows fragmentation pathways leading to ions with m/e 219 and m/e 279.

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